QD P447o 1890

60740170R

NLM 05028982 8

NATIONAL LIBRARY OF MEDICINE

20 4x net

7/0

SURGEON GENERAL'S OFFICE

LIBRARY.

ANNEX

Section,

No. 170361.

3—1639

DUE ~~TWO WEEKS FROM~~ LAST DATE

SEP 24 1962

ORGANIC CHEMISTRY

BY

W. H. PERKIN, JUN., Ph.D., F.R.S.
PROFESSOR OF ORGANIC CHEMISTRY IN OWENS COLLEGE, MANCHESTER

AND

F. STANLEY KIPPING, Ph.D., D.Sc. (LOND.), F.R.S.
PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, NOTTINGHAM

LIBRARY
SURGEON GENERAL'S OFFICE
JUL 21 1900
170361.

PHILADELPHIA
J. B. LIPPINCOTT COMPANY

Annex
QD
P447.
1890

PREFACE.

Our original intention was to write a small text-book on Organic Chemistry, based on the syllabus drawn up by the Science and Art Department, in the hope that it would be useful to students attending the elementary or advanced classes in the subject, and not without value to teachers as a handy book of reference. As, however, it soon became apparent that, by making comparatively few additions, the subject-matter might be made to include the facts usually dealt with in a course of about sixty lectures, the scope of the work was enlarged to this extent, so as at the same time to make it more useful to general students as an introduction to Organic Chemistry.

Part I., which deals with the fatty compounds, contains, in the first place, a general account of the methods most frequently employed in the separation, purification, and analysis of organic compounds, and in the determination of molecular weight. The preparation and properties of typical compounds are then described, attention being directed to those changes which come under the heading of general reactions rather than to isolated facts regarding particular substances. Questions of constitution are also discussed at some length, and in the case of most of the typical compounds, the facts on which the given constitutional formula is based are specifically mentioned. This course was adopted, not only in order to avoid the introduction of a long chapter on structure at an earlier stage, but also because, in our opinion, a constant use of constitutional formulæ, accompanied by a clear conception of their meaning, is one of the greatest helps, even to a beginner, in committing the facts to memory.

The opening chapters of Part II. contain an account of coal-tar and its treatment. This leads naturally to a description of the preparation and properties of benzene, and to a discussion of its constitution in the light of facts previously dealt with; the student is thus made acquainted with the principal characteristics of aromatic, as distinct from fatty, compounds, and is then in a position to understand the classification of organic substances into these two main divisions.

The more important classes of aromatic compounds are then described, but in a somewhat different manner from that adopted in Part I., inasmuch as a general account of the properties of each class of substances is given before, instead of after, the more detailed description of typical compounds; this course is to a great extent free from the disadvantages which are found to attend its adoption at earlier stages, as the student has by this time acquired some experience of the more systematic method from a study of the summaries given in Part I.

Special attention has been given, as before, to questions of constitution, one of the objects being to train the student to think out such matters, and to try and deduce a constitutional formula for a given substance, by comparing its properties with those of others of known constitution; with this end in view, it has often been thought desirable to withhold the most important evidence in favour of the accepted constitutional formula until the subject had been discussed at some length.

The concluding chapters on dyes, alkaloids, and stereo-isomerism will doubtless offer the greatest difficulties, but, considering the importance of the matters with which they deal, their omission or curtailment was deemed inadvisable. The account of the alkaloids should be useful, more particularly to medical students, whilst the chapter on dyes deals with a variety of substances of even greater practical value, and indicates the methods employed in one of the most important applications of organic chemistry. The chapter on stereo-isomerism was included because, owing to the importance to which this theory has now attained, a text-book on organic chemistry would be incomplete without a brief discussion of the subject. The full directions which are given for the use of models will, it is hoped, lead to a clear conception of the views set forth.

A considerable proportion of the text, dealing as a rule either with matters of less importance or of a more advanced nature, is printed in small type, and should be left out of consideration until the rest of the subject-matter has been mastered, or, at any rate, studied. The consideration of the 'summary and extension' at the conclusion of some of the more important chapters, should also be postponed until the student has acquired some knowledge of the subject, as the method here adopted is not well suited to the requirements of a beginner.

One of the principal objects throughout has been to treat the subject from a practical point of view (as far as this could be done in a text-book on theoretical chemistry), because, unless a thorough course of practical work accompanies the theoretical, no really satisfactory progress can be made. The student should himself perform many of the simple exercises involved in the purification and analysis of organic compounds, and should prepare typical substances in order to become practically acquainted with their properties. Such general operations as oxidation, reduction, hydrolysis, nitration, sulphonation, &c., and the more important general reactions for the identification of the several classes of compounds, should also be included in the practical course.

In many respects we have made free use of the excellent text-books of V. Meyer and Jacobson and von Richter, of Beilstein's *Handbuch*, and of Ost's *Lehrbuch der technischen Chemie*. We are also much indebted to Dr A. Harden for help in revising the proof-sheets, and in preparing the index.

Since this preface was written, a chapter dealing with some of the more important constituents of plants and animals has been added—in the form of an Appendix, with a separate index. We hope that this new chapter will be found useful by all readers, but especially by medical students, for whom more particularly it has been written.

CONTENTS.

ORGANIC CHEMISTRY.

PART I.

CHAPTER I.

COMPOSITION, PURIFICATION, AND ANALYSIS OF ORGANIC COMPOUNDS.

Origin and Present Meaning of the Term 'Organic.'—Although spirits of wine, sugar, fats, and other substances obtained directly or indirectly from animals or plants have always claimed a large share of attention from chemists, their investigation met with only slight success until towards the close of the last century, when the composition of many of these natural products was established by the French chemist Lavoisier (1743–94). Lavoisier it was who first showed that vegetable substances are generally composed of carbon, hydrogen, and oxygen, whilst animal substances, although consisting for the most part of the same three elements, frequently contain nitrogen, and sometimes phosphorus and sulphur.

The peculiar composition of these natural products, and the fact that they behaved differently from mineral compounds, led to the belief that all animal and vegetable substances were produced under the influence of some peculiar **vital** force, and that their formation was regulated by laws quite different from those which governed the formation of mineral substances; consequently, it was thought impossible to prepare any animal or vegetable product artificially or synthetically in the laboratory.

For these reasons compounds obtained from animals and plants—that is to say, directly or indirectly from living *organisms*—were called **organic,** and were classed separately from **inorganic** or mineral substances.

This distinction between organic and inorganic compounds appears to have been generally accepted until 1828, when Wöhler succeeded in obtaining urea, an excretion of certain animal organisms, from ammonium cyanate, a substance which was at the time considered to be inorganic or mineral, because it could be produced in the laboratory; this synthesis showed conclusively that the influence of a living organism was not necessary for the production of the 'organic' substance urea.

After this important discovery it was soon found that many other so-called 'organic' substances could be prepared in the laboratory from 'inorganic' materials without the help of a vital force, and ultimately it came to be generally acknowledged that the formation of 'organic' and 'inorganic' substances is governed by precisely the same laws.

The supposed difference between the two classes of compounds having been shown to be purely an imaginary one, the terms 'organic' and 'inorganic' lost their original meaning; they are, nevertheless, still made use of in the classification of chemical compounds. The atoms of carbon are distinguished from those of all other elements by their extraordinary capability of combining with one another and with hydrogen to form compounds, such as CH_4, C_6H_6, $C_{10}H_8$, &c., the molecules of which are often composed of a very large number of atoms; the atoms of other elements, however, rarely combine with hydrogen to form more than one or two compounds, and have only to a very limited extent the power of combining with one another. In consequence of the properties just mentioned, carbon forms a larger number of compounds than any other element, and, speaking generally, these compounds are related to one another, but widely different to those of other elements.

For these reasons it is convenient to consider the carbon compounds separately, and to distinguish them by the term *organic*, which recalls the fact that carbon is a most important constituent of all animal and vegetable substances; organic chemistry, therefore, is the *chemistry of the carbon compounds.*

Some of the simpler compounds of carbon, such as carbon dioxide, carbon monoxide, carbon bisulphide, &c., which are of general importance, are always described in works on inorganic chemistry for the sake of convenience; they are, nevertheless, organic compounds, because they contain carbon.

Composition of Organic Compounds.—In spite of their great number, organic compounds are almost always comparatively simple in composition, being made up, as a rule, of not more than four or five elements.

Organic substances, such as sugar, starch, and tartaric acid, which occur in the vegetable kingdom, almost invariably consist of carbon, hydrogen, and oxygen, although a few—morphine and strychnine, for example—contain nitrogen as well. Those occurring in the animal kingdom generally contain nitrogen as well as carbon, hydrogen, and oxygen: urea and uric acid, for instance, are composed of these four elements; a few animal substances also contain sulphur and phosphorus.

Artificially prepared organic compounds may contain any element. Some—benzene, for example—are composed of carbon and hydrogen only, but the majority contain oxygen as well; nitrogen and the halogens are very often present in carbon compounds produced in the laboratory; so also are the metals calcium, sodium, silver, &c., which form salts with organic, just as they do with inorganic acids.

General Principles of Organic Analysis.—The qualitative analysis of organic compounds is carried out by methods quite different from those employed in the case of inorganic substances. Most organic compounds are insoluble in water and in acids, and could not be examined by the ordinary wet methods of analysis: even those which are soluble do not show, except in rare cases, a sufficiently characteristic behaviour to enable them to be identified by their reactions. There is, again, this wide difference between inorganic and organic analysis, that, whereas a mixture of inorganic compounds may be directly submitted first to qualitative and then to quantitative examination, in the case of a mixture of carbon compounds it is usually necessary to separate and purify each constituent before its composition can be determined.

* For these reasons organic analysis usually consists of several processes: Firstly, the substance is submitted to a preliminary qualitative examination, the object of which is to find out how many distinct compounds are present, and to separate and purify each of them. The nature of each constituent is then determined; this may sometimes be done by proving it to be identical with some known compound by methods to be described later. If this be impossible, a further qualitative examination is made to ascertain what elements the substance contains; the pure compound is then submitted to quantitative or elementary analysis, from the results of which its percentage composition is obtained.

Separation and Purification of Organic Compounds.—The separation of a pure organic compound from a mixture of any kind is often a matter of considerable difficulty, and it is usually necessary to employ different processes for different mixtures. Although, therefore, it is impossible to give a method which would be applicable in every case, the more important steps in the general examination and purification of organic substances may be briefly indicated.

In the case of any substance of unknown composition, a small portion is ignited on platinum foil, in order to ascertain

---

* Generally speaking, portions of the text which are printed in smaller type are intended only for those who have already acquired an elementary knowledge of organic chemistry.

whether it contains inorganic matter; if it leaves a non-combustible residue, it is probably a salt of some organic acid, or it contains inorganic compounds as impurity.

The separation of an organic from an inorganic substance can usually be accomplished by shaking or boiling the substance with some solvent, such as alcohol, ether, benzene, chloroform, petroleum, &c. Most organic compounds are soluble in one or other of these liquids, whereas the majority of inorganic compounds are insoluble, or nearly so. Water or dilute acids may often be employed for the same purpose, since many inorganic substances are soluble, many organic substances insoluble, in these liquids.

The separation of two or more organic substances may sometimes be effected in a similar manner. In the case of a mixture of cane-sugar, tartaric acid, and benzoic acid, for example, the last-named compound only can be dissolved out with ether, the tartaric acid being then separated from the sugar by treating with alcohol, in which it is much more readily soluble than sugar.

Solid or liquid organic substances in aqueous solution, or suspended in water in a fine state of division, may often be isolated by agitating the solution or mixture with some solvent, such as ether, benzene, chloroform, &c., which does not mix with water. For this purpose a **separating funnel** (fig. 1) is employed, and after being shaken vigorously, the mixture is allowed to stand until it forms two layers; the two solutions are now separated by turning the stopcock (*a*, *a′*) and running off that which is underneath, the extraction being repeated, if neces-

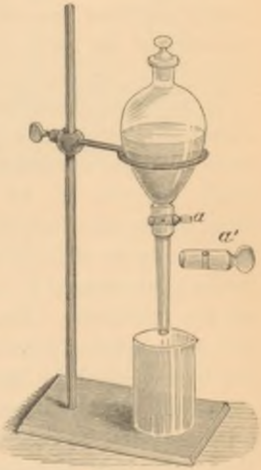


Fig. 1.

sary, with a fresh quantity of the organic solvent. The combined extracts are then dried (p. 17), and the solvent distilled or slowly evaporated.

The process of **crystallisation** is one of the simplest and best methods of separating and purifying organic substances, but before it can be successfully employed, a suitable solvent must be found. About a centigram of the substance is boiled for a short time in a test tube with 1–2 c.c. of some solvent (such as water, ether, alcohol, carbon bisulphide, benzene, light petroleum, &c.), and, if necessary, the hot liquid is filtered from any insoluble matter; if, on cooling, the substance be deposited in crystals, the rest of the material is treated in the same way, the insoluble portion, if any, being examined separately. Should no separation of crystals take place on cooling, the solution is concentrated by evaporation, and then allowed to cool; if, again, crystals be not deposited, some other solvent is tried. The crystals ultimately obtained are collected on a filter, washed with a small quantity of the solvent, and further purified by recrystallisation.

If only one constituent of a mixture be dissolved by the liquid employed, this particular substance is obtained in a state of purity without difficulty, because the others are easily got rid of by filtration; when, however, two or more of the constituents are soluble, their further separation can usually be effected by **fractional crystallisation**. In this process, advantage is taken of the difference in solubility of the substances. On slowly cooling the hot solution, the more sparingly soluble substance is first deposited, and can be separated by filtration from the more readily soluble compound, which does not crystallise until the solution is further cooled or concentrated; the two crops of crystals are then separately redissolved, and the process repeated until each substance is obtained in a pure state, as shown by a determination of its melting-point (p. 20).

Another method extensively used in the separation and purification of organic substances, both solid and liquid, is **distillation in a current of steam.** The substance and a little water are placed in a flask (A, fig. 2) which is connected with a condenser, and heated on a water- or sand-bath; a rapid current of steam, generated in a separate vessel (B), is then passed through the mixture. The distillate, which contains the volatile organic substance in solution, or in suspension, is afterwards extracted with ether, or filtered, or treated in some other way according to circumstances. In this simple manner it is often possible to isolate a compound when all other methods fail; it is, however, only applicable in the case of the comparatively few organic substances which are **volatile in steam.** Many compounds which cannot be distilled in the ordinary way because they undergo decomposition, are volatile in steam, and pass over unchanged, even when their boiling-points are much higher than that of water.

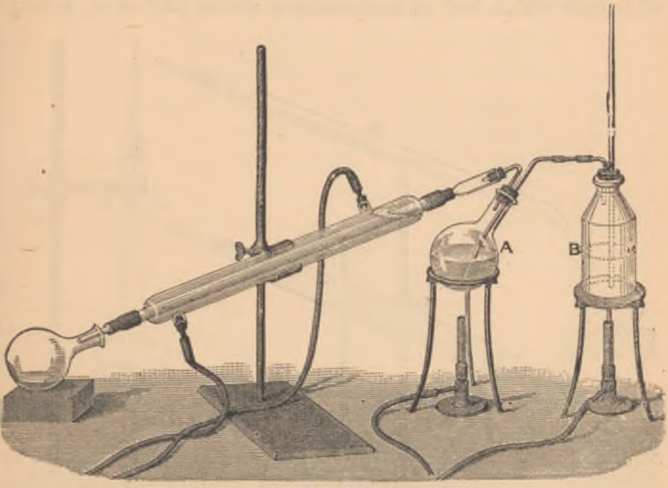


Fig. 2.

Organic substances which boil without decomposition can be purified by **distillation.** The substance is placed in a distilling flask (A, fig. 3), which is connected with a condenser, the neck of the flask being closed with a cork, through which a thermometer passes; the bulb of the thermometer is placed just below the opening of the side-tube (B), and a few scraps of unglazed porcelain or platinum are put in the distilling flask, to prevent 'bumping' or sudden ebullition. In the case of liquids which boil at temperatures above 130° or so, a long glass tube (C) without a water-jacket is used instead of a Liebig's condenser, which is apt to crack. If the compound to be purified contain only a small quantity of *non-volatile* impurities, the thermometer rises very rapidly as soon as the liquid begins to boil, but then remains practically stationary until almost the whole has distilled. Towards the end of the operation, however, it begins to rise again, and distillation is then stopped, the impurities remaining in the distilling flask. If the distillate be now transferred to a clean flask, and

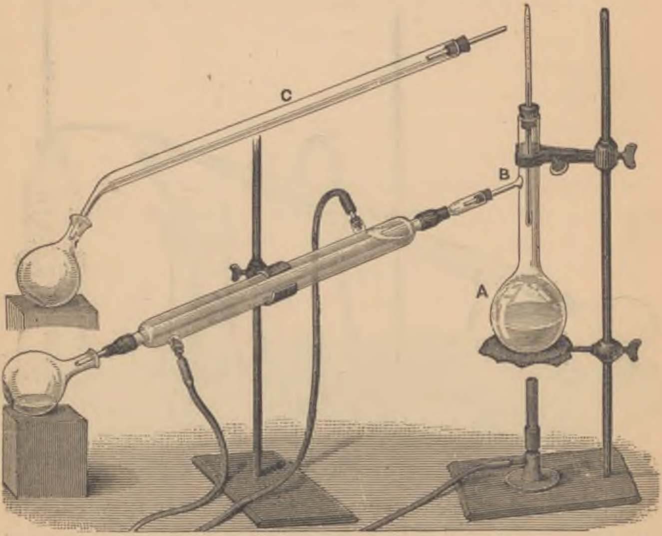


Fig. 3.

redistilled, it will boil at a constant temperature, which is the **boiling-point*** of the liquid.

All pure substances which boil without decomposition have a definite boiling-point (b.p.), which is dependent on the pressure. As the pressure diminishes, the boiling-point is lowered, so that, by carrying out the process under *reduced pressure*, it is often possible to distil a substance which would undergo decomposition under ordinary atmospheric pressure, because in the latter case it is heated more strongly.

The boiling-point is one of the most important physical constants of a substance, and affords a valuable means of identifying it. An observation of the boiling-point should always be made with an apparatus similar to that shown above, and a considerable quantity of the liquid should be distilled, in order to make sure that it has a constant boiling-point; if not, it is impure. Before distilling a substance, it should be carefully dried; in the case of liquids, this is done by shaking them with a few small pieces of fused calcium chloride, potassium carbonate, or other dehydrating agent, and then decanting or filtering.

When a mixture of two (or more) volatile substances is distilled in the manner described above, it begins to boil at some temperature lying between the boiling-points of the constituents. As distillation proceeds, the boiling-point rises, and towards the end of the operation, it usually becomes nearly the same as that of the liquid which boils at the higher temperature. In the case of a mixture of alcohol (b.p. 78·3°) and water (b.p. 100°), for example, the thermometer at first registers some temperature between 78·3 and 100° according to the proportion of the two substances, and the first portions of the distillate contain a larger proportion of alcohol than the original mixture. During distillation, the thermometer slowly and continuously rises, and at last registers 99–100°, the portions passing over at this temperature consisting of practically pure water. The change

---

* See foot-note, p. 21.

in boiling-point is due to a change in the composition of the mixture; the alcohol, being more volatile, passes off more quickly than the water. It is possible, therefore, to partially separate a mixture of liquids by collecting the distillate in portions or **fractions** at intervals of 5 or 10°, the operation being termed **fractional distillation.** By redistilling each fraction separately, a further separation is effected, and, after a sufficient number of operations, the constituents of the mixture are obtained in a practically pure condition, boiling at a constant temperature. Such a separation, however, can only be satisfactorily effected provided that there is a difference of at least 20-30° between the boiling-points of the liquids; in many cases, even when there is a greater difference than this, a complete separation cannot be accomplished.

As an illustration of the process of fractional distillation, the case of a mixture of 50 c.c. of benzene (b.p. 81°) and 50 c.c. of xylene (b.p. 140°) may be taken. The mixture begins to boil at about 87°, the thermometer rising gradually to 140°; if the receiver be changed every 10°, the following fractions are obtained:

87–100°	100–110°	110–120°	120–130°	130–140°
33 c.c.	16 c.c.	8·5 c.c.	8 c.c.	33 c.c.
(1)	(2)	(3)	(4)	(5)

The first and last are larger than the others, because the temperatures at which they are collected are approximately the boiling-points of the constituents. If, now, the fractions 1 and 5 be separately redistilled, they will yield a large fraction boiling at 81–85° and at 135–140° respectively, as well as small intermediate fractions, which are collected separately. By repeating these operations with the fractions 2, 3, and 4, a large proportion of the mixture is ultimately separated into two fractions, from which benzene and xylene respectively can be obtained in an almost pure condition by further fractional distillation.

The process of fractional distillation is greatly facilitated by employing a flask with a long neck, or by causing the mixed vapours to pass through a long vertical tube before they enter the condenser. By this means the vapour of the liquid of higher boiling-point is partially condensed, and runs back into the distilling flask instead of passing over with the more volatile liquid.

Fractional distillation is frequently carried out under reduced pressure for the reasons already stated in the case of ordinary distillation. A simple apparatus for this purpose is easily made by inserting the side-tube of one distilling flask (A, fig. 4) into the neck of a second flask (B), and connecting the side-tube (of B) with a water-pump. The liquid to be distilled is placed in A; the air is then exhausted, and the distillation carried out in the usual manner, the process being interrupted when the receiver is being changed.

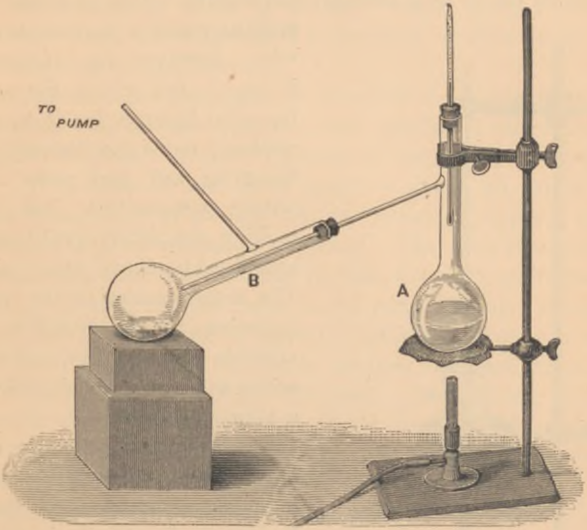


Fig. 4.

Tests of Purity.—Before attempting to determine the composition of an organic substance, its purity must be established. It would be useless to test for chlorine, for example, in an impure organic compound, since, even if a distinct indication were obtained, this element might be present (as a chloride) in the form of impurity. In the case of a compound, liquid or solid, which distils unchanged, its purity can generally be established by observing if its boiling-point is constant. A solid substance should be examined under the microscope in order to see whether it is homogeneous, and an observation of its melting-point should be made.

Pure substances which melt or liquefy without decomposition do so at a definite temperature, which is called the **melting-point** of the compound; when, however, the substance is impure, not only is the melting-point lowered, but it is also rendered indefinite, the mixture becoming soft and pasty at a certain temperature, and not melting completely until heated considerably above this point. The determination of the melting-point affords, therefore, a valuable test of purity, and also serves as a means of identifying a compound.

The apparatus generally employed for determining the melting-point consists of a small beaker (*a*, fig. 5) of about 50 c.c. capacity, containing concentrated sulphuric acid, and fitted with a glass stirrer (*b*). A minute quantity of the substance is placed in a capillary tube (*c*), closed below, which is attached to a thermometer (*d*) by means of a small india-rubber ring, or simply caused to adhere to it by capillary attraction. The acid is slowly heated, being constantly stirred, and the temperature at

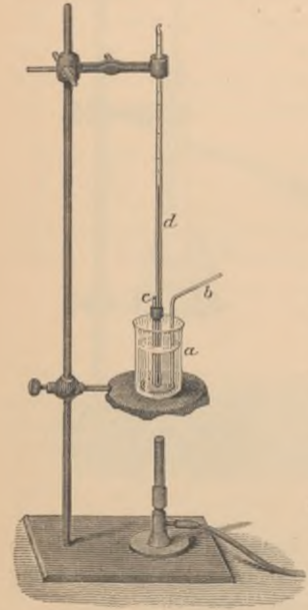


Fig. 5.

which the substance liquefies—that is to say, its melting-point (m.p.) *—is noted.

QUALITATIVE ELEMENTARY ANALYSIS.

A pure compound having been obtained, it is often possible, by noting its appearance, smell, crystalline form, solubility in various solvents, and by determining its melting- or boiling-point, to prove that it is identical with some substance the composition of which is known: when, however, this cannot be done, the next step is to ascertain of what *elements* the substance is composed.

In order, in the first place, to ascertain whether the substance contains **carbon**—that is to say, whether it really is an organic compound—a small quantity is heated on platinum foil. If it inflames and burns away, or swells up, giving a black mass, which on strongly heating entirely disappears, the substance is in all probability organic. The salts of organic acids usually char when treated in this way, and, on further heating, the carbonaceous matter burns away, leaving a residue which may be dissolved in water or acids and examined by the usual methods of inorganic analysis; sodium acetate, for example, yields sodium carbonate, silver acetate gives metallic silver, and copper acetate the oxide of the metal. If a halogen, or sulphur, be present in the acid, it is generally found in the residue in combination with the metal.

The behaviour of a substance when heated with concentrated sulphuric acid often affords an indication of the presence of carbon, as many organic substances blacken under these conditions owing to the separation of carbonaceous matter.

If neither of these tests give a decisive result, the compound is mixed with about ten times its weight of pure copper oxide, and the mixture heated to redness in a narrow tube of hard glass sealed at one end, the escaping gases being led into

---

* The *observed* melting- or boiling-point of a substance is usually rather lower than the true value, because, as a rule, the column of mercury is not wholly immersed in the heating liquid or vapour.

lime-water; under these conditions all organic substances* are decomposed, yielding carbon dioxide, the formation of which is proved by the lime-water becoming turbid.

The presence of **hydrogen** may sometimes be detected by heating the substance in a dry test tube and noticing whether any water is formed as the result of decomposition: as, however, many organic compounds do not yield water under these conditions, but simply distil unchanged, and as the detection of water itself in such small quantities is not a very simple matter, the only reliable test for hydrogen is to heat the substance with dry copper oxide in a stream of dry air or oxygen (see pp. 26–28); if hydrogen be present, it will be oxidised to water, the formation of which may be proved by passing the products of combustion through a weighed calcium chloride tube.

The presence of **chlorine, bromine,** or **iodine** in organic compounds cannot, as a rule, be detected by the methods employed in the examination of inorganic substances, as for example, by means of silver nitrate, or by heating with manganese dioxide and sulphuric acid; chloroform, for instance, contains a very large proportion of chlorine, but when pure it gives no precipitate with silver nitrate, and simply boils away when heated with manganese dioxide and sulphuric acid.

A simple but not quite conclusive test for the halogens is to take a piece of copper wire, and heat one end of it in the oxidising zone of the Bunsen flame until it is quite black and ceases to colour the flame green. A small quantity of the substance is then heated on the end of the wire in the flame, when, if a halogen be present, a green colouration is usually observed, due to the formation of a volatile halogen compound of copper. As, however, this test sometimes fails, and as, moreover, it does not give any information as to which of the halogens is present, one of the following methods is almost invariably adopted.

---

* Except the stable carbonates and cyanides of the alkalies and alkaline earths.

(*a*) A small quantity of the substance is placed in a narrow test tube, together with a bright piece of sodium (or potassium) about the size of a pea, and gently heated, care being taken, especially in the case of volatile compounds, that the metal is brought into contact with the substance and thoroughly chars it. The mixture is then heated more strongly, finally at a red heat, and after allowing to cool a little, the tube is broken by introducing the hot end into about 10 c.c. of water contained in an evaporating basin. The alkaline solution is filtered from carbonaceous matter, the filtrate acidified with pure nitric acid and a portion tested with silver nitrate; if a precipitate be formed, the presence of halogen in the original substance is proved, and its nature may be determined by submitting the rest of the solution, or the precipitate, to the usual examination. This test depends on the fact that when any organic substance containing chlorine, bromine, or iodine is heated with sodium, the halogen combines with the metal to form chloride, bromide, or iodide of sodium, which can then be tested for in the usual manner.

(*b*) A small quantity of the substance is heated with pure lime in a tube of hard glass, as described later (p. 35). The mixture is allowed to cool, carefully shaken into distilled water, the solution acidified with nitric acid, filtered from carbonaceous matter, and tested with silver nitrate. If the substance contained a halogen—chlorine, for instance—heating it with calcium oxide causes the formation of calcium chloride.

The presence of **nitrogen** in an organic substance is frequently indicated by the peculiar, unpleasant smell, like that of burning feathers, which is observed on heating the substance on platinum foil. A better test is to strongly heat a fairly large quantity of the substance with soda-lime * in a hard glass tube, when, if ammonia is evolved, the presence of

---

* Soda-lime is prepared by intimately mixing quicklime and caustic soda, and strongly heating the mixture until it is quite dry.

nitrogen is proved. As, however, certain organic compounds containing nitrogen do not yield ammonia when heated with soda-lime, the following test must be applied before the absence of nitrogen may be considered as satisfactorily proved. The substance is carefully heated with a bright piece of sodium or potassium exactly as described in testing for the halogens; the alkaline solution is filtered from carbonaceous matter, a few drops of ferrous sulphate added to the filtrate, the mixture warmed for a short time, acidified with pure hydrochloric acid, and tested with a drop of ferric chloride, when, if nitrogen were present in the original substance, a deep bluish-green coloration, or a precipitate of Prussian blue, is produced.

This test depends on the fact that the nitrogen and some of the carbon in the organic compound combine with the sodium to form sodium cyanide; when the alkaline solution of sodium cyanide is warmed with ferrous sulphate, ferrous hydrate is precipitated and sodium ferrocyanide is formed, $6NaCN + Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH$, so that on afterwards adding a ferric salt* to the acidified solution, Prussian blue is produced.

Sulphur and **phosphorus** may be detected by gradually adding a small quantity of the substance to a fused mixture of potassium carbonate and nitre, heated on a piece of platinum foil; under these conditions the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid. The residue, which should be colourless, the carbon having been burned to carbon dioxide, is dissolved in water, and the solution of potassium salts tested for the above-mentioned acids in the usual way. Another method, similar in principle, consists in oxidising the substance with nitric acid in a sealed tube, as described later (pp. 33–35).

---

* During the operation some of the ferrous hydrate generally becomes oxidised to ferric hydrate, which, on acidifying with hydrochloric acid, is converted into ferric chloride; a precipitate of Prussian blue is thus at once produced.

Sulphur may also be detected by heating the substance with sodium or potassium in the manner described above, and bringing a portion of the alkaline solution into contact with a bright silver coin; if the original substance contained sulphur, an alkaline sulphide will have been produced, the presence of which will be at once recognised by the formation of a black stain on the silver coin.

QUANTITATIVE ELEMENTARY ANALYSIS.*

When the qualitative examination has been completed, the quantitative analysis may be proceeded with, but not before: the reason of this is, that the presence of certain elements necessitates a slight change in the methods to be employed, as will be shown below.

Estimation of Carbon and Hydrogen.—All organic compounds † are decomposed when brought into contact with red-hot copper oxide, or with any substance which readily gives up oxygen, the carbon being converted into *carbon dioxide*, the hydrogen into *water;* by employing a known weight of substance, and collecting and weighing these products of combustion, the percentage of carbon and hydrogen may be readily determined. The apparatus generally used for this purpose is shown in the accompanying figures.

Fig. 6.

The **calcium chloride** or **drying tube** (fig. 6) is filled with granulated anhydrous calcium chloride, or with fragments of pumice moistened with concentrated sulphuric acid, and serves

---

* The following account of the methods most commonly adopted in the quantitative analysis of organic compounds is only intended to indicate the nature of the processes; the details of manipulation, upon which success depends, can only be learned by practice in the laboratory.

† With the exceptions already mentioned in the foot-note, p. 22.

to absorb the water; the **potash bulbs** (fig. 7) are partly filled, as shown, with strong potash (sp. gr. about 1·28), the small tube (*a*), which contains anhydrous calcium chloride, serving to retain the aqueous vapour which is taken up in the passage of the gases through the potash. The calcium chloride tube and the potash bulbs are carefully weighed before and after the combustion, the caps (*b*, *b*) with which they are closed being removed in both cases; the gain in weight of the former corresponds with the amount of water produced, that of the latter representing the amount of carbon dioxide absorbed.

Fig. 7.

The combustion is carried out in a piece of hard glass combustion tube (*a*, *b*, fig. 8), which is usually about 90 cm. long, and open at both ends; part of the tube (*f* to *f*) is filled with a layer of granulated copper oxide kept in its place by loose asbestos plugs (*e*, *e*). Before commencing the analysis the tube is heated in a combustion furnace (*k*), at a dull red heat, a current of air, carefully freed from carbon dioxide and moisture—by passing first through potash contained in the wash bottle (*g*), and then through the two towers (*h*, *j*)* containing pumice moistened with concentrated sulphuric acid—being led through it in order that any moisture or traces of organic matter may be removed; the *empty* section of the tube (*a*, *f*) is then allowed to cool.

The drying tube (*l*) having been fitted into the end (*b*) through an india-rubber cork, and the potash bulbs (*m*) attached by means of a short piece of india-rubber tubing, 0·15 to 0·2 gram of the substance, accurately weighed out in a narrow porcelain or platinum *boat* (*d*), is introduced into the tube; a roll of platinum foil (*c*) is then placed behind

---

* In practice, two such sets of drying apparatus are usually employed, one for the air, the other for the oxygen.

the boat in order to prevent as far as possible any backward diffusion of the products of combustion. When a volatile liquid is to be analysed, the substance is weighed out in a thin glass bulb (shown on a larger scale at *n*), which is afterwards placed in the boat (at *d*).

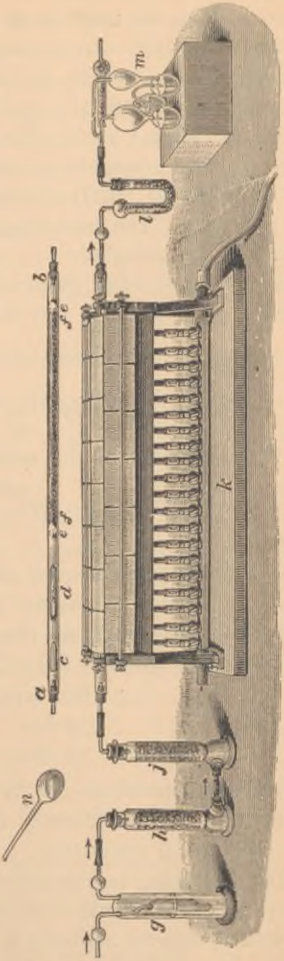


Fig. 8.

A slow stream of air carefully freed from moisture and carbon dioxide, as before, is now passed through the tube, the combustion of the substance being started and regulated by turning on the gas taps (beginning at *c*). As soon as the whole of the tube has been gradually raised to a dull red heat, the current of air is turned off, and a stream of pure oxygen is passed, in order to burn any remaining organic matter, and to oxidise the copper which has been formed by the reduction of some of the copper oxide; finally, air is again passed until the oxygen is expelled from the apparatus. The whole operation occupies from 1½ to 3 hours, according to the nature of the substance. The calcium chloride tube and the potash bulbs are then disconnected, their ends closed with the india-rubber caps, and allowed to stand for one or two hours, when they are again weighed.

Now, since the gain in weight of the potash bulbs is due to the absorption of carbon dioxide, which has been formed during the combustion, $\frac{12}{44}$ths or $\frac{3}{11}$ths (C/CO_2) of this gain in weight represents the quantity of carbon in the amount of substance taken; as also the gain in weight of the calcium chloride tube corresponds with the amount of water formed, $\frac{2}{18}$ths or $\frac{1}{9}$th (H_2/H_2O) of this increase represents the amount of hydrogen. The percentage of carbon and hydrogen may therefore be calculated.

Example.—0·1582 gram of substance gave on combustion 0·0614 gram of H_2O and 0·3620 gram of CO_2; therefore, 0·1582 gram of substance contains $0·0614 \times \frac{1}{9} = 0·0068$ gram of hydrogen, and $0·3620 \times \frac{3}{11} = 0·0987$ gram of carbon, so that 100 parts of the substance contain $\frac{0·0068 \times 100}{0·1582} =$ 4·31 parts of hydrogen, and $\frac{0·0987 \times 100}{0·1582} = 62·40$ parts of carbon.

If the substance consist of carbon, hydrogen, and oxygen *only*, the difference between the sum of the above numbers and 100 must represent the quantity of oxygen; the percentage composition of the substance is therefore

C.........62·40 per cent.
H......... 4·31 "
O.........33·29 " (by difference).

The percentage of oxygen is always obtained by difference, there being no satisfactory method by which this element may be directly estimated.

The following points remain to be noticed in connection with the determination of carbon and hydrogen. If the substance contain *nitrogen*, it is necessary to insert a roll of bright copper gauze, about four inches long, into the front part (*b*) of the tube; this is kept red hot during the combustion, and serves to decompose any oxides of nitrogen* produced during the operation, which would otherwise be absorbed by the water in the calcium chloride tube and by the potash, and thus lead to erroneous results. When the substance contains a *halogen*, a roll of silver gauze must be used in order to prevent any halogen or halogen compound of copper from passing into the absorption apparatus; usually, in analysing a substance containing *halogens*, *sulphur*, or *phosphorus*, the space *f* to *f* (fig. 8) is filled with lumps of fused lead chromate instead of copper oxide. Lead chromate, like copper oxide, is a powerful oxidising agent at high temperatures, its action being probably represented by the equation

$$4PbCrO_4 = 4Pb + 2Cr_2O_3 + 10O.$$

Any sulphur dioxide, phosphorus pentoxide, or halogen produced during the combustion is completely retained by the lead chromate, as $PbSO_4$, $PbCl_2$, &c., and thus its passage into the absorption apparatus is prevented.

Quantitative Determination of Nitrogen.—Nitrogen may be estimated in two ways, either volumetrically by Dumas' method, or gravimetrically, as ammonia, by Will and Varrentrap's process.

1. Volumetric Estimation by Dumas' Method.—This process is based on the fact that when ignited with copper oxide, nitrogenous organic substances are entirely decomposed into carbon dioxide, water, and nitrogen. If the gaseous products of combustion be collected over potash, the carbon dioxide is absorbed, and the residual gas consists of practically pure nitrogen; by measuring the volume of the gas obtained

---

* $2NO_2 + 4Cu = N_2 + 4CuO$; $N_2O_3 + 3Cu = N_2 + 3CuO$. In order to render the roll of gauze as efficient as possible, it is heated in a blowpipe flame until thoroughly oxidised, and, while red hot, dropped into a little pure methyl alcohol contained in a test tube; the methyl alcohol reduces the copper oxide, giving a very bright surface of copper. The roll is then completely freed from methyl alcohol by heating at 160-180° for half an hour, just before commencing the combustion.

from a known weight of substance, the percentage of nitrogen can be readily ascertained.

The analysis is carried out in a combustion tube similar to that used in the determination of carbon and hydrogen (fig. 8), but containing in the front end (*b*) a roll of copper gauze, which serves to decompose any oxides of nitrogen formed during the combustion (see foot-note, p. 29). Instead, however, of placing the substance in a boat, the weighed quantity is intimately mixed with finely-powdered copper oxide, this mixture occupying the space *c* to *e*. Before commencing to heat the substance, a stream of carbon dioxide is passed through the tube until the air has been expelled, which is the case when the bubbles are almost entirely absorbed* in passing through the potash; at the same time the roll of copper gauze and the front part of the tube are raised to dull redness. The combustion is then started by gradually heating the mixture of substance and copper oxide, the escaping gases being either collected over mercury in a eudiometer containing potash, or more conveniently in the apparatus shown in fig. 9.

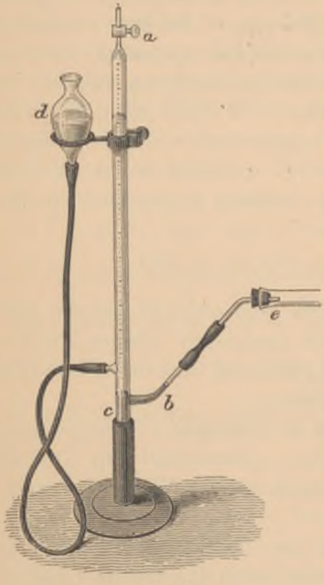


Fig. 9.

As soon as the whole of the tube has been raised to a dull or cherry-red heat, and gases cease to be evolved, a current

---

* The bubbles are never completely absorbed, as it is impossible to drive out the last traces of air.

of carbon dioxide is led through the combustion tube until the rest of the nitrogen has been expelled. The eudiometer is then closed with the thumb, inverted in a cylinder of water, and the thumb removed so that the mercury may fall out and the strong potash mix with the water. After about half an hour's time, the tube is held vertically in such a position that the level of the water inside and outside is the same, and the volume (*v*) of the nitrogen is observed, the temperature (t°) of the gas—that is, of the water surrounding the tube—and the height (P) of the barometer being also noted.

The apparatus (Schiff's nitrometer) shown in fig. 9, which is now very generally used in nitrogen determinations, consists of a graduated tube (*ac*), provided with a stopcock (*a*) and a reservoir (*d*), by means of which the tube may be filled with potash (sp. gr. 1·3), and which also serves for regulating the pressure in the apparatus; the lower part of the tube (*cb*) is filled with mercury, which forms a seal and prevents the passage of the potash into the combustion tube (*e*). After carbon dioxide has been passed through the combustion tube for a considerable time, the tube (*b*) is connected, and the reservoir (*d*) lowered. If the bubbles are almost completely absorbed as they ascend through the potash, the combustion is proceeded with, the nitrogen remaining in the tube at the end of the operation being swept into the apparatus by means of carbon dioxide, as described above. The apparatus is now placed aside for about an hour to cool; the reservoir (*d*) is then raised until the potash in it and in the tube (*ac*) is at the same level, and the volume of nitrogen (*v*) is read off, the temperature (t°) and the barometric pressure (P) being noted.

The weight of nitrogen in the quantity of substance taken is readily ascertained when its volume (in cubic centimetres) has been determined by either of the methods described. Since the volume v is measured at t° under a pressure $P - w$, where w = the tension of aqueous vapour in mm. of mercury* at the temperature t°, the volume V at 0° and 760 mm. would be $v \times \frac{P - w}{760} \times \frac{273}{273 + t^\circ}$. As, now, 1 c.c. of nitrogen weighs 0·001256 gram at N.T.P.,† the weight of V c.c. will be V × 0·001256 gram.

Example.—0·2248 gram of substance gave 7·1 c.c. of nitrogen measured at 16°; $P = 753{\cdot}5$ mm., $w = 13{\cdot}5$ mm. The weight of the gas, therefore, is $7{\cdot}1 \times \frac{740}{760} \times \frac{273}{289} \times 0{\cdot}001256 = 0{\cdot}00805$ gram, and the percentage of nitrogen $\frac{0{\cdot}00805 \times 100}{0{\cdot}2248} = 3{\cdot}58$.

2. The Gravimetric Estimation of Nitrogen as Ammonia, by Will and Varrentrap's method, depends on the fact already stated, that many nitrogenous organic substances, when heated with caustic alkalies, are decomposed in such a way that the whole of their nitrogen is converted into ammonia: by estimating the amount of ammonia produced by the decomposition of a known weight of the substance, the percentage of nitrogen can be determined.

The apparatus (fig. 10) employed for this purpose consists of a piece of hard glass tube (*ad*), about 35 cm. long, drawn out and sealed at one end (*a*); an asbestos wad is loosely fitted into the end (*a*), and the space *a* to *b* is filled with coarsely powdered soda-lime; the part *b* to *c* contains a mixture of the weighed substance and finely powdered soda-lime, the remainder of the tube (*c* to *d*) being filled with coarsely powdered soda-lime only, the whole being kept in position by an asbestos wad (at *d*).

---

* Some of the values of w which are most frequently required are the following:

$t =$	10°	12°	14°	16°	18°	20°
$w =$	9·14	10·43	11·88	13·51	15·33	17·36 mm.

When the apparatus shown in fig. 9 is employed, the vapour tension of the strong potash is much less than that of pure water; if the potash has a sp. gr. = 1·3 it is usual, in practice, to deduct from P half the tension of aqueous vapour at the temperature t.

† Normal temperature and pressure—that is, 0° and 760 mm.

The absorption apparatus (*e*) contains dilute hydrochloric acid, and serves to absorb the ammonia; it is fitted into the open end of the tube by means of an india-rubber cork. The tube is gradually heated in a combustion furnace, as in determining nitrogen volumetrically (commencing at *d*), and when the whole has been raised to a red heat, the ammonia remaining in the tube is drawn into the absorption bulb by breaking off the sealed end and aspirating air through the apparatus.

Fig. 10.

The amount of ammonia which has been produced may be determined gravimetrically by precipitation with platinic chloride, or, if a known volume of standard hydrochloric acid has been introduced into the bulbs, the quantity neutralised by the ammonia may be estimated volumetrically by titration with standard alkali.

The soda-lime method is not altogether satisfactory, because, owing to the decomposition of some of the ammonia formed during the operation, the results are usually too low. This decomposition may, to some extent, be prevented by adding a little sugar to the mixture of the substance and soda-lime. Furthermore, the method is not of universal application, as many nitrogenous organic substances, especially those belonging to the aromatic group, do not yield the whole of their nitrogen in the form of ammonia when heated with soda-lime.

Quantitative Determination of Chlorine, Bromine, and Iodine.—The halogens in an organic compound are very readily estimated by the method devised by Carius, which consists in oxidising the substance with nitric acid at a high temperature in presence of silver nitrate. Under these conditions the carbon is completely oxidised to carbon dioxide, and the hydrogen to water, the halogen combining with the silver; the chloride, bromide, or iodide of silver thus produced is collected and weighed in the ordinary way. The decomposition is carried out in a strong glass tube (*ab*, fig. 11), about 40 cm. long, sealed at one end (*a*); the substance is weighed out in a small glass receptacle, which is placed in the tube together with a few crystals of silver nitrate. Pure concentrated nitric acid having been added in quantity sufficient to fill $\frac{1}{6}$th to $\frac{1}{3}$d of the tube, the open end is drawn out and sealed, as shown at *b*. The tube is then placed in an iron case, and heated in a specially constructed apparatus (fig. 11) at a temperature necessary to ensure complete decomposition, usually at about 180°, for four hours; in the case of very stable substances, a much higher temperature and prolonged heating are required, and fuming nitric acid must be used. When *quite cold* the tube is opened,* the

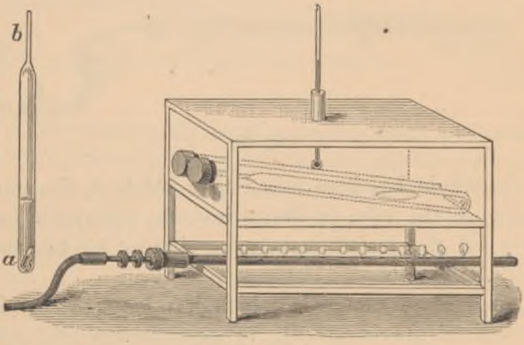


Fig. 11.

---

* Very great care must always be taken in working with sealed tubes, as they frequently explode, and serious accidents may occur. The tube is wrapped in a cloth as it is being removed from the iron case; after the pressure has been released by holding the capillary point in a flame, the tube is cut with a file in the usual way.

contents poured into distilled water, and the halogen silver salt treated in the usual way.

Another method of estimating the halogens, especially useful in the case of substances which are difficult to decompose, consists in heating the compound with pure, freshly ignited quicklime (prepared by calcining marble) in a narrow piece of combustion tube, about 50 cm. long, and closed at one end. In charging the tube a little lime is first introduced, and then the mixture of the substance with about ten times its weight of quicklime, the remainder of the tube being nearly filled with quicklime. After tapping gently to form a small channel for the passage of the gases, the tube is heated in a combustion furnace, the front part being raised to a bright red heat before the decomposition of the substance is proceeded with. When quite cold, the contents of the tube are cautiously shaken into excess of dilute nitric acid, the acid solution filtered from carbonaceous matter, and the halogen precipitated by the addition of silver nitrate.

Sulphur and **Phosphorus** may be estimated by heating the substance in a sealed tube with nitric acid, as described above, but without the addition of silver nitrate. The whole of the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid, which may then be estimated by the ordinary methods of analysis.

Another method for determining sulphur and phosphorus (applicable only in the case of organic acids and some non-volatile neutral compounds), consists in heating the substance with a mixture of potassium carbonate and nitre in a platinum crucible, until the product is colourless. Here, again, the substance is completely oxidised, and the sulphate or phosphate produced may be estimated in the solution of the residue.

CHAPTER II.

DEDUCTION OF A FORMULA FROM THE RESULTS OF ANALYSIS AND DETERMINATION OF MOLECULAR WEIGHT.

The quantitative analysis of an organic compound is usually made with one of two objects: either to prove that a particular compound is what it is supposed to be, or to ascertain the percentage composition of some pure substance, the nature of which is quite unknown.

In the first case, the results of the analysis are compared with the calculated percentage composition, and if the two series of values agree within the limits of experimental error, the fact is taken as evidence that the substance in question is what it was believed to be.

Example.—A substance obtained by oxidising a fat with nitric acid is suspected to be succinic acid, $C_4H_6O_4$, and, on analysis, it gives the following results: $C = 40{\cdot}56$, $H = 5{\cdot}12$, $O = 54{\cdot}32$ (by difference) per cent. Since the percentage composition of succinic acid, calculated from its formula, is $C = 40{\cdot}68$, $H = 5{\cdot}08$, $O = 54{\cdot}24$ per cent., the analysis affords strong confirmation of the conclusion previously arrived at.

In the second case, the nature of the substance being entirely unknown, it is necessary to deduce a formula from the analytical results—that is to say, to find the relative number of the atoms in the molecule of the compound.

Example.—The percentage composition of a substance is found to be $C = 84{\cdot}0$, $H = 16{\cdot}0$; deduce its formula. Since an atom of carbon weighs twelve times as much as an atom of hydrogen, the ratio between the number of *atoms* of carbon and the number of *atoms* of hydrogen is $\frac{84}{12} : \frac{16}{1}$ or $7 : 16$; the formula C_7H_{16} may therefore be given to the substance, this formula having been obtained by dividing the percentage of each element by the atomic weight of that element.

Example.—The percentage composition of a substance is $C = 39{\cdot}95$, $H = 6{\cdot}69$, $O = 53{\cdot}36$; deduce its formula. Proceeding as before, the ratio between the number of atoms is found to be 3·33 : 6·69 : 3·33,

$$C = \frac{39{\cdot}95}{12} = 3{\cdot}33,\ H = \frac{6{\cdot}69}{1} = 6{\cdot}69,\ O = \frac{53{\cdot}36}{16} = 3{\cdot}33;$$

dividing now each term by 3·33 to simplify, and allowing for experimental errors, the ratio of the atoms C : H : O = 1 : 2 : 1; the formula obtained in this way is therefore CH_2O.

In order, then, to calculate a formula from the percentage composition, the quantity of each element is divided by the atomic weight of that element, and the ratio is then expressed in whole numbers by dividing each term by the smallest, or by some simple fraction of the smallest term.

Example.—The percentage composition of a substance is $C = 19{\cdot}88$, $H = 6{\cdot}88$, $N = 46{\cdot}86$, $O = 26{\cdot}38$; deduce its formula.

$$C = \frac{19{\cdot}88}{12} = 1{\cdot}657 \div 1{\cdot}649 = 1$$

$$H = \frac{6{\cdot}88}{1} = 6{\cdot}880 \div 1{\cdot}649 = 4$$

$$N = \frac{46{\cdot}86}{14} = 3{\cdot}347 \div 1{\cdot}649 = 2$$

$$O = \frac{26{\cdot}38}{16} = 1{\cdot}649 \div 1{\cdot}649 = 1$$

The formula, therefore, is CH_4N_2O; the ratio of the atoms determined experimentally is, of course, not exactly 1 : 4 : 2 : 1, owing to unavoidable errors.

The formula calculated from the results of analysis is the *simplest* expression of the *ratio* of the atoms, and is termed an **empirical formula**; such a formula may, or may not, show how many atoms of each element the molecule of the substance contains, because substances such as formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, have the same percentage composition, and would all be found, on analysis, to have the same empirical formula, CH_2O.

Determination of Molecular Weight.

Further investigation is necessary in order to deduce the **molecular formula** of a compound, by which is meant a formula expressing not only the ratio, but also the actual number of the atoms in the molecule; in other words, the **molecular weight** of the compound must be determined. If, for example, it can be proved that a compound of the empirical formula CH_2O has a molecular weight = 60, this fact shows that the molecular formula is $C_2H_4O_2$ ($C_2 = 24$, $H_4 = 4$, $O_2 = 32$; total 60), and not CH_2O or $C_3H_6O_3$; that is to say, the molecule consists of two atoms of carbon, four of hydrogen, and two of oxygen.

The determination of the molecular weight of a substance is therefore of great importance, and for this purpose certain physical methods, described later, are adopted whenever possible; no purely chemical methods are known by which the molecular weight can be established with certainty, although such methods often afford some indication of the probable molecular weight, as will be seen from the following examples.

Chemical Methods.—In the case of organic acids, the analysis of a salt of the acid is often of value; the silver salt is generally employed for this purpose, a weighed quantity being ignited in a porcelain crucible, when complete decomposition ensues, and a residue of pure silver is obtained.

Example.—The percentage composition of an organic acid is $C = 39{\cdot}95$, $H = 6{\cdot}69$, $O = 53{\cdot}36$; its empirical formula is therefore CH_2O. Its silver salt was prepared; 0·2960 gram of the pure salt gave on ignition 0·1620 gram of silver, so that the percentage of silver in the salt is $\frac{0{\cdot}1620 \times 100}{0{\cdot}2960} = 54{\cdot}73$

Now, since 54·73 parts of silver are contained in 100 parts of the salt, 107·7 parts of silver will be contained in $\frac{100 \times 107 \cdot 7}{54 \cdot 73} = 196 \cdot 78$ parts of salt; but 107·7 is the atomic weight of silver, so that if the salt contain one atom of silver, its molecular weight must be 196·78, and, as the salt is formed from the acid by displacing 1 part of hydrogen by 107·7 parts of silver, the molecular weight of the acid must be $196 \cdot 78 - 107 \cdot 7 + 1 = 90 \cdot 08$. Since, however, the acid is composed of carbon, hydrogen, and oxygen, the atomic weights of which are all taken as whole numbers, the molecular weight of the acid must also be a whole number—that is to say, 90—the value found experimentally being not quite correct, owing to errors in the analysis. The molecular weight of the acid being 90, its *molecular formula* is not CH_2O (= 30) or $C_2H_4O_2$ (= 60), but $C_3H_6O_3$ (= 90), that of the silver salt being $C_3H_5O_3Ag$ (= 196·7).

This conclusion is based on the assumption that the silver salt contains only 1 atom of silver—that is to say, that the acid is monobasic; until this assumption is proved to be correct, the analysis of the silver salt does not establish the molecular formula of the acid. If the acid had the molecular formula $C_6H_{12}O_6$, and contained two atoms of displaceable hydrogen—that is to say, were dibasic—the silver salt $C_6H_{10}O_6Ag_2$ would contain, as before, 54·75 per cent. of silver, and the molecular weight, calculated as above, would again appear to be 90. But if the acid were dibasic, it would probably be possible to displace only one atom of hydrogen, and obtain an acid salt, $C_6H_{11}O_6Ag$, the analysis of which would point to the molecular formula $C_6H_{12}O_6$. If this were found impossible, the fact would be taken as evidence against this molecular formula, and the conclusion would be drawn that the probable molecular formula is $C_3H_6O_3$.

Most organic bases combine with hydrochloric acid to form salts which, like ammonium chloride, form double salts with platinic chloride and with auric chloride. These double salts usually have the composition B'_2,H_2PtCl_6, and $B',HAuCl_4$, where B′ represents one molecule of a monacid base, such as methylamine CH_5N, ethylamine C_2H_7N, &c. When these salts are ignited in a porcelain crucible, pure finely divided platinum, or gold, remains; so that the percentage of metal in the salt is very easily determined. Assuming that one molecule of the salt contains 1 atom of platinum or gold, and that the salt has the above composition, the molecular weight of the base can be calculated.

Example.—The platinum double salt (*platinochloride*) of an organic base gave on ignition 37·2 per cent. of platinum; what is its probable molecular weight? Since 37·2 parts of platinum are contained in 100 parts of the salt, 197 parts of the metal are contained in $\frac{100 \times 197}{37 \cdot 2} = 529 \cdot 4$ parts of salt, and, as 197 is the atomic weight of platinum, the molecular weight of the salt is 529·4. The molecular weight of the base (C_3H_9N) is therefore $\frac{B'_2,H_2PtCl_6 - H_2PtCl_6}{2}$ or

$$\frac{529 \cdot 4 - (2 + 197 + 212 \cdot 4)}{2} = \frac{529 \cdot 4 - 411 \cdot 4}{2} = 59.$$

As in the case of acids, so in that of bases, the molecular weight calculated from the analytical results may be incorrect, because it is not known whether the compound is a monacid base or not. Some bases are diacid, and form platinochlorides of the composition B'',H_2PtCl_6, so that a diacid base of the molecular weight 118 would yield a platinochloride containing the same percentage of platinum as the salt of a monacid base of the molecular weight 59.

It will be seen from the above examples, that, assuming that there is only one atom of any particular element in the molecule of the compound, the probable molecular weight may be calculated from the results of analysis.

This being the case, the probable molecular formula of a compound may often be determined by preparing and analysing some simple derivative.

Example.—A liquid hydrocarbon has the percentage composition C = 92·31, H = 7·69; its empirical formula is therefore CH. On treating this hydrocarbon with bromine, it yields hydrogen bromide and a bromo-derivative consisting of C = 45·86, H = 3·18, Br = 50·96 per cent. The empirical formula of this derivative is

$$\left.\begin{aligned} C &= \frac{45{\cdot}86}{12} = 3{\cdot}82 \div 0{\cdot}637 = 6 \\ H &= \frac{3{\cdot}18}{1} = 3{\cdot}18 \div 0{\cdot}637 = 5 \\ Br &= \frac{50{\cdot}96}{80} = 0{\cdot}637 \div 0{\cdot}637 = 1 \end{aligned}\right\} = C_6H_5Br.$$

Now since, from experience, there are strong grounds for supposing that the number of atoms of carbon in the molecule is not changed on treating with bromine, the probable molecular formula of the hydrocarbon is C_6H_6; it cannot be less than this, but it may be greater. A hydrocarbon $C_{12}H_{12}$, for example, might give a bromo-derivative $C_{12}H_{10}Br_2$, and these compounds would have the same percentage composition as C_6H_6 and C_6H_5Br respectively.

The probable molecular weight may often be deduced with tolerable certainty by studying the methods of formation, and the chemical and physical properties of a substance. When, for example, acetone is distilled with concentrated sulphuric acid, it is converted into a hydrocarbon which, on analysis, is found to have the empirical formula C_3H_4. The fact that this hydrocarbon boils at 163° affords very strong evidence that the molecular formula is not C_3H_4, or C_6H_8, but probably C_9H_{12}, because other hydrocarbons which contain only 3 or 6 atoms of carbon boil at a temperature much below 163°, and an increase in molecular weight is generally accompanied by a rise in boiling-point.

Physical Methods.—One of the most important physical methods by which the molecular weight of a compound can be ascertained is by determining its vapour density. This method is based on the hypothesis that equal volumes of all gases measured under the same conditions of temperature and pressure, contain the same number of molecules (Avogadro's Law). If, therefore, the weights of equal volumes of various gases be determined under the same conditions, these weights must be in the same proportion as the weights of the molecules of the gases. In other words, the molecular weight of a substance can be determined by ascertaining the weight of a given volume of the vapour of the substance, compared with the weight of the same volume of hydrogen measured under the same conditions. The former divided by the latter is the *specific gravity* or *vapour density* (V.D.) of the gas compared with hydrogen as unity.

Now, since the vapour density is a number expressing how many times a given volume of the gas is heavier than the same volume of hydrogen, it also expresses how many times one molecule of the substance is heavier than one *molecule* of hydrogen (= 2), because equal volumes contain an equal number of molecules. The molecular weight, on the other hand, is a number expressing how many times one molecule of the substance is heavier than one *atom* of hydrogen (= 1); therefore the molecular weight is double the vapour density, because the standard with which it is compared is half as great: M.W. = V.D. × 2.

Sometimes air is taken as unit weight in stating the specific gravity or vapour density of a gas; since air is 14·43 times heavier than hydrogen, the sp. gr. compared with air is $\frac{1}{14 \cdot 43}$ of the value when compared with hydrogen; so that, in order to obtain the molecular weight, the sp. gr. is in such cases multiplied by $28 \cdot 86 = 2 \times 14 \cdot 43$.

Determination of Vapour Density.

The vapour density of a substance is ascertained experimentally, (*a*) by measuring the volume occupied by the vapour of a known weight of the substance at known temperature and pressure, or (*b*) by ascertaining the weight of a known volume of the vapour of the substance at known temperature and pressure. The observed volume of the vapour is then reduced to 0° and 760 mm., and the weight of a volume of hydrogen at 0° and 760 mm. equal to the corrected volume of the vapour is calculated; the weight of the vapour divided by that of the hydrogen is the vapour density.

Example.—An organic liquid has the empirical formula $C_4H_{10}O$; 0·062 gram of the liquid gave 23·2 c.c. of vapour at 50° and 720 mm., what is its molecular formula?

$$\text{The volume at } 0^\circ \text{ and } 760 = 23{\cdot}2 \times \frac{720}{760} \times \frac{273}{273+50} = 18{\cdot}57 \text{ c.c.}$$

and 1 c.c. of hydrogen at N.T.P. weighs 0·0000896 gram; therefore 18·57 c.c. weigh 0·00164 gram.

$$\frac{\text{The weight of the vapour}}{\text{The weight of the hydrogen}} = \frac{0{\cdot}062}{0{\cdot}00164} = 37{\cdot}7 = \text{V.D.}$$

$$\text{The molecular weight} = \text{V.D.} \times 2 \text{ or } 37{\cdot}7 \times 2 = 75{\cdot}4.$$

Since the molecular weight of a compound of the empirical formula $C_4H_{10}O$ is calculated to be 74, the determination of the vapour density proves that the molecular formula of the liquid is $C_4H_{10}O$, so that in this case the empirical is identical with the molecular formula. The molecular weight determined experimentally from the vapour density frequently differs from the theoretical value by several units, owing to experimental errors; this, however, is of little importance, since all that is required in most cases is to decide between multiples of the empirical formula, in the above example, between $C_4H_{10}O = 74$, $C_8H_{20}O_2 = 148$, &c.

The determination of the vapour density is only possible when a substance can be converted into vapour without decomposition under the conditions of the experiment. In many cases, however, a non-volatile compound, or a compound which cannot be vaporised without decomposition, can be converted into some simple derivative which is volatile, so that, by determining the vapour density of the latter, the molecular weight of the parent substance can be ascertained.

The following are some of the methods employed in determining vapour density:

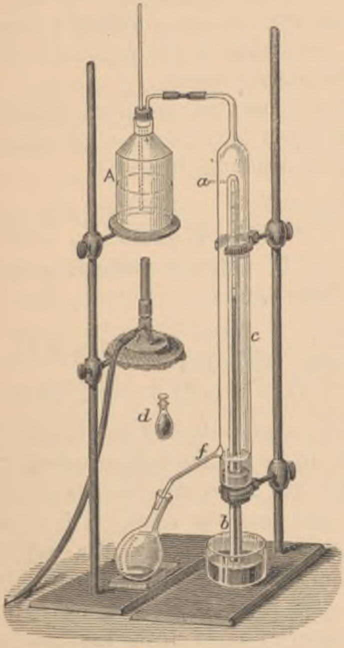


Fig. 12.

Gay-Lussac's or Hofmann's Method.—A graduated barometer tube (*ab*, fig. 12), about 85 cm. long, and 35 mm. wide, filled with and then inverted in mercury, is surrounded by a wider tube (*c*), through which the vapour of some liquid boiling at a known and constant temperature is passed. For this purpose the upper end of the outer tube (*c*) is connected with a vessel (A), usually made of copper, containing the heating liquid, which is kept in rapid ebullition. The liquids most commonly employed are water (b.p. 100°), xylene (b.p. 140°), aniline (b.p. 183°), and ethyl benzoate (b.p. 213°). The condensed liquid escapes through the side-tube (*f*), and is collected for subsequent use.

As soon as the barometer tube is at a constant temperature, a weighed quantity (about 0·05 gram) of the substance contained in a small stoppered vessel (*d*), which it fills completely, is introduced into the open end (*b*). The vessel immediately rises to the surface of the mercury in the tube, the substance vaporises into the Torricellian vacuum, and the mercury is forced downwards; as soon as the level remains stationary, the *volume* of the vapour is noted. The *temperature* of the vapour is the boiling-point of the liquid employed to heat the barometer tube. The *pressure* is determined by subtracting the height of the column of mercury in the inner tube (*ab*), above the level in the trough, from the height of the barometer, both readings having been first reduced to 0°.* The *weight* of the vapour is that of the substance taken.

The great advantage of this method lies in the fact that it affords a means of determining the vapour density of substances under greatly reduced pressures, and therefore at temperatures very much below their ordinary boiling-points, so that it can often be employed with success in the case of substances which are only volatile without decomposition under reduced pressure.

Dumas' Method.—A globe-shaped vessel of about 200 c.c. capacity (*a*, fig. 13), the neck of which is drawn out to a fine tube, is carefully weighed, the temperature ($t'°$) and pressure (P′) being noted. A fairly large quantity of the substance (about 8–10 grams) is now introduced by gently heating the globe and quickly dipping the tube into the liquid. The vessel is then immersed in an oil-bath (shown in section in fig. 13) containing a thermometer (*b*), and heated at a constant temperature, at least 20° above the boiling-point of the compound. The air in the apparatus is quickly expelled by the rapid vaporisation of the substance, and the vessel is filled with the vapour of the liquid. As soon as the whole of the liquid has been vaporised, which is known by the fact that gas ceases to issue from the fine tube, the point of the latter is sealed before the blowpipe, the *temperature* of the oil-bath ($t°$) and the *height of the barometer*

Fig. 13.

---

* By correcting for the expansion of the mercury.

(P) being noted. The globe is allowed to cool, and is then cleaned, dried, and weighed.

The point of the tube is now broken under water (or mercury), which rushes in and fills the globe completely, except for the minute quantity of liquid produced by the condensation of the vapour in the globe; the globe is again weighed, and its capacity or *volume* (v) calculated from the weight of the water contained in it, the weight in grams being equivalent to the volume in c.c. The volume may also be measured directly by transferring the liquid from the globe to a graduated vessel.

When the globe is weighed the first time it is full of air, but at the second weighing it is full of vapour; if, therefore, the first weight be subtracted from the second, the difference, W, is the weight of the volume, v, of vapour *less* the weight of the volume, v, of air.* The weight of the air is calculated by reducing the volume, v, at t'° and P′ to N.T.P., and multiplying by 0·001293, the weight of 1 c.c. of air at N.T.P.; this weight added to W gives the weight of the volume, v, of vapour at t° and P. The volume, v, of vapour at t° and P is then reduced to N.T.P., the weight of an equal volume of hydrogen at N.T.P. calculated, and divided into the weight of the vapour.

Victor Meyer's Method.—Owing to its simplicity, and the rapidity with which the determination may be made, this method is now used whenever possible; the apparatus is represented in fig. 14. The bulb tube (ab) is closed (at a) by means of an india-rubber stopper, and heated by the vapour of some constant boiling liquid † contained in the outer vessel (c); as the air expands it escapes through the narrow tube (d), which dips under the water in the vessel (e). As soon as the

---

* Changes in the temperature of the air, height of the barometer, and volume of the globe occurring during the experiment may be neglected.

† See page 44; in determining the vapour density of substances of high boiling-point, diphenylamine (b.p. 310°) or sulphur (b.p. 448°) may be used, or the bulb tube (ab) may be heated at a constant temperature in a metal bath.

temperature of the bulb tube (*ab*) becomes constant—that is to say, when bubbles of air cease to escape (from *d*)—the graduated tube (*g*) is filled with water and inverted over the end of *d;* the stopper (*a*) is now removed, and a small bottle or bulb (*d*, fig. 12) completely filled with a weighed quantity (about 0·1 gram) of the liquid dropped into the apparatus,* the stopper being replaced as quickly as possible. The substance immediately vaporises, and the vapour forces the air out of the apparatus into the graduated vessel (*g*). When air ceases to issue (from *d*), the stopper (*a*) is at once taken out to prevent the water (in *e*) from passing into the apparatus.

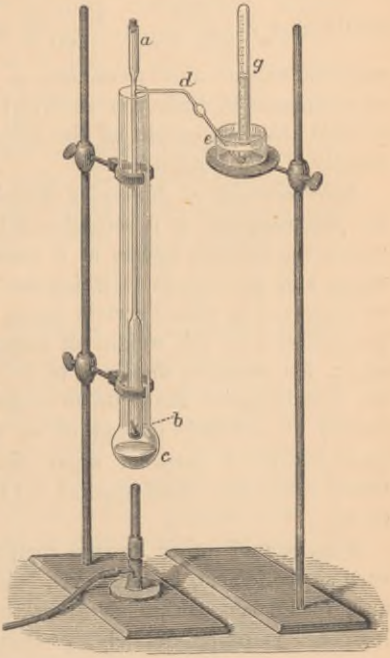


Fig. 14.

The *volume* of the vapour is ascertained by measuring the volume (*v*) of the air in the graduated tube, its *temperature* (t°) and the barometric *pressure* (P) being noted. The volume of the air (in *g*) is not the same as that actually occupied by the hot vapour (in *ab*), because the air displaced has been cooled, and is measured under a different pressure. Its volume now is equal to that which the given weight of vapour would

---

* In order to prevent fracture, a little mercury or sand is usually placed in *b*.

occupy under the same conditions of temperature and pressure.

The temperature of the volume, v, of air being t°, and the height of the barometer P, the volume at N.T.P. would be $v \times \frac{273}{273 + t} \times \frac{P - w}{760}$, w being the tension of aqueous vapour at t° (foot-note, p. 32). The weight of an equal volume of hydrogen at N.T.P. is then calculated and divided into the weight of the substance taken; the vapour density is thus obtained.

Determination of Molecular Weight from the depression of the freezing-point of a solvent.—When sugar is dissolved in water, the solution freezes at a lower temperature than pure water, and the extent to which the freezing-point is lowered or depressed is, within certain limits of concentration, directly proportional to the weight of sugar in solution; 1 part of sugar, for example, dissolved in 100 parts of water depresses the freezing-point about 0·058°—that is to say, the solution freezes at – 0·058° instead of at 0°, the freezing-point of pure water; 2 parts of sugar dissolved in 100 parts of water lower the freezing-point 0·116°, 3 parts 0·174°, and so on.

Solutions of other organic compounds in other solvents, such as acetic acid, benzene, &c., behave in a similar manner, and, in sufficiently dilute solutions, the depression of the freezing-point is (approximately) proportional to the number of molecules of the dissolved substance in a given weight of the solvent, and independent of the nature of the substance. If, then, molecular proportions of various substances be separately dissolved in a given (and sufficiently large) quantity of the same solvent, the depression of the freezing-point is the same in all the solutions, but different with different solvents. In other words, if the molecular weight in grams of any substance be dissolved in 100 grams of a given solvent, the depression of the freezing-point is a constant quantity, K, which is termed the molecular depression of that solvent.

When, therefore, this constant has been determined for any solvent, the molecular weight, M, of a substance can be ascertained by observing the depression of the freezing-point of a sufficiently dilute solution, containing a known quantity of the substance. If 1 gram of the substance were dissolved in 100 grams of the solvent, the observed depression, D, would be $K \times \frac{1}{M}$, because K is the depression produced by the molecular weight in grams—that is to say, by M grams—and the depression varies directly with the weight of dissolved substance. If, again, P grams of the substance were dissolved in 100 grams of the solvent, the depression, $D = K \times \frac{P}{M}$; hence the molecular weight $M = \frac{K \times P}{D}$, so that K and P being known, if the depression be ascertained experimentally, the molecular weight, M, can be calculated.

This method of determining the molecular weight of organic compounds was first applied by Raoult, and is usually known as Raoult's or the *cryoscopic method*. The observation is usually made with the aid of the apparatus devised by Beckmann (fig. 15) in the following manner: A large tube (A), about one inch in diameter, and provided with a side-tube (B), is closed with a cork (C), through which pass a stirrer (*a*) and a thermometer (*b*) graduated to $\frac{1}{100}$°. A weighed quantity (about 25 grams) of the solvent is placed in the tube, which is then fitted into a wider tube (D), which serves as an air-jacket and prevents a too rapid change in temperature. The apparatus is now introduced through a hole in the metal plate (E) into a vessel which is partly filled with a liquid, the temperature of which is about 5° lower than the freezing-point of the solvent. The solvent (in A) is now constantly stirred, when the thermometer rapidly falls and sinks below the freezing-point of the solvent, until the latter begins to freeze; the thermometer now rises again, but soon becomes stationary at a temperature which is the *freezing-point of the solvent*. A weighed quantity of the substance is now introduced through the side-tube (B), and after first allowing the solvent to melt completely, the *freezing-point of the solution* is ascertained as before. The difference between the two freezing-points is the depression (D); the molecular weight of the substance is then calculated with the aid of the above formula.

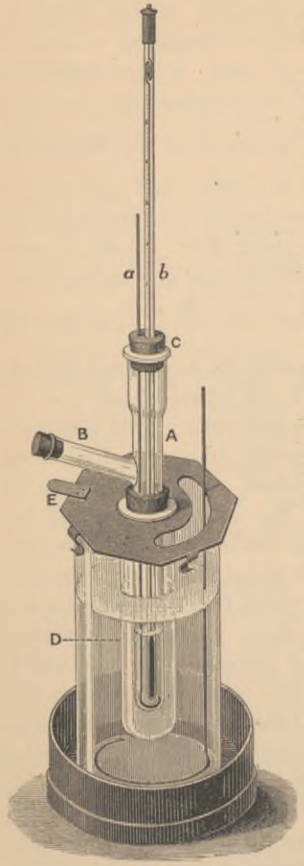


Fig. 15.

Example.—4·9818 grams of cane-sugar ($C_{12}H_{22}O_{11}$) dissolved in 96·94 grams of water caused a depression in the freezing-point of 0·295° (D). Since 96·94 grams of the solvent contain 4·9818 grams of substance P, the quantity in 100 grams = 5·139 grams. The constant, K, for water is 19; hence the molecular weight, M, of cane-sugar is found to be $\frac{19 \times 5{\cdot}139}{0{\cdot}295}$ = 331, the true value being 342.

As in the determination of molecular weight from the vapour density, the experimental and theoretical values frequently differ by several units, this is of little importance for the reasons already stated.

The constants, K, for the solvents most frequently used are: acetic acid, 39; benzene, 49; water, 19.

CHAPTER III.

CONSTITUTION OR STRUCTURE OF ORGANIC COMPOUNDS.

Even when the molecular formula of an organic compound has been established by the methods described in the foregoing pages, the most difficult and important steps in the investigation of the substance have still to be taken.

Many cases are known in which two or more compounds have the same molecular formula, and yet are different in chemical and physical properties; there are, for example, two compounds of the molecular formula $C_2H_4O_2$, three of the molecular formula C_5H_{12}, and so on. Now, if the properties of a compound depended simply on the nature and number of the atoms of which it is composed, there could not be two or more different substances having the same molecular formula.

The only possible conclusion to be drawn from the proved existence of such compounds is, therefore, that the difference between them is a difference in **constitution**; in other words, that the atoms of which their molecules are composed are differently arranged.

There is nothing at all improbable in this conclusion: in the case of simple inorganic compounds, the behaviour of any particular atom depends on the nature of the other atoms or groups of atoms with which it is united. The hydrogen atoms in ammonia, NH_3, for example, are not, but the hydrogen atoms in sulphuric acid, H_2SO_4, are displaceable by zinc, and the only difference between them is a difference in their state of combination. It is just the same in the case of organic compounds; the state of combination determines the behaviour of the atoms, and therefore the properties of the compound depend on the state of combination of all the atoms of which its molecule is composed.

Now, although the actual arrangement or structure of the molecule cannot be directly determined, it is possible to obtain some idea of the state of combination of the atoms by studying the chemical behaviour of the compound. Methyl alcohol, CH_4O, for example, is readily acted on by sodium, yielding a compound of the composition CH_3NaO, which is formed by the displacement of one hydrogen atom (*a*) by one atom of the metal; the other three hydrogen atoms in methyl alcohol cannot be displaced, no matter how large a quantity of sodium be employed. Again, when methyl alcohol is treated with hydrogen chloride under certain conditions, one atom of hydrogen and one atom of oxygen are displaced by one atom of chlorine, a compound of the composition CH_3Cl being formed,

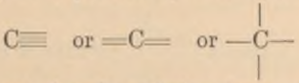
$$CH_4O + HCl = CH_3Cl + H_2O.$$

When this compound is heated with water, it is transformed into methyl alcohol, one atom of chlorine being displaced by one atom of oxygen and one atom of hydrogen; the change is, in fact, the reverse of that represented above.

From these and other experiments it is concluded that methyl alcohol contains one atom of hydrogen (*a*) combined differently from the other three; also that one atom of hydrogen is closely associated with the oxygen atom, because the two are constantly displaced and replaced together; as, further, the compound CH_3Cl does not contain a hydrogen atom which can be displaced by sodium, it is concluded that the particular hydrogen atom (*a*) in methyl alcohol which is displaceable by sodium is the same as that which is closely associated with the oxygen atom. These conclusions may be expressed by the formula $CH_3(OH)$.

Now any compound, such as ethyl alcohol, C_2H_6O, propyl alcohol, C_3H_8O, &c., which behaves like methyl alcohol under the same conditions, may be assumed to contain one atom of hydrogen and one atom of oxygen in the same state of combination as in methyl alcohol, and may be represented by formulæ such as $C_2H_5(OH)$, $C_3H_7(OH)$, &c.; in other words, the constitution of any compound may be ascertained by comparing its behaviour under various conditions with that of some compound of known constitution. Atoms or groups of atoms which are found to show the same behaviour are considered to be in a similar state of combination. In this way it is possible to determine the state of combination of many or of all the atoms of which the molecule is composed, and then, by using suitable formulæ, not only the state of combination or constitution, but also the chemical behaviour, of the substance may be expressed. Formulæ employed for this purpose are called **rational** or **constitutional** formulæ.

Another way of representing compounds is by means of **graphic formulæ**, the object of which is to express still more fully and clearly the constitution and chemical behaviour of the substance. Before giving examples of the use of graphic formulæ, it will be necessary to consider the molecular formulæ of some of the simpler organic compounds. For this purpose attention may be directed in the first place to compounds such as (*a*) CH_4 and $CHCl_3$; (*b*) CO_2 and COS; (*c*) $COCl_2$; and (*d*) HCN, which contain only one atom of carbon in the molecule. In all these compounds the atom of carbon is combined with (*a*) 4 monovalent or monad atoms, (*b*) 2 dyad atoms, (*c*) 1 dyad and 2 monad atoms, or (*d*) 1 triad and 1 monad atom—that is to say, with four monad atoms or their valency equivalent. With the doubtful exception of carbon monoxide, CO,* no compound containing only one carbon atom is known, in which the carbon atom is combined with *more* or *less* than four monad elements or their valency equivalent; carbon, therefore, is *tetravalent*, and this fact may be expressed by writing its symbol,



$$\mathrm{C}\!\equiv\!\!\!- \quad \text{or} \quad =\!\mathrm{C}\!= \quad \text{or} \quad -\overset{|}{\underset{|}{\mathrm{C}}}-$$

or in any other way, four lines being drawn simply to express its tetravalent character.

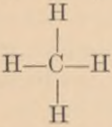
For similar reasons the monovalent hydrogen atom may be

---

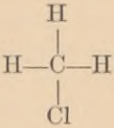
* Oxygen may be assumed to be a tetrad in CO.

represented by H—, divalent oxygen by O= or —O—, trivalent nitrogen by N≡ or , and so on, the number of lines serving to recall the valency of the atom.

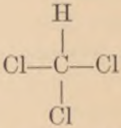
If, now, in the case of substances such as CH_4, CH_3Cl, $CHCl_3$, in which the carbon atom is united with four monad atoms, each of the latter be placed at the extremity of one of the four lines which represent the valency of carbon, the following formulæ are obtained :



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

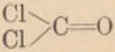
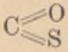


$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ Cl \end{array}$$

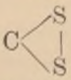


$$\begin{array}{c} H \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

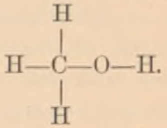
If in the case of substances such as CO_2, $COCl_2$, COS, each of the dyad atoms be given two lines, the compounds will be represented by the formulæ

$O=C=O$  

Similarly, HCN may be expressed by the formula $H-C\equiv N$.

Formulæ of this kind are termed *graphic formulæ*. They are intended to express in a purely diagrammatic manner the constitution of the several compounds—that is to say, the state of combination and the valency of each of the atoms in the molecule. In all such formulæ, therefore, the number of lines running to or from any given symbol must be the same as the number of monad atoms with which the element represented by that symbol is known to combine. The constitution of carbon bisulphide, for example, cannot be expressed by the formula , or that of carbon dioxide by a formula such as O—C—O, because the valency of the elements is not correctly indicated by the number of lines.

These lines are sometimes called **valencies**, more frequently **bonds** or **linkings**; in the graphic formula $H-C\equiv N$, the hydrogen atom is said to be combined with carbon by one bond or linking, the nitrogen atom by three. The hydrogen and nitrogen atoms are not directly combined, but are both united with carbon.

It must not be supposed, however, that these lines are intended to represent the actual force or attraction which causes the atoms to combine. They are simply expressions of valency or combining capacity, and may be shortened or lengthened at will without altering their significance: as a rule, they are shortened, as in the formulæ $H\cdot C\vdots N$ and $O:C:S$, or brackets are employed instead, as in $CH_3(OH)$, which signifies the same as $CH_3\cdot OH$ and  $H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$. All these, except the last, would be termed constitutional rather than graphic formulæ, but there is no sharp difference between them.

All such formulæ are based on considerations of valency and on a study of the chemical behaviour of the compounds which they represent; they express, in fact, in a concise and simple manner the most important chemical properties of the compound.

CHAPTER IV.

THE PARAFFINS, OR HYDROCARBONS OF THE METHANE SERIES.

It has already been noted that carbon differs from all other elements in forming an extraordinarily large number of compounds with hydrogen; these compounds, composed of hydrogen and carbon only, are called **hydrocarbons.**

Methane, or **Marsh-gas,** CH_4, is the simplest hydrocarbon. It is met with, as its name implies, in marshes and other places in which the decomposition or decay of vegetable matter is taking place under water. On stirring a marshy pond or swamp, bubbles consisting of marsh-gas, carbon dioxide, and other gases, frequently rise. It is one of the principal constituents of the gas which streams out of the earth in the petroleum districts of America and Russia; it also occurs in coal-mines, the gas (fire-damp) which issues from the fissures in the coal sometimes containing as much as 80–90 per cent. of methane, to the presence of which, mixed with air, explosions in coal-mines are due. Ordinary coal-gas usually contains about 40 per cent. of methane.

Methane is formed* when zinc methyl† (p. 216) is decomposed with water,

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2.$$

It is also obtained when sulphuretted hydrogen or steam, together with the vapour of carbon bisulphide, is passed over heated copper,

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$$
$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO;$$

and by reducing carbon tetrachloride with sodium amalgam (p. 93),

$$CCl_4 + 4H_2 = CH_4 + 4HCl.$$

Since carbon bisulphide and hydrogen sulphide may be produced by the direct union of their constituent elements, and carbon tetrachloride is formed on treating carbon bisulphide with chlorine, these reactions are of considerable theoretical importance, as they afford a means of synthesising methane from its elements. They are often quoted as examples of the synthesis of an organic compound from inorganic materials, but such a view is rather misleading, because carbon and carbon bisulphide are just as truly 'organic' as methane.

---

* The words *formed*, *obtained*, and *produced* are used when the method is of theoretical importance, and not suitable for the actual *preparation* of the compound.

† Compounds, such as zinc methyl, are often unavoidably introduced long before their properties are described; in such cases references are given. The groups of atoms, CH_3-, C_2H_5-, C_3H_7-, and C_4H_9-, are termed *methyl*, *ethyl*, *propyl*, and *butyl* respectively.

Methane is prepared by heating one part of anhydrous sodium or potassium acetate with four parts of soda-lime in a hard glass tube or retort, and collecting the gas over water,

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

The gas obtained in this way contains small quantities of hydrogen, ethylene (p. 72), and other impurities.

Pure methane is prepared by slowly running methyl iodide from a dropping funnel into a flask containing a zinc-copper couple* covered with dilute alcohol, to which a few drops of sulphuric acid have been added. The methyl iodide is reduced by the nascent hydrogen formed by the action of the dilute acid on the zinc-copper couple, and a constant stream of methane is obtained without application of heat,

$$CH_3I + 2H = CH_4 + HI.$$

In a similar manner, all halogen derivatives of marsh-gas (p. 171) are converted into marsh-gas on treatment with nascent hydrogen, generated from zinc and hydrochloric acid, from sodium amalgam and water, or in any other suitable manner (p. 93).

Methane is a colourless, tasteless gas; it condenses to a liquid at − 11° under a pressure of 180 atmospheres. It burns with a pale-blue, non-luminous flame, and forms a highly explosive mixture with certain proportions of air or oxygen,

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O \\ \text{2 vols.} & + & \text{4 vols.} & = & \text{2 vols.} & + & \text{4 vols.} \end{array}$$

It is almost insoluble in water, but rather more soluble in alcohol. It is very stable; when passed through bromine, potash, nitric acid, sulphuric acid, solution of potassium permanganate, and solution of chromic acid, it is not absorbed or changed in any way. When mixed with chlorine in the dark, no action takes place; but if a mixture of 1 vol. of

---

* Granulated zinc coated with a thin layer of copper by immersion in a dilute solution of copper sulphate and subsequent drying.

methane and 2 vols. of chlorine be exposed to direct sunlight, explosion ensues, and carbon is deposited,

$$CH_4 + 2Cl_2 = C + 4HCl.$$

In diffused sunlight there is no explosion, but after some time a mixture of hydrochloric acid and four other compounds is produced, the proportion of each depending on the quantity of chlorine present, and on the conditions of the experiment.

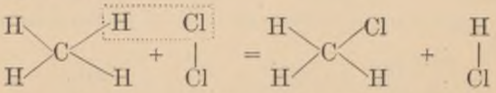
$CH_4 + Cl_2 = CH_3Cl + HCl.$
Methyl Chloride.

$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl.$
Methylene Chloride.

$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$
Chloroform.

$CH_4 + 4Cl_2 = CCl_4 + 4HCl.$
Carbon Tetrachloride.

All these compounds are formed by the displacement of one or more hydrogen atoms by an equivalent quantity of chlorine. The carbon atom cannot combine with more than four monad atoms, so that hydrogen must be displaced if any action at all take place. Now it may be supposed that in the formation of methyl chloride, CH_3Cl, for example, one of the hydrogen atoms is drawn away from the carbon by the superior attraction of the chlorine, and that one atom of chlorine takes up the vacant place in the molecule without the other atoms being disturbed or their state of combination altered; this change may then be represented graphically thus:



In the formation of methylene chloride, CH_2Cl_2, it may be supposed that a repetition of this process occurs, and so also in the case of the other products; in other words, it may be assumed that in all the above examples the action of the chlorine is not such that the molecule of marsh-gas is completely broken up into atoms, which then, by combination with chlorine, form totally new molecules, but that certain atoms simply change places. To such changes as these, in which certain atoms are simply displaced by an equivalent quantity of other atoms, without the state of combination of the rest of the molecule being altered, the term **substitution** is applied, and the compounds formed as the result of the change are called **substitution products.**

The four compounds mentioned above are substitution products of methane and of one another: methyl chloride, CH_3Cl, is a mono-substitution product, methylene chloride, CH_2Cl_2, a di-substitution product of marsh-gas, and so on; chloroform, $CHCl_3$, is a tri-substitution product of methane, a di-substitution product of methyl chloride. If, by treatment with nascent hydrogen in the manner described above, any of these substitution products be reconverted into marsh-gas or into one another, the change would be termed **inverse substitution.**

The only way in which it is possible to produce a change in marsh-gas, or in any of its chloro-substitution products, is by a process of direct or inverse substitution. The atom of carbon already holds in combination the maximum number of atoms, and some of them must be displaced if any other atom enter the molecule. Compounds such as these, in which the maximum combining capacity of all the carbon atoms is exerted, and which can only yield derivatives by substitution, are termed **saturated.**

Ethane, ethyl hydride, or dimethyl, C_2H_6, like methane occurs in the gas which issues from the earth in the petroleum districts. It is formed when methyl chloride or methyl iodide, CH_3I, is treated with sodium,

$$2CH_3I + 2Na = C_2H_6 + 2NaI;$$

this reaction affords a means of preparing ethane from its elements, because methane can be formed from its elements, as already described, and then converted into methyl chloride by treatment with chlorine.

Ethane is also formed when zinc ethyl (p. 215) is decomposed with water,

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2;$$

when ethylene (p. 72) is treated with nascent hydrogen,

$$C_2H_4 + 2H = C_2H_6;$$

and when methyl iodide is treated with zinc methyl,

$$2CH_3I + Zn(CH_3)_2 = 2C_2H_6 + ZnI_2.$$

Ethane is prepared by reducing ethyl iodide with the zinc-copper couple, exactly as described in the preparation of pure methane,

$$C_2H_5I + 2H = C_2H_6 + HI,$$

or by the electrolysis of dilute acetic acid, or of a concentrated aqueous solution of potassium acetate (Kolbe). When acetic acid is used, ethane and carbon dioxide are evolved at the positive, hydrogen at the negative pole,

$$\begin{matrix} CH_3{\cdot}CO_2H \\ CH_3{\cdot}CO_2H \end{matrix} = \overbrace{C_2H_6 + 2CO_2} + H_2;$$

when potassium acetate is employed, the following decompositions occur:

$$\begin{matrix} CH_3{\cdot}CO_2K \\ CH_3{\cdot}CO_2K \end{matrix} = \overbrace{C_2H_6 + 2CO_2} + 2K$$

and

$$2K + 2H_2O = 2KOH + H_2,$$

so that the same gases are evolved as before.

Ethane is a colourless, tasteless gas, which liquefies at 4° under a pressure of 46 atmospheres; it is practically insoluble in water, slightly soluble in alcohol. It is inflammable, burns with a feebly luminous flame, and can be exploded with air or oxygen.

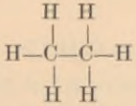
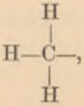
$$\begin{matrix} 2C_2H_6 & + & 7O_2 & = & 4CO_2 & + & 6H_2O \\ 4 \text{ vols.} & + & 14 \text{ vols.} & = & 8 \text{ vols.} & + & 12 \text{ vols.} \end{matrix}$$

It is very stable, and is not acted on by alkalies, nitric acid, sulphuric acid, bromine, or oxidising agents at ordinary temperatures. When mixed with chlorine and exposed to diffused sunlight, it gives various substitution products, 1, 2, 3, 4, 5, or 6 atoms of hydrogen being displaced by an equivalent quantity of chlorine.

$$\underset{\text{Ethyl Chloride.}}{C_2H_6+Cl_2=C_2H_5Cl+HCl} \qquad \underset{\text{Ethylene Chloride.}}{C_2H_6+2Cl_2=C_2H_4Cl_2+2HCl}$$

$$\underset{\text{Perchlorethane.}}{C_2H_6+6Cl_2=C_2Cl_6+6HCl.}$$

Ethane, like methane, cannot combine directly with chlorine or with any element; it is a saturated compound.

The *constitution* of ethane may be deduced theoretically in the following manner: the two atoms of carbon must be directly united, because hydrogen, being monovalent, cannot link the two carbon atoms together; as, moreover, carbon is tetravalent, one of the six hydrogen atoms must be placed at the end of each of the remaining six lines; in this way the graphic formula  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$ is obtained. This view, based entirely on considerations of valency, is confirmed by a study of the methods of formation and properties of ethane. When methyl iodide is treated with sodium or with zinc methyl, the metal combines with the halogen, and a group of atoms, CH_3-, is left; as, however, carbon is tetravalent, this group  $H-\underset{H}{\overset{H}{C}}-$, like the atom of hydrogen H–, cannot exist alone, and immediately combines with a similar group forming ethane, CH_3-CH_3, or dimethyl, which is a saturated compound, because all the carbon atoms in the molecule are exerting their maximum valency or combining capacity.

Propane, propyl hydride, or methyl-ethyl, C_3H_8, occurs in petroleum, and can be obtained by reducing propyl iodide or isopropyl iodide (p. 178) with zinc and hydrochloric acid, or with the zinc-copper couple,

$$C_3H_7I + 2H = C_3H_8 + HI.$$

It is also obtained by treating a mixture of ethyl and methyl iodides with sodium,

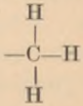
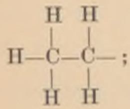
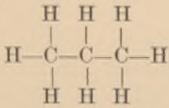
$$C_2H_5I + CH_3I + 2Na = C_3H_8 + 2NaI,$$

and by treating zinc ethyl with methyl iodide,

$$Zn(C_2H_5)_2 + 2CH_3I = 2C_3H_8 + ZnI_2.$$

Propane is a gas, and closely resembles methane and ethane in chemical properties. It condenses to a colourless liquid at temperatures below − 17° under ordinary atmospheric pressure. It burns with a more luminous flame than ethane. When treated with chlorine in diffused sunlight, it yields propyl chloride and other substitution products, one or more hydrogen atoms being displaced,

$$C_3H_8 + Cl_2 = C_3H_7Cl + HCl.$$

Constitution.—Since propane is produced by the action of sodium on a mixture of methyl and ethyl iodides, and also by the action of zinc ethyl on methyl iodide, it is concluded that propane is formed by the combination of  $-\overset{H}{\underset{H}{C}}-H$ and  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$; its constitution is therefore represented by the formula  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$, or $CH_3 \cdot CH_2 \cdot CH_3$, and it may be regarded as derived from ethane, just as ethane may be considered as derived from methane, by substituting the monovalent group of atoms CH_3- for one atom of hydrogen.

Butanes, C_4H_{10}.—Two hydrocarbons of the molecular formula C_4H_{10} are known. One of them, **butane**, diethyl or methyl-propyl, occurs in petroleum, and can be obtained by treating ethyl iodide with sodium,

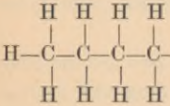
$$2C_2H_5I + 2Na = C_4H_{10} + 2NaI.$$

The other, **isobutane**, or trimethylmethane, is formed when tertiary butyl iodide (p. 178) is treated with nascent hydrogen,

$$C_4H_9I + 2H = C_4H_{10} + HI.$$

These two hydrocarbons have been proved to have the same molecular formula, but to be different in properties. Although they are both gases under ordinary conditions, butane liquefies at about 0°, isobutane not until about $-17°$ under atmospheric pressure, so that they are certainly distinct substances. In chemical properties they closely resemble propane and one another. They give substitution products with chlorine, but the compounds obtained from butane are not identical with those produced from isobutane, although they have the same molecular formula.

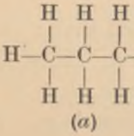
Constitution of the two Butanes.—The production of butane from ethyl iodide in the above-mentioned manner indicates that this hydrocarbon is di-ethyl. It is therefore represented by the formula



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H, \text{ or } C_2H_5-C_2H_5, \text{ or } CH_3\cdot CH_2\cdot CH_2\cdot CH_3,$$

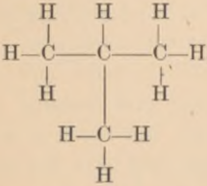
Butane.
(I.)

which not only brings to mind the method of formation of the hydrocarbon, but also indicates its relation to propane. Butane, in fact, may be regarded as propane in which one atom of hydrogen has been displaced by the monovalent CH_3- group. When, however, the graphic formula of propane is carefully considered, it will be seen that the eight atoms of hydrogen are not all in the same state of combination relatively to the rest of the molecule, but that two of them (a),

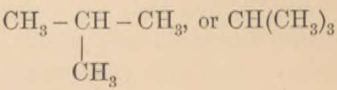


$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\underset{\displaystyle (a)}{\displaystyle H}}{|}}{\overset{\overset{\overset{\displaystyle (a)}{\displaystyle H}}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H, \text{ or } CH_3-\underset{(a)}{CH_2}-CH_3, \text{ or } \underset{(a)}{CH_2}(CH_3)_2$$

are united with a carbon atom which is itself combined with two carbon atoms, whereas each of the other six atoms of hydrogen is combined with a carbon atom which is united with only one other. If, then, one of the (*a*) hydrogen atoms be displaced by a CH_3– group, the constitution of the product would be represented by the formula



or

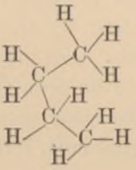


$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3, \text{ or } CH(CH_3)_3$$

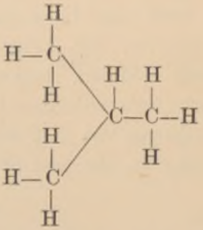
Isobutane.
(II.)

whereas, if one of the other hydrogen atoms were displaced, a hydrocarbon of the constitution represented by formula I. would be formed. As in these two cases the atoms would not all be in the same state of combination, the properties of the compounds represented by these formulæ would be different.

It is next important to note that the above two are the only formulæ which can be constructed with four atoms of carbon and ten atoms of hydrogen, if it be assumed that carbon is tetravalent and hydrogen monovalent. All formulæ such as



or

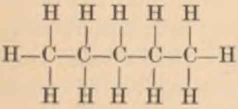


will, on examination, be found to be identical with I. or II., as they express the same state of combination. Since, then, formula I. represents the constitution of butane, that of isobutane or trimethylmethane is expressed by formula II. This conclusion is confirmed by a study of the methods of formation and chemical behaviour of isobutane.

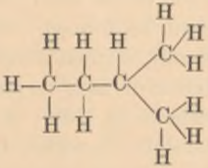
Pentanes.—Three hydrocarbons of the molecular formula C_5H_{12} are known; two of them—namely **pentane** (b.p. 37°), and **isopentane** (b.p. 30°)—occur in petroleum, and are colourless mobile liquids. The third, **tetramethylmethane** (b.p. 9·5°), can be obtained by treating tertiary butyl iodide with zinc methyl,

$$2(CH_3)_3CI + Zn(CH_3)_2 = 2(CH_3)_3C\cdot CH_3 + ZnI_2.$$

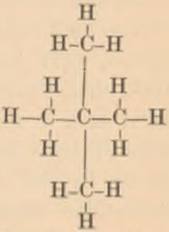
For reasons similar to those stated in the case of the simpler hydrocarbons, the constitutions of the three pentanes are represented by the formulæ



Pentane.



Isopentane.



Tetramethylmethane.

They may all be regarded as derived from the butanes (pentane and isopentane from normal butane, tetramethylmethane from isobutane) by the substitution of a CH_3– group for one atom of hydrogen.

Isomerism.—Compounds, such as the two hydrocarbons C_4H_{10}, and the three hydrocarbons C_5H_{12}, which have respectively the same molecular formula, but different properties, are said to be **isomeric.** The phenomenon is spoken of as **isomerism,** and the compounds themselves are called **isomers** or **isomerides.** Isomerism is due to a difference in constitution or arrangement of the atoms.

When graphic formulæ are employed to represent the constitutions of the hydrocarbons, it will be found possible to construct as many different formulæ as there are isomerides. It is possible, for example, to construct three different graphic formulæ for a substance of the molecular formula C_5H_{12}, and three isomerides only are known; more could not be represented by graphic formulæ, assuming always that carbon is tetravalent. This agreement between theoretical conclusions and observed facts is strong evidence of the tetravalent character of carbon.

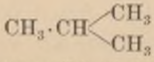
Ethane may be regarded as derived from methane, propane from ethane, and the butanes from the propanes by substituting the monovalent group of atoms CH_3- for one atom of hydrogen, and, theoretically, this process can be continued without limit. If one hydrogen atom in each of the three pentanes be displaced by a CH_3- group, a number of isomeric hydrocarbons, C_6H_{14}, would be obtained, from each of which, by a repetition of the same process, at least one hydrocarbon, C_7H_{16}, might be formed, and so on. It is evident then, that, theoretically, a great number of hydrocarbons may exist, and, as a matter of fact, very many have actually been isolated from petroleum (p. 70). As the number of carbon atoms in the molecule increases, the number of possible isomerides rapidly becomes larger; 7 isomerides of the molecular formula C_7H_{16}, 18 of the formula C_8H_{18}, and no less than 802 of the formula $C_{13}H_{28}$ could, theoretically, be formed. In many cases, all the possible isomerides have not been prepared, but there can be little doubt that they could be obtained by suitable reactions.

The several isomerides are usually distinguished by the terms *normal* or *primary*, *iso-* or *secondary*, and *tertiary*. A normal or primary hydrocarbon is one in which no carbon atom is directly combined with more than two others, as, for example,

$CH_3\cdot CH_2\cdot CH_2\cdot CH_3$
Normal Butane.

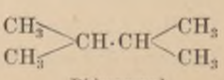
$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$.
Normal Hexane.

A secondary or iso-hydrocarbon contains at least one carbon atom directly united with three others,



$$CH_3\cdot CH{<}\begin{matrix}CH_3\\ CH_3\end{matrix}$$

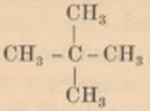
Isobutane or Trimethylmethane.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}{>}CH\cdot CH{<}\begin{matrix}CH_3\\ CH_3\end{matrix}$$

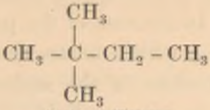
Di-isopropyl.

A tertiary hydrocarbon contains at least one carbon atom directly combined with four others,



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ CH_3- & C & -CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Tertiary Pentane
(or Tetramethylmethane).



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ CH_3- & C & -CH_2-CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Tertiary Hexane
(or Trimethylethylmethane).

In the case of iso- and tertiary hydrocarbons, it is convenient to use a name which readily expresses the constitution of the compound ; examples of such names are given above in brackets.

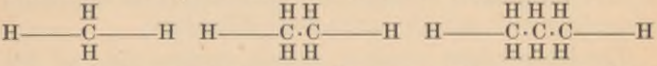
The hydrocarbons methane, ethane, propane, &c., are not only all produced by similar reactions, but they also show very great similarity in chemical properties ; for these reasons they are classed together as the **paraffins**, or hydrocarbons of the methane series. The class, or generic name 'paraffin,' was assigned to this group because paraffin-wax consists principally of the higher members of the methane series. Paraffin-wax is a remarkably inert and stable substance, and is not acted on by strong acids or alkalies ; the name paraffin, from the Latin *parum affinis* (small or slight affinity), was given to it for this reason.

Homologous Series.—When the paraffins are arranged in order of molecular weight, they form a series, each member of which contains one atom of carbon and two atoms of hydrogen more than the preceding member.

Methane, CH_4	difference CH_2
Ethane, C_2H_6	" CH_2
Propane, C_3H_8	" CH_2
Butane, C_4H_{10}	" CH_2.
Pentane, C_5H_{12}	

The members of this series are similar in constitution and in chemical properties ; but, as the molecular weight increases, the physical properties undergo a gradual and regular variation. Such a series is termed **homologous**, and the several members are spoken of as **homologues** of one another ; there are many homologous series of organic compounds.

General Formulæ.—The molecular composition of all the members of a homologous series can be expressed by a **general formula.** In the case of the paraffin series the general formula is C_nH_{2n+2}, which means, that in any member containing n atoms of carbon in the molecule, there are $2n + 2$ atoms of hydrogen; in propane, C_3H_8, for example, $n = 3$; $2n + 2 = 8$. That this is so can be readily seen by writing the graphic formulæ of some of the paraffins in the following manner:



$$\text{H}\text{———}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{———H}\quad \text{H}\text{———}\overset{\text{H H}}{\underset{\text{H H}}{\text{C}\cdot\text{C}}}\text{———H}\quad \text{H}\text{———}\overset{\text{H H H}}{\underset{\text{H H H}}{\text{C}\cdot\text{C}\cdot\text{C}}}\text{———H}$$

when it is at once obvious that for every atom of carbon there are two atoms of hydrogen, the molecule containing, in addition, two extra hydrogen atoms.

Since the members of a homologous series can, as a rule, be obtained by similar or *general methods*, if these be given it is usually unnecessary to describe the preparation of each member separately. In view, also, of the great similarity in chemical properties, a detailed account of each compound may be omitted if the *general properties* of the members of the series be described; the physical properties may also be treated in a general manner, since they undergo a regular and gradual variation as the molecular weight increases.

The following is a summary of the principal facts relating to the paraffins treated in this way; it will be found advantageous to omit this and other summaries until some knowledge of other series has been acquired.

SUMMARY AND EXTENSION.

The Paraffin or Methane Series.—Saturated hydrocarbons of the general formula C_nH_{2n+2}. The more important members of the series are the following, the number of possible isomers being indicated by the figures in brackets:

Methane (1), CH_4
Ethane (1), C_2H_6
Propane (1), C_3H_8
Butane (2), C_4H_{10}
Pentane (3), C_5H_{12}
Hexane (5), C_6H_{14}
Heptane (9), C_7H_{16}
Octane (18), C_8H_{18}
Nonane (35), C_9H_{20}
Decane (75), $C_{10}H_{22}$

Nomenclature.—The names of all the hydrocarbons of this series have the distinctive termination **ane**, those of the higher members having prefixes which denote the number of carbon atoms in the molecule.

Occurrence.—The paraffins are found in nature in enormous quantities as petroleum or mineral naphtha, in smaller quantities as natural gas, and as earth-wax, or ozokerite.

Methods of Preparation.—(1) By the dry distillation of an alkali salt of a fatty acid (p. 142) with potash, soda, or soda-lime,

$$CH_3{\cdot}COONa + NaOH = CH_4 + Na_2CO_3$$
$$C_3H_7{\cdot}COOK + KOH = C_3H_8 + K_2CO_3.$$

(2) By the action of nascent hydrogen on the alkyl* halogen compounds,

$$CH_3Cl + 2H = CH_4 + HCl$$
$$C_2H_5I + 2H = C_2H_6 + HI.$$

(3) By the action of sodium or zinc on the alkyl halogen compounds (Frankland),

$$2C_2H_5I + 2Na = C_2H_5{\cdot}C_2H_5 + 2NaI$$
$$2CH_3I + 2Na = CH_3{\cdot}CH_3 + 2NaI.$$

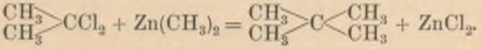
(4) By decomposing the zinc alkyl compounds (p. 215) with water,

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2$$
$$Zn(C_3H_7)_2 + 2H_2O = 2C_3H_8 + Zn(OH)_2.$$

(5) By the action of the alkyl halogen compounds on the zinc alkyl derivatives,

$$2CH_3I + Zn(CH_3)_2 = 2CH_3{\cdot}CH_3 + ZnI_2$$
$$2CH_3I + Zn(C_2H_5)_2 = 2CH_3{\cdot}C_2H_5 + ZnI_2.$$

Tertiary hydrocarbons, such as tetramethylmethane, may be similarly prepared by acting with the zinc alkyl compounds on certain dihalogen derivatives of the paraffins (p. 139),



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CCl_2 + Zn(CH_3)_2 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

(6) By the electrolysis of aqueous solutions of the sodium or potassium salts of the fatty acids,

$$2CH_3{\cdot}COOK + 2H_2O = CH_3{\cdot}CH_3 + 2KHCO_3 + H_2.$$

(7) By the destructive distillation of coal, cannel, turf, shale, and other products of vegetable origin.

Physical Properties.—The first four members of the series are colourless gases under ordinary conditions, but on the application of pressure at a low temperature they condense to liquids, and the

---

[*] The meaning of the word *alkyl* is given on p. 115.

more readily the greater the number of carbon atoms in the molecule. Methane liquefies at − 11° under a pressure of 180 atmospheres, ethane at 4° under 46 atmospheres, butane at 0° under ordinary atmospheric pressure. The hydrocarbons containing from 4 to about 16 atoms of carbon are colourless liquids under ordinary conditions, the boiling-point rising as the series is ascended. Normal pentane boils at 37°, normal hexane at 69°, and normal heptane at 98°, the difference between the boiling-points of consecutive normal hydrocarbons being about 30°. The higher members of the series, from about $C_{16}H_{34}$ (m.p. 18°), are colourless solids, the melting-point rising with increasing molecular weight.

The specific gravity of the hydrocarbons from butane, C_4H_{10}, to octane, C_8H_{18}, varies from 0·600 to about 0·718; from octane upwards the sp. gr. increases until the solid hydrocarbons are reached, when it becomes almost constant at 0·775 − 0·780, this value being determined at the melting-point.

The paraffins are insoluble, or nearly so, in water, but soluble in alcohol, ether, and other organic liquids.

Chemical Properties.—The paraffins are all characterised by great stability. At ordinary temperatures they are not acted on by nitric acid, fuming sulphuric acid, alkalies, or such powerful oxidising agents as chromic acid and potassium permanganate, and even at higher temperatures only a very slow action occurs. They are, however, attacked by chlorine and, less readily, by bromine in sunlight with formation of substitution products. Iodine has no action on the paraffins.

The paraffins are saturated compounds, and cannot combine directly with any element.

Paraffins of Commercial Importance.—In Pennsylvania, North America, in Baku, South-east Russia, and in other parts of the world, a gas escapes from the earth under considerable pressure. This *natural gas* is variable in composition, but usually contains a large proportion of methane and hydrogen, small quantities of other gaseous paraffins, and other hydrocarbons. It is employed as a fuel at Pittsburgh in Pennsylvania for a variety of industrial purposes.

In the localities already mentioned, enormous quantities of *petroleum* or *mineral naphtha* are also obtained, either from natural springs or from artificial borings. The origin of natural gas and petroleum is unknown, but it is supposed that they are produced by the destructive distillation in the lower layers of the earth's crust of the fatty remains of (sea) animals.

Crude petroleum is specifically lighter than water, and varies greatly in consistency and colour, being generally a thick yellow or brown liquid with a greenish colour when viewed by reflected light. It consists almost entirely of a mixture of hydrocarbons, that obtained from Pennsylvania being composed chiefly of paraffins, that from Baku of hydrocarbons belonging to a different (naphthene) series.

Petroleum is not only, next to coal-gas, one of the most important illuminating agents of the present day, but is also the source of a number of substances of considerable commercial value. The crude oil is not directly employed for illuminating purposes, owing partly to the fact that it contains very volatile hydrocarbons which render it too inflammable. In order to obtain the various substances in a condition suitable to the purposes for which they are required, the crude oil is distilled from large iron vessels and the distillate collected in fractions. American petroleum, treated in this way, yields: *Petroleum ether* (b.p. 40–70°), *gasoline* (b.p. 70–90°), and *ligroin* or *light petroleum* (b.p. 80–120°), colourless mobile liquids used as solvents for resins, oils, caoutchouc, &c.; *cleaning oil* (b.p. 120–170°), employed for cleaning purposes, and as a substitute for oil of turpentine in the preparation of varnishes; *refined petroleum*, *kerosene*, or burning oil (b.p. 150–300°), used for illuminating purposes; the portions collected above 300° are employed as lubricating oils. The residue consists of heavy lubricating oils, *vaseline*, and tarry matter. Russian petroleum also yields a variety of products, such as *benzine*, *kerosene*, *Vulcan oil*, *vaseline*, and tarry matter, which, though slightly different in composition, are similar in properties and uses to those obtained from American oil.

Ordinary paraffin-wax is obtained from the tar which is produced by the destructive distillation of cannel-coal or shale. When this tar is fractionally distilled, it yields several liquid products similar to those obtained from petroleum—such as *photogene* and *solar oil*, which are used as solvents and for illuminating purposes—and solid paraffins, or paraffin-wax, which is purified by treatment with concentrated sulphuric acid and redistillation. Paraffin-wax is a colourless, semi-crystalline, waxy substance, soluble in ether, &c., but insoluble in water; its melting-point ranges from about 45–65°, according to its composition; its principal use is for the preparation of candles (p. 170).

Ozokerite is a naturally occurring solid paraffin or *earth-wax* which is found in Galicia and Roumania; it is purified by treatment with concentrated sulphuric acid and distillation.

CHAPTER V.

UNSATURATED HYDROCARBONS—

THE OLEFINES, OR HYDROCARBONS OF THE ETHYLENE SERIES.

When the halogen mono-substitution products of the paraffins, such as ethyl bromide (p. 176), propyl chloride, &c., are heated with an alcoholic solution of potash, they are converted into hydrocarbons,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O$$
$$C_3H_7Cl + KOH = C_3H_6 + KCl + H_2O.$$

The compounds obtained in this way, and by other methods to be described later, contain two atoms of hydrogen less than the corresponding paraffins, and form a homologous series of the general formula C_nH_{2n}; their names are derived from those of the corresponding paraffins by changing the termination *ane* into *ylene*,

Methane, CH_4;	Ethane, C_2H_6;	Propane, C_3H_8;	Butane, C_4H_{10}.
——	Ethylene, C_2H_4;	Propylene, C_3H_6;	Butylene, C_4H_8.

The simplest member of the series is *ethylene;* the hydrocarbon CH_2 (methylene), which would correspond with methane, is unknown, and all attempts to prepare it have been unsuccessful.

The word 'olefine' is derived from 'olefiant' or 'oil-making' gas, a name originally given to ethylene on account of its property of forming an oily liquid (ethylene dichloride or Dutch liquid) with chlorine; the generic or class name 'olefine' is now applied to all the hydrocarbons of the series.

Ethylene, ethene, or olefiant gas, C_2H_4, is formed during the destructive distillation of many organic substances, and occurs in coal-gas, of which it forms about 6 per cent. by volume; the luminosity of the burning gas is to a great extent due to ethylene.

It is formed when acetylene (p. 81) is reduced with zinc dust and ammonia,

$$C_2H_2 + 2H = C_2H_4,$$

and when methylene iodide is heated with copper,

$$2CH_2I_2 + 4Cu = C_2H_4 + 2Cu_2I_2,$$

a reaction which is very similar to the formation of ethane by the action of sodium on methyl iodide (p. 59); also when ethyl bromide is heated with alcoholic potash,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O,$$

and when a solution of potassium succinate (p. 235) is submitted to electrolysis,

$$C_2H_4(COOK)_2 = C_2H_4 + 2CO_2 + 2K.$$

In the latter case, a mixture of ethylene and carbon dioxide is obtained at the positive pole, the alkali metal which separates at the negative pole acting on the water with liberation of hydrogen. This interesting method of formation of ethylene is similar to the production of ethane by the electrolysis of potassium acetate (p. 60).

Ethylene is prepared by heating a mixture of 1 vol. of ethyl alcohol and 6 vols. of concentrated sulphuric acid in a capacious flask (fig. 16), the gas thus produced being passed through wash-bottles containing potash, to free it from sulphur dioxide and carbon dioxide, and then collected over water; when the evolution of gas slackens, a further supply may be obtained by dropping a mixture of 1 vol. of alcohol and 2 vols. of sulphuric acid through the funnel. The reaction may be expressed by the equation

$$C_2H_5{\cdot}OH = C_2H_4 + H_2O,$$

but in reality it is not quite so simple (p. 183).

Ethylene is a colourless gas, has a peculiar sweet but not unpleasant smell, and liquefies at 10° under a pressure of 60 atmospheres; it is only sparingly soluble in water, more readily in alcohol and ether. It burns with a luminous flame, and forms a highly explosive mixture with air or oxygen,

$$\begin{array}{c} C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \\ 2 \text{ vols.} + 6 \text{ vols.} = 4 \text{ vols.} + 4 \text{ vols.} \end{array}$$

Its chemical behaviour is totally different from that of the paraffins. It combines directly with hydrogen at high temperatures (in presence of spongy platinum at ordinary temperatures) forming ethane,

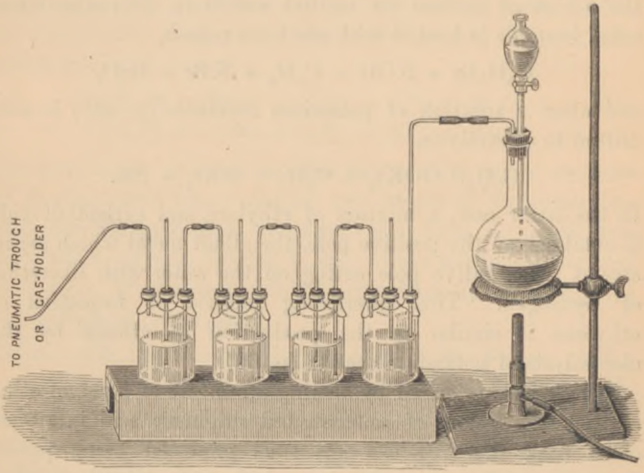


Fig. 16.

$$C_2H_4 + H_2 = C_2H_6.$$

Although it is not acted on by hydrochloric acid, it combines directly with concentrated hydrobromic and hydriodic acids at 100°, forming ethyl bromide and ethyl iodide respectively,

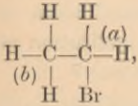
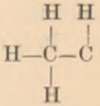
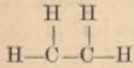
$$C_2H_4 + HBr = C_2H_5Br \qquad C_2H_4 + HI = C_2H_5I.$$

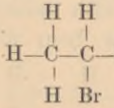
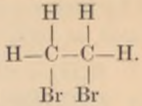
It is absorbed by, and combines with, fuming sulphuric acid, and, more slowly, with ordinary sulphuric acid, yielding ethyl hydrogen sulphate (p. 182), from which ethyl alcohol is produced on boiling with water,

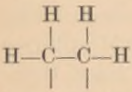
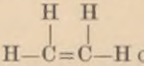
$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4$$
$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4.$$

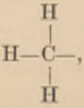
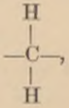
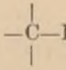
It combines directly with chlorine and bromine, and also with iodine in alcoholic solution,

$$C_2H_4 + X_2 = C_2H_4X_2 \qquad (X = Cl, Br, I).$$

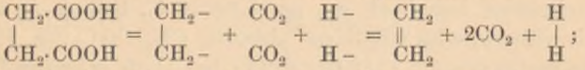
Constitution of Ethylene.—Ethylene is formed when ethyl bromide, a mono-substitution product of ethane, is heated with alcoholic potash, which simply takes away one atom of hydrogen and one atom of bromine ($C_2H_5Br = C_2H_4 + HBr$); since, therefore, the constitution of ethyl bromide is represented by the formula  $\mathrm{H{-}\underset{(b)\ H}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}{-}^{(a)}H}$, that of ethylene would be  $\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}}$ (I.), assuming that one of the (*a*) hydrogen atoms were taken away,  $\mathrm{H{-}\overset{H}{C}{-}\overset{H}{C}{-}H}$ (II.) if one of the (*b*) hydrogen atoms were removed.

But if ethylene have the constitution (I.), ethylene dibromide $C_2H_4Br_2$ (p. 78), the compound formed by the *direct combination* of ethylene with bromine, must be represented by the formula (III.),  $\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}{-}Br}$, because, from the behaviour of the paraffins, it is known that the carbon atom in the CH_3–group cannot combine with bromine except by substitution. As, however, a substance $C_2H_4Br_2$ (ethylidene dibromide, p. 78), whose constitution must be represented by the formula (III.), is known, and is not identical with ethylene dibromide, the latter cannot have the same constitution, but must be represented by the only alternative formula  $\mathrm{H{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{Br}{C}}{-}H}$.

This being the case, the constitution of ethylene might be expressed by formula (II.). But such a formula does not indicate that carbon is tetravalent, nor does it recall the fact that ethylene combines directly with Cl_2, Br_2, HBr, &c. These deficiencies might be remedied by writing ethylene  $\mathrm{H{-}\overset{H}{\underset{|}{C}}{-}\overset{H}{\underset{|}{C}}{-}H}$ to show that the carbon atoms are tetravalent, but that their combining capacity is not fully exercised; this formula would express the fact that each of the carbon atoms has still the power of combining with one monad atom or group. It is usual, however, to represent the constitution of ethylene by the formula  $\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}H}$ or $CH_2 = CH_2$ or $CH_2{:}CH_2$, the two carbon atoms being joined by two lines, **bonds**, or **linkings**; this formula is not quite the same as that just given, because it indicates that the particular portion of the combining power of each of the carbon atoms, which before was represented as doing nothing, or free, is in some way exerted in 'satisfying,' or combining with, the other carbon atom.

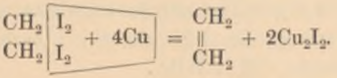
There are at least two very good reasons for writing the formula in this way and not with unoccupied lines, or **free bonds**; firstly, because it has been found impossible to prepare hydrocarbons such as  $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}}$,  $\mathrm{{-}\overset{H}{\underset{H}{C}}{-}}$, or  $\mathrm{{-}\overset{|}{\underset{|}{C}}{-}H}$, a fact which indicates that no carbon compound, in which the maximum combining capacity of the carbon atom or atoms is not exerted in some way, can exist; secondly, because whenever a compound contains one carbon atom which is not combined with the maximum quantity of four monad atoms or their valency equivalent, the carbon atom directly united with it is in the same 'unsatisfied' condition. One has never been found to exist without the other, and so it is assumed that they have some action on one another.

The above view of the constitution of ethylene receives support from the formation of the gas by the electrolysis of succinic acid, as is clearly seen if the decomposition be represented thus:



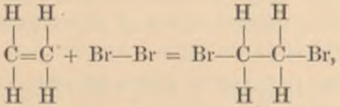
$$\begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH_2-\\ |\\ CH_2-\end{array} + \begin{array}{c}CO_2\\ \\ CO_2\end{array} + \begin{array}{c}H-\\ \\ H-\end{array} = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + 2CO_2 + \begin{array}{c}H\\ |\\ H\end{array};$$

again, the formation of ethylene by the action of copper on methylene iodide can only be explained on the assumption that ethylene has this constitution,



$$\begin{array}{l}CH_2\\ CH_2\end{array}\boxed{\begin{array}{l}I_2\\ I_2\end{array} + 4Cu} = \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2Cu_2I_2.$$

All organic compounds, which, like ethylene, contain carbon atoms having the power of combining directly with other atoms or groups, are said to be **unsaturated.** In the graphic formulæ of all such substances, these particular carbon atoms are represented as joined by a **double bond** or **double linking.** When an unsaturated compound enters into direct combination, the double bond is said to be broken, and the two carbon atoms, which before were written with two lines between them, are now joined by only one; the combination of ethylene with bromine, for example, is expressed graphically,



$$\begin{array}{ccc}H&&H\\ |&&|\\ C&=&C\\ |&&|\\ H&&H\end{array} + Br—Br = \begin{array}{ccccccc}&&H&&H&&\\ &&|&&|&&\\ Br&—&C&—&C&—&Br\\ &&|&&|&&\\ &&H&&H&&\end{array},$$

to show that ethylene dibromide, like the paraffins, is a saturated substance, and cannot combine except by substitution.

The substances formed by the direct union of unsaturated compounds with atoms or groups of atoms are called **additive products**, in contradistinction to substitution products. Unsaturated compounds always combine with 2, 4, 6, &c. monovalent atoms or groups, because they always contain an even number of unsaturated carbon atoms.

Derivatives of Ethylene.—*Ethylene dichloride*, $C_2H_4Cl_2$, or $CH_2Cl{\cdot}CH_2Cl$, was originally called Dutch liquid, or oil of Dutch chemists, by whom it was discovered. It is obtained by the direct combination of ethylene and chlorine, and is a colourless liquid of sp. gr. 1·28 at 0°, boiling at 85°. It is isomeric with ethylidene chloride, $CH_3{\cdot}CHCl_2$ (p. 139). *Ethylene dibromide*, $C_2H_4Br_2$, or $CH_2Br{\cdot}CH_2Br$, is prepared by passing ethylene into bromine until the colour of the latter disappears; the product is purified by fractional distillation. It is a colourless crystalline substance, melts at 9·5°, and boils at 131°; its sp. gr. is 2·21 at 0°. It is isomeric with ethylidene bromide, $CH_3{\cdot}CHBr_2$.

Substitution products of ethylene, such as *chlorethylene* or *vinyl chloride*, $CH_2{:}CHCl$, *bromethylene* or *vinyl bromide*, $CH_2{:}CHBr$, cannot be obtained by treating ethylene with a halogen, because additive products are produced in this way. They are prepared by heating the halogen additive products of ethylene with alcoholic potash,

$$CH_2Br{\cdot}CH_2Br + KOH = CH_2{:}CHBr + KBr + H_2O.$$

Vinyl chloride is a gas, vinyl bromide a colourless liquid, boiling at 16°; they are unsaturated compounds, and combine directly with Br_2, HBr, &c.

Propylene or methyl-ethylene, C_3H_6, or $CH_3{\cdot}CH{:}CH_2$, is formed by the dehydrating action of phosphorus pentoxide on propyl alcohol (p. 104),

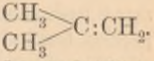
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_3{\cdot}CH{:}CH_2 + H_2O.$$

It is prepared by boiling either propyl or isopropyl bromide with alcoholic potash,

$$\begin{array}{ll}\text{Propyl bromide,} & CH_3{\cdot}CH_2{\cdot}CH_2Br \\ \text{Isopropyl bromide,} & CH_3{\cdot}CHBr{\cdot}CH_3\end{array} = CH_3{\cdot}CH{:}CH_2 + HBr.$$

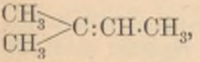
It is a gas very similar to ethylene in properties; it liquefies at ordinary temperatures under a pressure of 7–8 atmospheres, and being an unsaturated compound, combines readily with bromine, forming *propylene dibromide*, $CH_3{\cdot}CHBr{\cdot}CH_2Br$, an oily liquid boiling at 141°.

The higher members of the olefine series are obtained by methods similar to those employed in the case of propylene. Three isomeric **butylenes** of the molecular formula C_4H_8 are known, namely,

$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$	$CH_3{\cdot}CH{:}CH{\cdot}CH_3$	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{:}CH_2.$
Normal or α-butylene.	β-Butylene.	Iso- or γ-butylene.

They are all colourless gases, and combine directly with chlorine, bromine, hydrobromic acid, &c.

Five isomeric **amylenes** or **pentylenes**, C_5H_{10}, are known, the most important being *trimethylethylene* or *β- iso-amylene*, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{:}CH{\cdot}CH_3$, which is obtained by treating fusel oil (pp. 99, 104–5) with zinc chloride; it is a colourless liquid, and boils at 32°.



SUMMARY AND EXTENSION.

The Olefine or **Ethylene Series.**—Unsaturated hydrocarbons of the general formula C_nH_{2n}. The following are the more important members of this series, the number of possible isomerides being given in brackets:

Ethylene (1), C_2H_4	Amylene (5), C_5H_{10}
Propylene (1), C_3H_6	Hexylene (13), C_6H_{12}.
Butylene (3), C_4H_8	

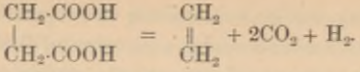
Methods of Preparation.—By the action of dehydrating agents, such as H_2SO_4, $ZnCl_2$, P_2O_5, &c., on the alcohols (p. 88),

$$CH_3{\cdot}CH_2{\cdot}OH = CH_2{:}CH_2 + H_2O.$$

By the action of alcoholic potash on the alkyl halogen compounds (p. 171),

$$CH_3{\cdot}CH_2Br + KOH = CH_2{:}CH_2 + KBr + H_2O$$
$$CH_3{\cdot}CHBr{\cdot}CH_3 + KOH = CH_3{\cdot}CH{:}CH_2 + KBr + H_2O.$$

By the electrolysis of certain dibasic acids (p. 229), or, better, of their potassium salts,



$$\begin{array}{l} CH_2{\cdot}COOH \\ \vert \\ CH_2{\cdot}COOH \end{array} = \begin{array}{l} CH_2 \\ \Vert \\ CH_2 \end{array} + 2CO_2 + H_2.$$

Physical Properties.—The first four members of the series are gases; the following fourteen or so, liquids; the higher members, solids at ordinary temperatures: the boiling-point and the melting-point rise on passing up the series, as in the case of the paraffins. They are insoluble, or nearly so, in water, but more readily soluble in alcohol.

Chemical Properties.—The olefines burn with a luminous smoky flame, and can be exploded with oxygen or air. They are unsaturated hydrocarbons, and differ very considerably in chemical properties from the saturated hydrocarbons of the paraffin series; whereas the latter are either not acted on, or form substitution products when treated with Cl_2, Br_2, HCl, HBr, HClO, H_2SO_4, &c., the olefines, as a rule, readily enter into direct combination with all these substances, forming saturated additive products.

The olefines are converted into paraffins on treatment with nascent hydrogen,

$$C_nH_{2n} + 2H = C_nH_{2n+2}.$$

They combine with chlorine and bromine, sometimes with iodine, forming saturated compounds which may be regarded as di-substitution products of the paraffins,

$$CH_3{\cdot}CH{:}CH_2 + Cl_2 = CH_3{\cdot}CHCl{\cdot}CH_2Cl.$$

They combine with hydrobromic and hydriodic acids, but not, as a rule, with hydrochloric acid, yielding alkyl halogen compounds,

$$CH_2{:}CH_2 + HBr = C_2H_5Br \qquad CH_3{\cdot}CH{:}CH_2 + HI = CH_3{\cdot}CHI{\cdot}CH_3,$$

combination generally taking place in such a manner that the halogen atom unites with that carbon atom which is combined with the smallest number of hydrogen atoms; propylene, for example, yields with hydrobromic acid isopropyl bromide, $CH_3{\cdot}CHBr{\cdot}CH_3$, and not propyl bromide, $CH_3{\cdot}CH_2{\cdot}CH_2Br$; normal butylene, $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, with hydriodic acid, gives secondary butyl iodide, $CH_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$, and so on.

Fuming sulphuric acid, in some cases ordinary sulphuric acid, readily absorbs the olefines, forming alkyl hydrogen sulphates,

$$CH_2{:}CH_2 + H_2SO_4 = C_2H_5{\cdot}HSO_4.$$

Hypochlorous acid, in aqueous solution, converts the olefines into chlorohydrins (p. 222),

$$CH_2{:}CH_2 + HOCl = CH_2Cl{\cdot}CH_2{\cdot}OH.$$

Unlike the paraffins, the olefines are readily oxidised by chromic acid and potassium permanganate. When oxidation is carried out carefully under suitable conditions, products containing the same number of carbon atoms as the original olefine are obtained; ethylene, for example, giving ethylene glycol (p. 219); butylene, the corresponding butylene glycol,

$$CH_2{:}CH_2 + O + H_2O = CH_2(OH){\cdot}CH_2{\cdot}OH$$

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + O + H_2O = CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

Generally speaking, when a substance contains the group $—CH = CH—$, this group, on oxidation, is in the first place converted into the group $—CH(OH){\cdot}CH(OH)—$. The compounds thus formed readily undergo further oxidation in such a way that the originally unsaturated carbon atoms are forced asunder. Propylene, on vigorous oxidation, yields acetic and formic acids; α-butylene gives propionic and formic acids,

$$CH_3{\cdot}CH{:}CH_2 + 4O = CH_3{\cdot}COOH + H{\cdot}COOH$$

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + 2O_2 = CH_3{\cdot}CH_2{\cdot}COOH + H{\cdot}COOH.$$

HYDROCARBONS OF THE ACETYLENE SERIES.

The relation between the hydrocarbons of the acetylene series and those of the olefine series is the same as that between the olefines and the paraffins; in other words, the members of the acetylene series contain two atoms of hydrogen less than the corresponding olefines, and the general formula of the series is C_nH_{2n-2}.

Paraffins, C_nH_{2n+2}	*Olefines*, C_nH_{2n}	*Acetylenes*, C_nH_{2n-2}
Methane, CH_4	——	——
Ethane, C_2H_6	Ethylene, C_2H_4	Acetylene, C_2H_2
Propane, C_3H_8	Propylene, C_3H_6	Allylene, C_3H_4

Acetylene, C_2H_2, the simplest member of the series, occurs in small quantities (about 0·06 per cent. by vol.) in coal-gas. It is produced during the incomplete combustion of methane, ethyl alcohol, coal-gas, and other substances; also when the vapour of such substances is passed through a red-hot tube. It is formed when hydrogen is led through a globe in which the electric arc is passing between carbon poles,

$$C_2 + H_2 = C_2H_2.$$

This synthesis of acetylene from its elements is of great interest, because ethylene can be produced from acetylene by the action of nascent hydrogen, and ethylene is readily converted into ethyl alcohol by treating with sulphuric acid and water consecutively (p. 75). As, moreover, a large number of organic substances can be produced from ethyl alcohol, it is possible to prepare all these compounds, starting with carbon and hydrogen.

Acetylene is also produced by the electrolysis of a solution of the potassium salt of fumaric or maleïc acid (p. 241), hydrogen being evolved at the negative pole (as the result of the action of the liberated potassium on the water) a mixture of acetylene and carbon dioxide at the positive pole,

$$C_2H_2(COOK)_2 = C_2H_2 + 2CO_2 + 2K.$$

Acetylene is prepared by heating ethylene dibromide with excess of alcoholic potash,

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

In the first place, the potash takes away one molecule of hydrogen bromide ($C_2H_4Br_2 + KOH = C_2H_3Br + KBr + H_2O$), and the vinyl bromide thus produced is then further acted on ($C_2H_3Br + KOH = C_2H_2 + KBr + H_2O$). A more convenient method of preparation is to burn coal-gas with a supply of oxygen insufficient for complete combustion, the products being aspirated through an ammoniacal solution of cuprous chloride, when the red copper derivative of acetylene is precipitated. When this compound is decomposed with hydrochloric acid, acetylene is evolved.

Acetylene is a colourless gas, which liquefies at 1° under a pressure of 48 atmospheres. It has a characteristic smell, resembling that of garlic, and quite different from that which is noticed when a Bunsen is burning below, although the latter is often erroneously ascribed to the presence of acetylene. It is slightly soluble in water, much more readily in alcohol. It burns with a luminous, very smoky flame, this behaviour being shown by all hydrocarbons which contain a very large percentage of carbon.

Copper acetylene, the brownish-red amorphous compound which is precipitated when acetylene is passed into a solution of cuprous chloride in ammonia, has probably the composition $C_2H_2Cu_2O$, and its formation serves as a delicate test for acetylene. The dry substance explodes when struck on an anvil or when heated at about 120°. It is decomposed by hydrochloric acid with formation of acetylene and traces of vinyl chloride, but when warmed with a solution of potassium cyanide, it yields pure acetylene. Silver acetylene, $C_2H_2Ag_2O$, is a colourless amorphous compound obtained on passing acetylene into an ammoniacal solution of silver nitrate. It is more explosive than the copper compound.

When acetylene is passed over heated sodium or potassium, hydrogen is evolved, and a metallic substitution product formed,

$$2C_2H_2 + 2Na = 2C_2HNa + H_2.$$

Acetylene combines directly with nascent hydrogen, being converted first into ethylene, then into ethane,

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6.$$

It combines directly with chlorine, forming dichlorethylene and tetrachlorethane,

$$C_2H_2 + Cl_2 = C_2H_2Cl_2 \qquad C_2H_2 + 2Cl_2 = C_2H_2Cl_4,$$

with bromine, forming dibromethylene and tetrabromethane, and with halogen acids under certain conditions, giving in the first place substitution products of ethylene. Thus, when the copper compound of acetylene is decomposed with hydrochloric acid, small quantities of vinyl chloride or chlorethylene are produced.

Sulphuric acid absorbs acetylene. When the solution is diluted with H_2O, and then distilled, acetaldehyde (p. 120) passes over,

$$C_2H_2 + H_2O = C_2H_4O.$$

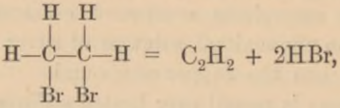
Acetaldehyde is also formed when acetylene is passed through an aqueous solution of mercuric bromide.

This remarkable reaction—that is, the addition of the elements of water to the group HC≡CH, by treatment with sulphuric acid or with halogen mercuric salts—appears to be a general one, and is frequently employed as a method of synthesis in organic investigations.

When acetylene is heated at a dull red heat, it is converted into benzene (part ii.),

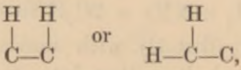
$$3C_2H_2 = C_6H_6.$$

Constitution of Acetylene.—The formation of acetylene from ethylene dibromide may be expressed by the equation



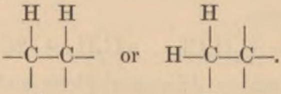
$$\mathrm{H{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{Br}{C}}{-}H} = C_2H_2 + 2HBr,$$

so that the constitution of the hydrocarbon might be represented by one of the formulæ



$$\mathrm{\overset{H}{C}{-}\overset{H}{C}} \quad \text{or} \quad \mathrm{H{-}\overset{H}{C}{-}C},$$

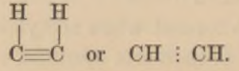
which, in order to recall the fact that carbon is tetravalent, and that acetylene combines directly with four monad atoms, must then be written



$$\underset{\text{I.}}{\mathrm{{-}\overset{H}{\underset{|}{C}}{-}\overset{H}{\underset{|}{C}}{-}}} \quad \text{or} \quad \underset{\text{II.}}{\mathrm{H{-}\overset{H}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}}}.$$

I. II.

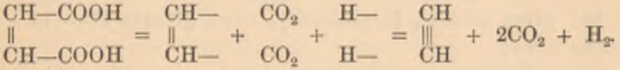
Since, however, as stated in discussing the constitution of ethylene, one unsaturated carbon atom is never found to exist alone, but requires the presence of another, it must be assumed that the particular portion of the combining capacity of each of the carbon atoms which is not exerted in uniting with hydrogen, is in some way exerted in combining with or satisfying the other carbon atom. For these reasons, formula I. is written



$$\mathrm{\overset{H}{C}{\equiv}\overset{H}{C}} \quad \text{or} \quad \mathrm{CH \vdots CH}.$$

But it is impossible to write formula II. in any such manner, and at the same time to represent both carbon atoms as actively tetravalent. For these and other reasons the constitution of acetylene is expressed by the formula $CH \vdots CH$, which recalls the fact that it contains *doubly unsaturated* carbon atoms, and is capable of combining directly with two pairs of monad groups or atoms to form additive compounds. This view of the constitution of acetylene accords well with its whole chemical behaviour.

The formation of acetylene by the electrolysis of fumaric acid affords support to this view, as will be readily understood if the decomposition be represented thus:



$$\begin{array}{l}CH{-}COOH\\ \|\\ CH{-}COOH\end{array} = \begin{array}{l}CH{-}\\ \|\\ CH{-}\end{array} + \begin{array}{l}CO_2\\ \\ CO_2\end{array} + \begin{array}{l}H{-}\\ \\ H{-}\end{array} = \begin{array}{l}CH\\ |||\\ CH\end{array} + 2CO_2 + H_2.$$

Fumaric Acid.

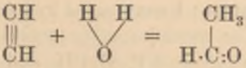
When the hydrocarbon combines with two monovalent atoms, such as 2H, Cl_2, Br_2, HBr, &c., it loses part of its unsaturated character, and the two carbon atoms, which before were represented as joined by three lines, or by a **treble binding** or **treble linking**, are now represented as joined by two only, as in the olefines,

$$CH \vdots CH + 2H = CH_2{:}CH_2 \qquad CH \vdots CH + Br_2 = CHBr{:}CHBr.$$

If, now, these compounds, which are still unsaturated, again combine with $2H, Br_2$, &c., they are converted into saturated compounds,

$$CH_2{:}CH_2 + 2H = CH_3{\cdot}CH_3$$
$$CHBr{:}CHBr + Br_2 = CHBr_2{\cdot}CHBr_2.$$

Acetylene can also combine with the valency equivalent of four monad atoms, with one atom of oxygen and two atoms of hydrogen, for example,



$$\begin{array}{l}CH\\ |||\\ CH\end{array} + \begin{array}{c}H\ \ H\\ \diagdown\!\diagup\\ O\end{array} = \begin{array}{c}CH_3\\ |\\ H{\cdot}C{:}O\end{array}$$

Homologues of Acetylene.—Two hydrocarbons of the molecular formula C_3H_4 are known; they may be represented by the formulæ

$$\underset{\text{Allylene or Methylacetylene.}}{CH_3{\cdot}C{\vdots}CH} \quad \text{and} \quad \underset{\text{Allene.}}{CH_2{:}C{:}CH_2.}$$

Allylene, like acetylene, contains two doubly unsaturated carbon atoms, whereas allene resembles rather ethylene in constitution, and may be considered as containing two pairs of (singly) unsaturated carbon atoms, $\overbrace{CH_2{:}C}\hspace{-0.7em}\underbrace{{:}CH_2}.$ This example shows that isomerism in the acetylene series may be due to a difference in the *position* of the unsaturated carbon atoms in the molecule, as well as to a difference in the *extent* of unsaturation, and consequently the number of isomerides in any given case is, theoretically, even greater than in the olefine series.

Allylene is prepared by heating propylene dibromide (dibromopropane) with alcoholic potash,

$$CH_3{\cdot}CHBr{\cdot}CH_2Br + 2KOH = CH_3{\cdot}C{\vdots}CH + 2KBr + 2H_2O.$$

It is a gas, very similar to acetylene in properties, and gives characteristic copper and silver compounds.

Allene is said to be produced in small quantities by heating allyl bromide (p. 255) with alcoholic potash,

$$CH_2{:}CH{\cdot}CH_2Br + KOH = CH_2{:}C{:}CH_2 + KBr + H_2O.$$

It is also a gas, but it differs from allylene in not forming metallic derivatives. Only those hydrocarbons which contain the group $-C{\vdots}CH$ yield metallic compounds with ammoniacal solutions of cuprous chloride and silver nitrate.

The higher homologues of acetylene have been comparatively little investigated.

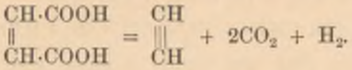
SUMMARY AND EXTENSION.

The Acetylene Series: Unsaturated hydrocarbons of the general formula C_nH_{2n-2}. The most important members of this series are *acetylene*, $CH{\vdots}CH$, *allylene*, $CH_3{\cdot}C{\vdots}CH$, and its isomeride allene, $CH_2{:}C{:}CH_2$, and *crotonylene*, $CH_3{\cdot}C{\vdots}C{\cdot}CH_3$.

Methods of Preparation.—By treating the monohalogen substitution products of the olefines, or the dihalogen substitution products of the paraffins, with alcoholic potash,

$$CH_2{:}CHBr + KOH = CH \vdots CH + KBr + H_2O$$
$$CH_3{\cdot}CHBr{\cdot}CH_2Br + 2KOH = CH_3{\cdot}C \vdots CH + 2KBr + 2H_2O.$$

By the electrolysis of the alkali salts of unsaturated dibasic acids,



$$\begin{matrix} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{matrix} = \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 2CO_2 + H_2.$$

Physical and Chemical Properties.—The members of the acetylene series up to $C_{12}H_{22}$ are gases or volatile liquids having a peculiar odour. They are sparingly soluble in water, more readily in alcohol, and burn with a luminous, very smoky flame. The hydrocarbons, C_nH_{2n-2} may be classed in two groups: (1) The true acetylene series, consisting of those compounds which, like *acetylene*, contain the group $-C \vdots C-$; and (2) the *di-olefines*, or hydrocarbons, such as *allene*, $CH_2{:}C{:}CH_2$, and *diallyl*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, which resemble the olefines in constitution. The former behave on the whole like acetylene, whereas the latter are similar to the olefines.

Those hydrocarbons of the true acetylene series which contain the group $-C \vdots CH$ form metallic compounds such as copper acetylene, $C_2H_2Cu_2O$, and silver acetylene, $C_2H_2Ag_2O$, when treated with ammoniacal solutions of cuprous chloride and silver nitrate. The copper compounds are red, the silver compounds white, and both classes are explosive, the latter more so than the former. These compounds are decomposed by hydrochloric acid, and by warm potassium cyanide solution, the acetylenes being regenerated. The di-olefines, and those members of the true acetylene series, such as $CH_3{\cdot}C \vdots C{\cdot}CH_3$, which do not contain the group $-C \vdots CH$, do not form these metallic derivatives.

The hydrocarbons of the true acetylene series may be caused to combine with the elements of water either by dissolving them in strong sulphuric acid, and then adding water and warming; or by shaking them with a concentrated aqueous solution of mercuric chloride or bromide, and then decomposing the precipitate which is formed with a dilute mineral acid,

$$CH \vdots CH + H_2O = CH_3{\cdot}CHO \qquad CH_3{\cdot}C \vdots CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3.$$

In the case of all the higher members, combination takes place in such a way that the oxygen atom becomes united with the carbon atom which is not combined with hydrogen; allylene, for example, yields acetone, as shown above, and not propaldehyde, $CH_3{\cdot}CH_2{\cdot}CHO$.

All the hydrocarbons of the C_nH_{2n-2} series combine directly with two molecules of chlorine, bromine, halogen acids, and with nascent hydrogen, &c., the action taking place in two stages,

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6$$
$$CH_3{\cdot}C{\vdots}CH + Br_2 = CH_3{\cdot}CBr{:}CHBr$$
$$CH_3{\cdot}CBr{:}CHBr + Br_2 = CH_3{\cdot}CBr_2{\cdot}CHBr_2.$$

Like the olefines, they are readily oxidised and converted into compounds containing a smaller number of carbon atoms in the molecule.

CHAPTER VI.

THE MONOHYDRIC ALCOHOLS.

The monohydric alcohols form a homologous series of the general formula $C_nH_{2n+1}{\cdot}OH$, or $C_nH_{2n+2}O$. They may be regarded as derived from the paraffins by the substitution of the monovalent hydroxyl-group HO– for one atom of hydrogen.

Methyl alcohol, $CH_3{\cdot}OH$, derived from methane, $CH_3{\cdot}H$
Ethyl " $C_2H_5{\cdot}OH$, " ethane, $C_2H_5{\cdot}H$
Propyl " $C_3H_7{\cdot}OH$, " propane, $C_3H_7{\cdot}H$, &c.

Methyl alcohol, *wood spirit*, or carbinol, $CH_3{\cdot}OH$, occurs in nature in several substances, amongst others in combination with salicylic acid, as methyl salicylate, in oil of wintergreen (*Gaultheria procumbens*). When this oil is distilled with dilute potash, an aqueous solution of pure methyl alcohol collects in the receiver. Methyl alcohol may be obtained from methane, by first converting the hydrocarbon into methyl chloride, and then heating the latter with dilute aqueous potash in closed vessels,

$$CH_3Cl + KOH = CH_3{\cdot}OH + KCl.$$

Methyl alcohol is prepared from the products of the destructive distillation of wood. When wood is heated in iron retorts out of contact with air, gases are evolved, water, tar, and other products collect in the receiver, and wood-coke or charcoal remains. After allowing the distillate to settle, the brown aqueous layer, which contains methyl alcohol, acetic acid, acetone, and other substances, is drawn off from the wood-tar and distilled from a copper vessel, the vapours being passed through hot milk of lime, to free them from acetic acid, and then collected in a receiver; this distillate is diluted with water to precipitate oily impurities, and then submitted to careful fractional distillation over quicklime. The liquid obtained in this way contains 98–99 per cent. of methyl alcohol. In order to free it from acetone and other impurities, it is mixed with powdered calcium chloride, with which the methyl alcohol combines, forming a crystalline compound of the composition $CaCl_2 + 4CH_4O$. This substance is freed from acetone by pressure between cloths, and then decomposed by distilling with water; the aqueous methyl alcohol is finally dehydrated by repeated distillation with quicklime, but it still contains traces of acetone and other impurities.

Pure methyl alcohol can be prepared by warming the impure product with oxalic acid, when methyl oxalate is produced (p. 233),

$$2CH_3{\cdot}OH + C_2O_4H_2 = C_2O_4(CH_3)_2 + 2H_2O;$$

this crystalline substance is decomposed by distilling with potash, and the aqueous solution of pure methyl alcohol dehydrated with caustic lime as before.

Methyl alcohol is a colourless, mobile liquid of sp. gr. 0·796 at 20°; it boils at 66°, has an agreeable vinous or winelike odour, and a burning taste. It mixes with water in all proportions, a slight contraction in volume taking place, and heat being developed; it burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$2CH_3{\cdot}OH + 3O_2 = 2CO_2 + 4H_2O.$$

It is largely used in the manufacture of organic dyes and varnishes, and for the preparation of methylated spirit (p. 100).

Sodium and potassium dissolve readily in methyl alcohol with evolution of hydrogen and formation of metallic compounds called *methylates* or *methoxides*,

$$2CH_3{\cdot}OH + 2Na = 2CH_3{\cdot}ONa + H_2,$$

a reaction which is similar to the decomposition of water by sodium. Sodium methoxide is readily soluble in methyl alcohol, but can be obtained in a solid condition by evaporating the solution in a stream of hydrogen; it is a colourless, crystalline, very deliquescent compound, which rapidly absorbs carbon dioxide from the air, and is immediately decomposed by water with regeneration of methyl alcohol,

$$CH_3{\cdot}ONa + H_2O = CH_3{\cdot}OH + NaOH.$$

Potassium methoxide has similar properties.

Although neutral to test-paper, methyl alcohol acts like a weak base, and combines with acids to form salts; when saturated with hydrogen chloride, it yields methyl chloride, corresponding with potassium chloride,

$$\begin{gathered} CH_3{\cdot}OH + HCl = CH_3Cl + H_2O \\ KOH + HCl = KCl + H_2O, \end{gathered}$$

and when warmed with sulphuric acid, it gives methyl hydrogen sulphate, corresponding with potassium hydrogen sulphate, and methyl sulphate, corresponding with potassium sulphate,

$$\begin{gathered} CH_3{\cdot}OH + H_2SO_4 = CH_3{\cdot}HSO_4 + H_2O \\ 2CH_3{\cdot}OH + H_2SO_4 = (CH_3)_2SO_4 + 2H_2O. \end{gathered}$$

When phosphorus pentachloride, trichloride, or oxychloride is added to methyl alcohol, a considerable development of heat occurs, and methyl chloride is formed,

$$\begin{gathered} CH_3{\cdot}OH + PCl_5 = CH_3Cl + HCl + POCl_3 \\ 3CH_3{\cdot}OH + PCl_3 = 3CH_3Cl + H_3PO_3 \\ 3CH_3{\cdot}OH + POCl_3 = 3CH_3Cl + H_3PO_4. \end{gathered}$$

The corresponding bromides of phosphorus act in a similar manner.

Methyl alcohol is readily oxidised,* being first converted into formaldehyde and then into formic acid,

$$\underset{\text{Formaldehyde.}}{CH_3{\cdot}OH + O = CH_2O + H_2O} \qquad \underset{\text{Formic Acid.}}{CH_2O + O = CH_2O_2.}$$

Constitution of Methyl Alcohol.—Since only one of the four hydrogen atoms in methyl alcohol, CH_4O, is displaceable by potassium or sodium, it must be concluded that this particular hydrogen atom is in a different state of combination from the other three; but methyl alcohol is formed by the action of dilute alkalies on methyl chloride,

$$CH_3Cl + KOH = CH_3{\cdot}OH + KCl,$$

---

* The substances most frequently used in oxidising organic compounds are: *Chlorine water*, *bromine water*, *nitric acid*, *chromic acid*, *manganese dioxide and sulphuric acid*, and *potassium permanganate*. Chlorine and bromine, in presence of water, act as oxidising agents by liberating oxygen,

$$Cl_2 + H_2O = 2HCl + O.$$

Nitric acid gives up some of its oxygen and is reduced to an oxide of nitrogen, the nature of which depends on that of the substance undergoing oxidation, and on the conditions of the experiment,

$$2HNO_3 = H_2O + N_2O_3 + 2O \qquad 2HNO_3 = H_2O + 2NO_2 + O, \text{ \&c.}$$

Chromic acid in the presence of sulphuric or acetic acid gives oxygen and a chromic salt,

$$2CrO_3 = Cr_2O_3 + 3O, \text{ or } 2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O.$$

A mixture of potassium dichromate and sulphuric acid, which is very often used instead of chromic acid, yields oxygen and a mixture of chromic sulphate and potassium sulphate, which frequently crystallises out in dark purple octahedra of chrome-alum, $K_2SO_4, Cr_2(SO_4)_3 + 24H_2O$,

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Potassium permanganate, in *alkaline* solution, is decomposed, yielding a precipitate of hydrated manganese dioxide,

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O;$$

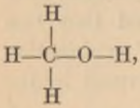
but in *acid* solution the same quantity of permanganate gives five instead of three atoms of oxygen,

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O,$$

because manganese dioxide and sulphuric acid yield oxygen,

$$2MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

and the three hydrogen atoms in methyl chloride, which are known to be combined with carbon, are not displaceable by metals. It is evident, therefore, that the displaceable hydrogen atom in methyl alcohol is not combined with carbon; the only other possibility is that it is combined with oxygen, and that methyl alcohol has the constitution



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}O{-}H}\\ |\\ \mathrm{H}\end{array}$$

which is usually written $CH_3{\cdot}OH$. When represented in this way, the whole chemical behaviour of methyl alcohol is summarised in its graphic formula; the fact that the oxygen atom cannot be taken away without one of the hydrogen atoms accompanying it—as, for example, when the alcohol is treated with HCl, PCl_5, PBr_5, &c.—is recalled by the two atoms being represented as directly united. The similarity between methyl alcohol and the metallic hydroxides is also accounted for; the alcohol may be regarded as derived from water, H–O–H, by substituting the monovalent CH_3–group for one atom of hydrogen, just as sodium hydroxide, Na–OH, is obtained by the substitution of one atom of sodium. Methyl alcohol, in fact, is *methyl hydroxide*, and, like other hydroxides, it forms salts and water when treated with acids,

$$CH_3{\cdot}OH + HCl = CH_3Cl + H_2O$$
$$Na{\cdot}OH + HCl = NaCl + H_2O.$$

Like water and certain metallic hydroxides, it contains displaceable hydrogen,

$$2CH_3{\cdot}OH + 2Na = 2CH_3{\cdot}ONa + H_2$$
$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

It may also be considered as a hydroxy-substitution product of the paraffin, methane; it is termed a monohydric alcohol because it contains one hydroxyl-group.

Ethyl alcohol, *spirits of wine*, alcohol, or methyl carbinol, $C_2H_5{\cdot}OH$, has been known from the earliest times, as it is contained in all wines prepared by the fermentation (p. 97) of grape juice.

It may be obtained from ethane by converting the hydrocarbon into ethyl chloride and heating the latter with dilute alkalies under pressure,

$$C_2H_5Cl + KOH = C_2H_5{\cdot}OH + KCl,$$

and by passing ethylene into fuming sulphuric acid, and then boiling the solution with water, a reaction of considerable theoretical importance,

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4$$
$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4;$$

also by reducing* acetaldehyde in aqueous solution with sodium amalgam,

$$C_2H_4O + 2H = C_2H_6O.$$

Alcohol may be prepared by placing a weak aqueous

---

* The substances most frequently used in reducing organic compounds are, *sodium*, *zinc*, *tin*, *iron*, *sodium amalgam*, *hydrogen iodide*, *sulphuretted hydrogen*, and *sulphur dioxide* in aqueous, acid, alkaline or alcoholic solution.

Sodium, acting on the alcoholic or moist ethereal solution of the substance, is one of the most powerful reducing agents known,

$$2Na + 2C_2H_5{\cdot}OH = 2C_2H_5{\cdot}ONa + 2H$$
$$2Na + 2H_2O = 2NaOH + 2H.$$

Sodium Amalgam, an alloy of sodium and mercury, acts on aqueous or dilute alcoholic solutions in the same way as metallic sodium, the action being, however, greatly moderated by the presence of the mercury.

Zinc and hydrochloric or sulphuric acid, or zinc dust and acetic acid, are perhaps the most commonly employed reducing agents; in some cases the action is much accelerated by coating the zinc with copper in the form of the zinc-copper couple (p. 57). Zinc dust is sometimes employed in alkaline solution, as, for instance, in the presence of potash, soda, or ammonia,

$$Zn + 2KOH = Zn(OK)_2 + 2H.$$

Substances which are reduced only with great difficulty are frequently mixed with zinc dust and heated at a high temperature.

Tin and hydrochloric acid act as reducing agents, stannous chloride being first produced,

$$Sn + 2HCl = SnCl_2 + 2H.$$

Stannous chloride is not acted on by hydrochloric acid alone, but, in solution of cane- or grape-sugar in a capacious flask, adding a small quantity of brewer's yeast, and keeping the mixture in a warm place (at about 20°). After some time it begins to froth and ferment (p. 97), and, if the flask be fitted with a cork and delivery tube, it can be proved that carbon dioxide is being evolved by passing the gas into lime-water. After about 24 hours' time the yeast is filtered off, and the solution distilled from a flask or retort connected with a condenser, the process being stopped when about one-third has passed over. In this way the more volatile alcohol is partially separated from the water (fractional distillation). The distillate has an unpleasant vinous smell, and consists of an aqueous solution of slightly impure alcohol. It is poured into a retort or flask connected with a condenser, and a considerable quantity of freshly-burnt lime in the form of small lumps is then slowly added; after some hours, the alcohol is distilled by heating on a water-bath. By repeating this process several times, employing fresh caustic lime in sufficient quantity, alcohol containing only about 0·2 per cent. of water is obtained, but it is impossible to free it completely from water by distillation over lime. When the alcohol contains less than about 0·5 per cent. of water, it is known commercially as *absolute* alcohol.

Wines, beers, and spirits contain alcohol, and its preparation from these liquids is very simple. The liquid is distilled, and the alcohol, thus freed from colouring matter and other

presence of reducible substances, it is a very powerful reducing agent, being converted into stannic chloride,

$$SnCl_2 + 2HCl = SnCl_4 + 2H.$$

Hydriodic Acid, in concentrated aqueous solution, is a very powerful reducing agent at high temperatures, the hydrogen iodide being decomposed into hydrogen and iodine.

Sulphuretted Hydrogen, being readily decomposed into sulphur and hydrogen, is frequently used as a mild reducing agent, generally in the form of ammonium sulphide.

Sulphur Dioxide has only a limited use; in presence of water and reducible substances, it is converted into sulphuric acid,

$$SO_2 + 2H_2O = H_2SO_4 + 2H.$$

solid substances, is then dehydrated by distillation with caustic lime.

Alcohol is a colourless, mobile liquid of sp. gr. 0·8062 at 0°; it has a pleasant vinous odour and a burning taste; it boils at 78°, but does not solidify until about – 130° (hence its use in alcohol thermometers). It burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$C_2H_5{\cdot}OH + 3O_2 = 2CO_2 + 3H_2O.$$

It mixes with water in all proportions with development of heat and diminution of volume; 52 vols. of alcohol and 48 vols. of water give a mixture occupying only 96·3 vols.

Ethyl alcohol closely resembles methyl alcohol in chemical properties. It quickly dissolves sodium and potassium with evolution of hydrogen and formation of *ethylates* or *ethoxides*,

$$2C_2H_5{\cdot}OH + 2Na = 2C_2H_5{\cdot}ONa + H_2.$$

These compounds are readily soluble in alcohol, but may be obtained in a solid condition by evaporating the solution in a stream of hydrogen. They are colourless, hygroscopic substances, rapidly absorb carbon dioxide from the air, and are immediately decomposed by water with regeneration of alcohol,

$$C_2H_5{\cdot}OK + H_2O = C_2H_5{\cdot}OH + KOH.$$

Although it has a neutral reaction, alcohol acts like a weak base, and when treated with acids, is converted into salts with formation of water,

$$C_2H_5{\cdot}OH + HI = C_2H_5I + H_2O.$$

When treated with the chlorides or bromides of phosphorus, it is converted into ethyl chloride or ethyl bromide, an energetic action taking place,

$$C_2H_5{\cdot}OH + PBr_5 = C_2H_5Br + HBr + POBr_3.$$

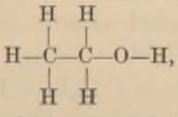
Alcohol is readily oxidised by chromic acid, yielding acetaldehyde, which on further oxidation is converted into acetic acid,

$$C_2H_5{\cdot}OH + O = \underset{\text{Acetaldehyde.}}{C_2H_4O} + H_2O \qquad C_2H_4O + O = \underset{\text{Acetic Acid.}}{C_2H_4O_2}.$$

By the action of the ferment, *mycoderma aceti*, it is, under certain conditions (p. 148), oxidised to acetic acid at ordinary temperatures by the oxygen of the air.

The presence of alcohol in aqueous solution may be detected by Lieben's *iodoform reaction* (p. 175). A small quantity of iodine is placed in the solution, and then caustic potash is added drop by drop until the colour of the iodine disappears. If alcohol be present in considerable quantity, a yellow precipitate of iodoform is produced almost immediately. In very dilute solutions of alcohol only a very slight precipitate is formed even after some time, but it may be recognised as iodoform by its odour, and by the characteristic appearance of its six-sided crystals when viewed under the microscope. By means of this reaction it is possible to detect 1 part of alcohol in 2000 parts of water. It is especially valuable as affording a means of distinguishing between ethyl and methyl alcohols, as the latter does not give the iodoform reaction, although many other substances, such as acetone, aldehyde, &c., do so.

The presence of water in alcohol can be detected by adding a little anhydrous copper sulphate. If water be present, the colourless powder turns blue, owing to the formation of the hydrated salt, but this test is not very delicate.

Constitution.—The formation of alcohol from ethyl chloride, the fact that only one of its six atoms of hydrogen is displaceable by metals, and its close resemblance to methyl alcohol in chemical properties, lead to the conclusion that it is a *hydroxide* of the constitution  $H{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}O{-}H$, or $C_2H_5{\cdot}OH$. It may be regarded as a mono-hydroxy-substitution product of ethane.

Production of Wines and Beers; Alcoholic Fermentation.

When the juice of grapes is kept for a few days at ordinary temperatures, it changes into wine; the sugars, dextrose and levulose (p. 262), present in the juice being decomposed into alcohol and carbon dioxide. This change is brought about by a small vegetable organism; the process is called *fermentation*, and the active agent which causes the change is termed a *ferment*. All wines, beers, and spirits, and the whole of the alcohol of commerce are prepared by the process of fermentation.

The ferment which brings about the conversion of grape-juice into wine is present on the grapes and stalks and in the air; it is a living organism, and during fermentation it rapidly grows and multiplies, feeding on the sugar, mineral salts, and nitrogenous substances contained in the juice. In order that fermentation may take place, the conditions must be favourable to the life and growth of the living ferment; sufficient food of a suitable kind must be at hand, and the temperature must be kept within certain limits.

Beer is prepared from malt and hops. Malt is the grain of barley which has been caused to sprout or germinate by first soaking it in water and then keeping it in a moist atmosphere at a suitable temperature. During the process of germination a ferment, *diastase*, is formed in the grain. The malt is now heated at 50–100° in order to stop germination and to cause the production of various substances which impart to it both colour and flavour, the character of the beer depending largely on the temperature and the duration of heating. It is then stirred up with water and kept at 60–65°, when fermentation sets in, the diastase converting the starch in the malt into *dextrin* and a sugar, *maltose*. This solution is now boiled in order to stop the *diastatic fermentation*, and then hops, the flower of the hop-plant, are added in order to impart a slight bitter taste, and also on account of the preservative properties of the hops. After cooling to from 5° to 20°, *yeast* is added, when *alcoholic fermentation* sets in, the sugar maltose being gradually converted into alcohol and carbon dioxide. The beer is then run off and kept until ready for consumption.

Beer usually contains 3–6 per cent. of alcohol, small quantities of dextrin, sugars, and colouring matters, and traces of succinic acid, glycerol, and other substances. It contains, moreover, carbon dioxide, to which it owes its refreshing taste, and small quantities of *fusel oil*, which help to give it a flavour.

The production of beer involves two distinct fermentations. In the first place, the starch in the malt is converted into maltose and dextrin by the diastase,

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5};$$

in the second place, the maltose is transformed into alcohol by the yeast,

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

One of the ferments cannot do the work of the other; yeast cannot convert starch into maltose, nor can diastase set up the alcoholic fermentation of sugar. Diastase is an amorphous substance, without definite form or structure, and apparently lifeless. Such ferments are termed *enzymes*, in contradistinction to living *organised* ferments of definite structure, of which yeast is an example.

Yeast (*saccharomyces*) consists of rounded, almost transparent living cells, which are usually grouped together in chain-like clusters. When placed in solutions of certain sugars containing small quantities of mineral substances, &c., which the organism requires for food, the cells soon begin to bud and multiply, provided also that the temperature is kept between about 5° and 30°; if it exceeds these limits, the plant stops growing, and fermentation ceases.

There are several sugars which can be fermented with yeast, the most important being dextrose or grape-sugar, $C_6H_{12}O_6$, levulose or fruit-sugar, $C_6H_{12}O_6$, and maltose, $C_{12}H_{22}O_{11}$. Cane-sugar, $C_{12}H_{22}O_{11}$, does not ferment with pure yeast, but does so with ordinary yeast, because the latter contains other ferments which rapidly convert the cane-sugar into equal molecules of dextrose and levulose:

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

The alcoholic fermentation of these sugars is expressed approximately by the equation,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2;$$

but small quantities of succinic, acetic, lactic, and butyric acids, glycerol, fusel oil, and other substances are also formed. *Fusel oil* is a mixture of the higher homologues of ethyl alcohol; it is usually present in small quantities in beers and spirits.

Manufacture of Alcohol and Spirits.—Alcohol is prepared on the large scale from potatoes, grain, rice, and other substances rich in starch. The raw material is reduced to a pulp or paste with water, mixed with a little malt, and the mixture kept at about 60° for 30–60 minutes, when diastatic fermentation takes place, and the starch is converted into dextrin and maltose. After cooling to about 15°, yeast is added, and the mixture kept until alcoholic fermentation is at an end. It is possible to obtain alcohol from starch without the use of malt, since starch is converted into dextrose when heated with dilute sulphuric acid, and, after neutralising with lime, the solution can be fermented with yeast. Alcohol is also prepared from beet-root, molasses (treacle), and other substances rich in sugar, by direct fermentation with yeast.

The weak solution of alcohol obtained by any of these methods is submitted to fractional distillation in specially constructed apparatus. The distillate is known as 'raw spirit,' and contains from 80–95 per cent. of alcohol and a small quantity of fusel oil, which passes over in spite of the fact that its constituents boil at a higher temperature than alcohol or water.

For the preparation of spirits, liqueurs, and other articles of consumption, the raw spirit must be freed as much as possible from fusel oil, which is very injurious to health. For this purpose it is diluted with water and filtered through charcoal, which absorbs some of the fusel oil. Finally, the spirit is again fractionally distilled, the portions which pass over first ('first runnings') and last ('last runnings') being collected separately; the intermediate portions consist of 'refined' or 'rectified spirit,' most of the fusel oil, which has not been removed, being present in the last runnings.

For most other purposes the separation of the fusel oil is unnecessary, and if a stronger alcohol be required, the raw spirit is again fractionated, or distilled over lime.

Alcohol is used in large quantities for the manufacture of ether, chloroform, &c., and in the purification of the alkaloids. It is employed as a solvent for gums, resins, and other substances, in the preparation of tinctures, varnishes, perfumes, &c., and is also used in spirit-lamps. In this country a heavy excise duty has long been levied on spirits of wine, a fact which acted as a serious impediment to its extended use; but since 1856 the Government has permitted the manufacture and sale of methylated spirit free of duty.

Methylated spirit contains about 90 per cent. of raw spirit (ethyl alcohol), about 10 per cent. of partially purified wood-spirit or methyl alcohol, and a small quantity of paraffin-oil, the addition of which renders the alcohol unfit for drinking purposes, without affecting its value as a solvent; methylated spirit is therefore used instead of alcohol whenever possible, as it is so much cheaper. Methylated spirit cannot be separated into its constituents by any commercial process, but the water and tarry and oily impurities can be got rid of almost completely by distilling with a little potash, and then dehydrating over lime; the purified spirit may be employed in most chemical experiments in the place of pure ethyl alcohol.

Alcoholometry.—In order to ascertain the strength of a sample of alcohol—that is, the percentage of alcohol in pure aqueous spirit, it is only necessary to determine its specific gravity at some particular temperature, and then to refer to published tables, in which the sp. gr. of all mixtures of alcohol and water is given. If, for example, the sp. gr. is found to be 0·8605 at 15·5°, reference to the tables would show that the sample contained 75 per cent. of alcohol by weight.

For excise and general purposes the sp. gr. is determined with the aid of hydrometers graduated in such a manner that the percentage of alcohol can be read off directly on the scale. The standard referred to in this country is *proof-spirit*, which contains 49·3 per cent. by weight, or 57·1 per cent. by volume of alcohol: it is defined by act of parliament as being 'such a spirit as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ths of an equal measure of distilled water.' Spirits are termed *under* or *over* proof according as they are weaker or stronger than proof-spirit: thus 20° over proof means that 100 vols. of this spirit diluted with water would yield 120 vols. of proof-spirit, whilst 20° under proof means that 100 vols. of the sample contain as much alcohol as 80 vols. of proof-spirit. The name *proof-spirit* owes its origin to the practice in vogue during the last century, of testing the strength of samples of alcohol by pouring them on to gunpowder and applying a light. If the sample contained much water, the alcohol burned away, and the water made the powder so damp that it did not ignite; but if the spirit were strong enough, the gunpowder took fire. A sample which just succeeded in igniting the powder was called proof-spirit.

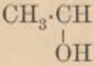
For the *determination of alcohol* in beers, wines, and spirits, a measured quantity of the sample is distilled from a flask connected with a condenser until about $\frac{1}{3}$d has passed over. The distillate, which contains the whole of the alcohol, is then diluted with water to the volume of the sample taken, and its sp. gr. determined with a hydrometer; the percentage of alcohol is found by referring to the tables already mentioned.

Distillation is necessary because the sugary and other extractive matters contained in the sample influence the sp. gr. to such an extent that a direct observation would be of no value.

The percentage of alcohol by weight in some of the best-known fermented liquors may be roughly taken as being as follows :

Brandy	50 %	Port	20 %	Hock	8 %
Whisky	50 %	Sherry	16 %	Burton Ale	5·5 %
Gin	40 %	Claret	7 %	Lager-bier	3 %

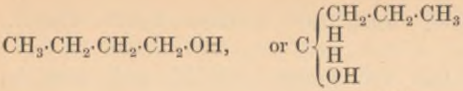
Homologues of Ethyl Alcohol.—The members of the series of monohydric alcohols may all be considered as derived from the paraffins by the substitution of the monovalent HO– group for one atom of hydrogen. Like the paraffins, they exist in isomeric forms, but, as two or more isomeric alcohols may be derived from one hydrocarbon, the number of isomerides is greater in the alcohol than in the paraffin series. Propane, $CH_3{\cdot}CH_2{\cdot}CH_3$, for example, exists in only one form, but two isomeric alcohols may be derived from it —namely, propyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and isopropyl alcohol,



$$CH_3{\cdot}\underset{\underset{OH}{|}}{CH}{\cdot}CH_3$$

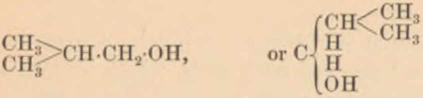
or $CH_3{\cdot}CH(OH){\cdot}CH_3$.

In order to distinguish between the various isomerides, the alcohols may be considered as derivatives of methyl alcohol or *carbinol*, $CH_3{\cdot}OH$, or $C\left\{\begin{array}{l}H\\H\\H\\OH\end{array}\right.$. Thus, propyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, may be termed ethyl-carbinol, because it may be considered as derived from carbinol by displacing one atom of hydrogen by the ethyl group C_2H_5–. Isopropyl alcohol, $(CH_3)_2CH{\cdot}OH$, may be called dimethyl-carbinol, and regarded as derived from carbinol, by substituting two methyl or CH_3– groups for two atoms of hydrogen. Such names as these serve to express the constitution of the substance, as will be seen by considering the case of the four isomeric butyl alcohols, $C_4H_9{\cdot}OH$,



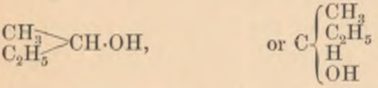
$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$, or $\mathrm{C}\begin{cases}\mathrm{CH_2{\cdot}CH_2{\cdot}CH_3}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{cases}$

Normal butyl alcohol, or propyl carbinol (primary).



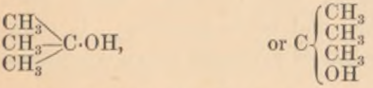
$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\!\mathrm{CH{\cdot}CH_2{\cdot}OH}$, or $\mathrm{C}\begin{cases}\mathrm{CH}\!<\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{OH}\end{cases}$

Isobutyl alcohol, or isopropyl carbinol (primary).



$\begin{matrix}\mathrm{CH_3}\\ \mathrm{C_2H_5}\end{matrix}\!>\!\mathrm{CH{\cdot}OH}$, or $\mathrm{C}\begin{cases}\mathrm{CH_3}\\ \mathrm{C_2H_5}\\ \mathrm{H}\\ \mathrm{OH}\end{cases}$

Methylethyl carbinol (secondary).



$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!-\!\mathrm{C{\cdot}OH}$, or $\mathrm{C}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{OH}\end{cases}$

Trimethyl carbinol (tertiary).

The alcohols are divided into three classes, namely, normal or primary, iso- or secondary, and tertiary alcohols.

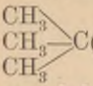
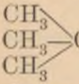
Primary or *normal alcohols* (such as normal propyl alcohol, $\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$), contain the group $-\mathrm{CH_2{\cdot}OH}$, and may be considered as mono-substitution products of carbinol. On oxidation with chromic acid, &c., they are converted first into aldehydes (p. 116) and then into fatty acids, (p. 142), the group $-\mathrm{CH_2{\cdot}OH}$ being transformed first into $-\mathrm{C}\!\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\!\diagdown\mathrm{O}\end{smallmatrix}$, and then into $-\mathrm{C}\!\begin{smallmatrix}\diagup\mathrm{O{-}H}\\ \diagdown\!\diagdown\mathrm{O}\end{smallmatrix}$

$$\mathrm{CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O}$$
$$\mathrm{CH_3{\cdot}CHO + O = CH_3{\cdot}COOH.}$$

These oxidation products contain the *same* number of carbon atoms in the molecule as the alcohols from which they are obtained.

Secondary alcohols, as, for example, isopropyl alcohol, $\mathrm{CH_3{\cdot}CH(OH){\cdot}CH_3}$, contain the group $>\mathrm{CH{\cdot}OH}$, and may be regarded as di-substitution products of carbinol. On oxidation they are converted into ketones (p. 127) containing the *same* number of carbon atoms, the group $>\mathrm{CH{\cdot}OH}$ becoming $>\mathrm{CO}$,

$$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.}$$

Tertiary alcohols, such as tertiary butyl alcohol,  $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right>C(OH)$, contain the group —C·OH, and may be regarded as tri-substitution products of carbinol. On oxidation they yield both ketones and fatty acids, which contain a *smaller* number of carbon atoms than the alcohol from which they are derived, the molecule of the latter being broken up. Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3C·OH$, for example, yields acetone, $CH_3·CO·CH_3$, acetic acid, $CH_3·CO·OH$, carbon dioxide, and other products. It could not be converted by simple loss of hydrogen into a compound,  $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right>CO$, containing the same number of carbon atoms—a change which would be analogous to that undergone by primary and secondary alcohols—because carbon is tetravalent and not pentavalent, as represented in this formula.

Propyl alcohol (normal ethyl carbinol), $CH_3·CH_2·CH_2·OH$, is one of the principal constituents of fusel oil, from which it is prepared by fractional distillation. It is formed when propyl iodide is heated with freshly precipitated silver hydroxide,

$$C_3H_7I + Ag·OH = C_3H_7·OH + AgI.$$

It is a colourless liquid of sp. gr. 0·817 at 0°, boils at 97°, and is miscible with water in all proportions. On oxidation with chromic acid, it is converted first into propaldehyde and then into propionic acid,

$$CH_3·CH_2·CH_2·OH + O = \underset{\text{Propaldehyde.}}{CH_3·CH_2·CHO} + H_2O$$

$$CH_3·CH_2·CH_2·OH + 2O = \underset{\text{Propionic Acid.}}{CH_3·CH_2·CO·OH} + H_2O.$$

Isopropyl alcohol, or dimethyl carbinol, $(CH_3)_2CH·OH$, is best prepared by the reduction of acetone in aqueous solution with sodium amalgam,

$$CH_3·CO·CH_3 + 2H = CH_3·CH(OH)·CH_3.$$

It is a colourless liquid of sp. gr. 0·789 at 0°, and boils at 81°, or about 16° lower than normal propyl alcohol. On oxidation it yields acetone,

$$CH_3 \cdot CH(OH) \cdot CH_3 + O = CH_3 \cdot CO \cdot CH_3 + H_2O.$$

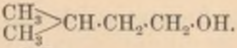
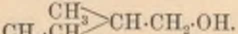
There are four isomeric **butyl alcohols**, $C_4H_9 \cdot OH$. *Normal butyl alcohol*, or propyl carbinol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$, may be prepared by the reduction of butaldehyde, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CHO$, and is produced during the fermentation of glycerol by certain bacteria. It boils at 117°.

Isobutyl alcohol, or isopropyl carbinol, $(CH_3)_2 \cdot CH \cdot CH_2 \cdot OH$, is contained in large quantities in fusel oil. It boils at 107°.

Methylethyl carbinol, $(CH_3) \cdot CH(OH) \cdot C_2H_5$, is obtained by the reduction of methyl ethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$ (p. 136), by means of sodium amalgam. It boils at 100°.

Trimethyl carbinol, $(CH_3)_3C \cdot OH$, may be prepared by the action of zinc methyl, $Zn(CH_3)_2$, on acetyl chloride, $CH_3 \cdot COCl$, a reaction which is described below (p. 107). It may also be obtained from isobutyl alcohol, as explained later (p. 108). Trimethyl carbinol is one of the few alcohols which are solid at ordinary temperatures. It melts at 28°, and boils at 83–84°.

Amyl alcohols, $C_5H_{11} \cdot OH$.—Of the eight isomerides theoretically capable of existing, the following two occur in fusel oil:

Isobutyl carbinol, (Isoamyl alcohol.)	 $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot CH_2 \cdot CH_2 \cdot OH.$	B.p. 131°.
Secondary butyl carbinol, (Active amyl alcohol.)	 $\begin{matrix} CH_3 \\ CH_3 \cdot CH_2 \end{matrix} > CH \cdot CH_2 \cdot OH.$	B.p. 127°.

These alcohols always occur in commercial amyl alcohol, and their boiling-points lie so close together that they cannot be separated by fractional distillation. A separation may, however, be accomplished by treating the mixture with sulphuric acid, and thus converting both alcohols into the alkyl hydrogen sulphates,

$$C_5H_{11} \cdot OH + H_2SO_4 = C_5H_{11} \cdot HSO_4 + H_2O.$$

By neutralising these acid salts with barium hydrate, the barium salts, $(C_5H_{11} \cdot SO_4)_2Ba$, are obtained; and, as the barium salt of isobutyl carbinol is more sparingly soluble than that of active amyl alcohol, the two may be separated by fractional crystallisation.

From the pure salts the respective alcohols are then obtained in a pure condition by distillation with dilute mineral acids,

$$C_5H_{11}{\cdot}HSO_4 + H_2O = C_5H_{11}{\cdot}OH + H_2SO_4.$$

Commercial amyl alcohol is prepared from fusel oil by fractionation, and is a mixture of about 87 per cent. of isobutyl carbinol and about 13 per cent. of active amyl alcohol. It has a pungent, unpleasant smell, boils at about 131°, and is used as a solvent, and in the preparation of essences and perfumes (p. 189).

SUMMARY AND EXTENSION.

The Monohydric Alcohols.—Hydroxy-derivatives of the paraffins of the general formula $C_nH_{2n+1}{\cdot}OH$.

The more important members of the series are the following. The letters p., s., t., in brackets, denote primary, secondary, and tertiary.

Name and composition.		B.p.	Sp. gr.
Methyl alcohol (p.)............	$CH_3{\cdot}OH$,	66°	0·812 at 0°
Ethyl alcohol (p.)..............	$C_2H_5{\cdot}OH$,	78°	0·806 „
Propyl alcohol (p.)...........	$C_3H_7{\cdot}OH$,	97°	0·817 „
Isopropyl alcohol (s.).......		83°	0·816 „
Butyl alcohol, (p.)...........	$C_4H_9{\cdot}OH$,	117°	0·823 „
Isobutyl alcohol (p.).......		108°	0·816 „
Tertiary butyl alcohol (t.)		83°	0·786 at 20°
Methylethyl carbinol (s.)		99°	0·827 „
Active amyl alcohol (p.)..	$C_5H_{11}{\cdot}OH$,	128°	— „
Isoamyl alcohol (p.)........		132°	0·825 „
Six other isomerides of little importance..........			

Methods of Preparation.—Methyl alcohol is prepared from the products of the dry distillation of wood. Ethyl alcohol is obtained by the alcoholic fermentation of sugar by means of yeast; the fusel oil produced at the same time contains propyl, isobutyl, active amyl, and isoamyl alcohols.

The alcohols are formed when the halogen substitution products of the paraffins are heated with water, dilute aqueous alkalies, or freshly precipitated silver hydroxide,

$$CH_3Br + KOH = CH_3{\cdot}OH + KBr \quad C_3H_7I + Ag{\cdot}OH = C_3H_7{\cdot}OH + AgI;$$

more readily by heating these halogen derivatives with silver or potassium acetate, and decomposing the products with potash,

$$C_2H_5I + \underset{\text{Silver Acetate.}}{C_2H_3O_2Ag} = \underset{\text{Ethyl Acetate.}}{C_2H_5{\cdot}C_2H_3O_2} + AgI$$

$$C_2H_5{\cdot}C_2H_3O_2 + KOH = C_2H_5{\cdot}OH + C_2H_3O_2K.$$

This method gives very good results, and is much used in the preparation of the higher alcohols, because the halogen derivatives of the higher paraffins (such as hexyl chloride, $C_6H_{13}Cl$), when treated directly with alkalies, are mainly converted into olefines,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl + KOH$$
$$= CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + KCl + H_2O,$$

so that the yield of alcohol is small.

Alcohols are also formed when the hydrocarbons of the olefine series are dissolved in sulphuric acid, and the solutions boiled with water,

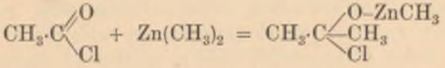
$$C_3H_6 + H_2SO_4 = C_3H_7{\cdot}HSO_4$$
$$C_3H_7{\cdot}HSO_4 + H_2O = C_3H_7{\cdot}OH + H_2SO_4,$$

and when aldehydes and ketones are reduced with nascent hydrogen, aldehydes giving primary, ketones secondary alcohols,

$$CH_3{\cdot}CH_2{\cdot}CHO + 2H = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$
$$CH_3{\cdot}CO{\cdot}CH_3 + 2H = CH_3{\cdot}CH(OH){\cdot}CH_3.$$

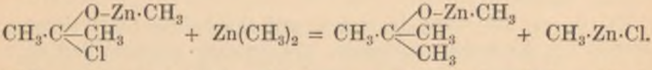
Tertiary alcohols are, as a rule, more difficult to obtain than the primary or secondary compounds; they are usually prepared by gradually adding the chloride of a fatty acid to excess of a zinc alkyl derivative. Thus acetyl chloride, $CH_3{\cdot}COCl$, acts on zinc methyl, $Zn(CH_3)_2$, forming a compound which, when treated with water, yields trimethyl carbinol, $(CH_3)_3C{\cdot}OH$.

In this reaction the zinc methyl and acetyl chloride form a crystalline compound



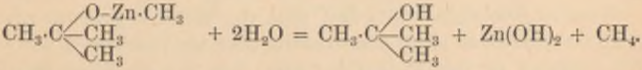
$$CH_3{\cdot}C\left\langle\begin{matrix}O\\Cl\end{matrix}\right. + Zn(CH_3)_2 = CH_3{\cdot}C\left\langle\begin{matrix}O{-}ZnCH_3\\CH_3\\Cl\end{matrix}\right.$$

which is then very slowly acted on by a further quantity of zinc methyl,



$$CH_3{\cdot}C\left\langle\begin{matrix}O{-}Zn{\cdot}CH_3\\CH_3\\Cl\end{matrix}\right. + Zn(CH_3)_2 = CH_3{\cdot}C\left\langle\begin{matrix}O{-}Zn{\cdot}CH_3\\CH_3\\CH_3\end{matrix}\right. + CH_3{\cdot}Zn{\cdot}Cl.$$

This product is decomposed by water, when trimethyl carbinol, methane, and zinc hydroxide are obtained,



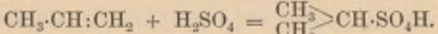
$$CH_3{\cdot}C\left\langle\begin{matrix}O{-}Zn{\cdot}CH_3\\CH_3\\CH_3\end{matrix}\right. + 2H_2O = CH_3{\cdot}C\left\langle\begin{matrix}OH\\CH_3\\CH_3\end{matrix}\right. + Zn(OH)_2 + CH_4.$$

Other tertiary alcohols may be prepared by employing other zinc alkyl compounds and other acid chlorides.

Conversion of Primary into Secondary and Tertiary Alcohols.—A secondary alcohol may be prepared from the corresponding primary compound by first converting the latter into an olefine by treating with dehydrating agents such as H_2SO_4, $ZnCl_2$, and P_2O_5,

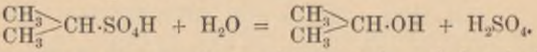
$$CH_3\cdot CH_2\cdot CH_2\cdot OH = CH_3\cdot CH{:}CH_2 + H_2O.$$

The olefine is then dissolved in fuming sulphuric acid, when an alkyl hydrogen sulphate is formed, the SO_4H– group uniting with that carbon atom which is combined with the least number of hydrogen atoms,



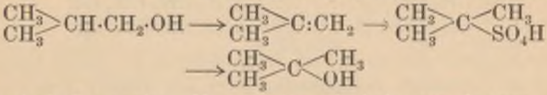
$$CH_3\cdot CH{:}CH_2 + H_2SO_4 = \begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\cdot SO_4H.$$

The alkyl hydrogen sulphate is finally converted into a secondary alcohol by boiling with water,



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\cdot SO_4H + H_2O = \begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\cdot OH + H_2SO_4.$$

In a similar manner, a primary alcohol, such as isobutyl alcohol, may be converted into the tertiary alcohol, trimethyl carbinol,



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\cdot CH_2\cdot OH \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{:}CH_2 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}CH_3\\SO_4H\end{matrix}$$
$$\longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}{>}C{<}\begin{matrix}CH_3\\OH\end{matrix}$$

Physical Properties.—No gaseous alcohols are known. The members up to $C_{12}H_{26}O$ are, with few exceptions, neutral, colourless liquids, possessing a characteristic odour and a burning taste. Trimethyl carbinol and all the higher alcohols, such as cetyl alcohol, $C_{16}H_{33}\cdot OH$, which occurs in spermaceti in combination with palmitic acid, and melissyl alcohol, $C_{30}H_{61}\cdot OH$, which is found in beeswax, also in combination with palmitic acid, are solids. Methyl, ethyl, and the propyl alcohols are miscible with water, but as the series is ascended, the solubility in water rapidly decreases, the amyl alcohols, for example, being only sparingly soluble. The alcohols are miscible in all proportions with most organic liquids.

The sp. gr. gradually increases, and the boiling-point rises on passing up the series; moreover, the primary alcohols boil at a higher temperature than the secondary, and the latter at a higher temperature than the tertiary isomerides, as shown in the table (p. 106).

Chemical Properties.—The fact that the alcohols interact with other compounds so much more readily than the paraffins is due to the presence of the hydroxyl group, the rest of the molecule remaining unchanged, except under exceptional circumstances. In many reactions the alcohols behave as alkyl substitution products of water; in others, their similarity to metallic hydroxides is more marked.

They dissolve sodium and potassium with evolution of hydrogen,

$$2C_3H_7\cdot OH + 2Na = 2C_3H_7\cdot ONa + H_2.$$

They interact with acids, forming neutral or acid ethereal salts, such as CH_3Cl, C_2H_5Br, $(C_2H_5)_2SO_4$, $C_3H_7\cdot HSO_4$.

They are converted into halogen derivatives of the paraffins, when treated with PCl_5, PCl_3, $POCl_3$, or with the corresponding bromo-derivatives,

$$PCl_5 + C_3H_7\cdot OH = C_3H_7Cl + POCl_3 + HCl.$$

They are converted into olefines by dehydrating agents, such as H_2SO_4, and $ZnCl_2$,

$$CH_3\cdot CH_2\cdot OH = CH_2{:}CH_2 + H_2O.$$

The action of oxidising agents varies with the nature of the alcohol. Primary alcohols are converted into aldehydes, and then into fatty acids, secondary alcohols into ketones, and in both cases the oxidation products contain the same number of carbon atoms in the molecule as the alcohol from which they are formed,

$$CH_3\cdot CH_2\cdot CH_2\cdot OH + O = CH_3\cdot CH_2\cdot CHO + H_2O$$
$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O.$$

Tertiary alcohols do not yield oxidation products containing the same number of carbon atoms as the alcohol, but are decomposed, giving simpler acids or ketones.

CHAPTER VII.

THE ETHERS.

The ethers, such as methyl ether, $CH_3\cdot O\cdot CH_3$, methyl ethyl ether, $CH_3\cdot O\cdot C_2H_5$, &c., are substances which contain an oxygen atom united to two hydrocarbon groups, such as CH_3-, C_2H_5-, and C_3H_7-. They are related to the metallic oxides in the same way as the alcohols to the metallic hydroxides.

$CH_3\cdot OH$ corresponds to $K\cdot OH$
$CH_3\cdot O\cdot CH_3$ " " $K\cdot O\cdot K$.

Methyl ether, $CH_3\cdot O\cdot CH_3$, may be prepared by the action of sulphuric acid or other suitable dehydrating agent on methyl alcohol,

$$2CH_3\cdot OH = CH_3\cdot O\cdot CH_3 + H_2O.$$

It is a gas which liquefies at −23°, and dissolves readily in water (1 vol. of water dissolves 37 vols. of methyl ether).

Ethyl ether, ether, or sulphuric ether,

$$C_4H_{10}O \text{ or } C_2H_5{\cdot}O{\cdot}C_2H_5,$$

is formed, together with sodium iodide, when sodium ethoxide is warmed with ethyl iodide,

$$C_2H_5{\cdot}ONa + C_2H_5I = C_2H_5{\cdot}O{\cdot}C_2H_5 + NaI.$$

It is also produced when ethyl alcohol is heated with sulphuric acid, zinc chloride, or other dehydrating agent,

$$2C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O.$$

Ethyl ether is prepared by the following method:

A mixture of five parts of 90 per cent. alcohol and nine parts of concentrated sulphuric acid is heated in a flask fitted with a tap funnel and thermometer, and connected with a condenser (fig. 17). As soon as the temperature rises to 140°

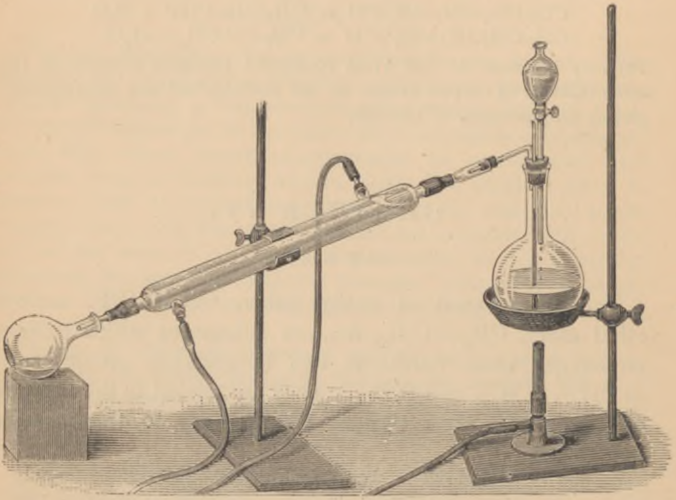


Fig. 17.

the mixture begins to boil, and ether distils over. Alcohol is now slowly run in from the tap funnel, the temperature being kept at 140–145°, and the process continued until a considerable quantity of ether has collected. The crude product in the receiver is a mixture of ether, alcohol, and water, and contains sulphur dioxide. It is shaken with dilute soda in a separating funnel; the layer of ether which collects on the surface is then separated, dried over calcium chloride or quicklime, and purified by redistillation from a water-bath. The ether still contains traces of water and alcohol, which may be got rid of by adding pieces of bright sodium, allowing to stand for some time, and again distilling. Sodium ethoxide and sodium hydroxide remain, and pure ether passes over.

The formation of ether from alcohol takes place in two stages. When alcohol is heated with sulphuric acid, it is converted into ethyl hydrogen sulphate (p. 182),

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O;$$

this compound then interacts with alcohol, yielding ether and sulphuric acid,

$$C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2SO_4.$$

That this is the true explanation of the formation of ether, is shown by the fact that ether is formed when pure ethyl hydrogen sulphate is heated with alcohol.

Now, since the sulphuric acid necessary for the conversion of the alcohol into ethyl hydrogen sulphate is regenerated when the latter is heated with alcohol, a given quantity of the acid might, theoretically, convert an unlimited quantity of alcohol into ether. As a matter of fact, a small quantity of sulphuric acid can transform a very large quantity of alcohol into ether, but the process has a limit, because the acid becomes diluted by the water formed in the first stage of the reaction, and part of it is reduced by the alcohol with formation of sulphur dioxide. This method of preparing ether, by the *continuous* addition of alcohol to a solution of alcohol in sulphuric acid, is termed the *continuous process.*

Ether is a colourless, mobile, neutral, pleasant-smelling liquid of sp. gr. 0·736 at 0°. It boils at 35°, and does not solidify at $-80°$. It is very volatile, and highly inflammable, its vapour forming an explosive mixture with air or oxygen,

$$C_4H_{10}O + 6O_2 = 4CO_2 + 5H_2O,$$

so that all experiments in which ether is used should be conducted at a considerable distance from all flames or hot objects. Ether is soluble in about ten times its own volume of water, and is miscible with alcohol and other organic liquids in all proportions.

Compared with alcohol, ether is a very indifferent substance. It is not acted on by sodium or potassium, by alkalies or weak acids, or by phosphorus pentachloride in the cold. Concentrated acids, however, decompose ether, with formation of ethereal salts (p. 171),

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + H_2O$$
$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Ether is used in considerable quantities in surgery as an anæsthetic, since, like chloroform, it causes insensibility when inhaled; it is also very largely employed as a solvent for resins, fats, oils, alkaloids, &c.

Constitution of Ether.—Since ether is produced by the action of ethyl iodide, C_2H_5I, on sodium ethoxide, $C_2H_5{\cdot}ONa$, it may be concluded that it is formed by the substitution of the monovalent C_2H_5- group for the sodium atom, and its constitution may be expressed by the formula $C_2H_5{\cdot}O{\cdot}C_2H_5$. The same conclusion is arrived at from the fact that ether is formed when 1 mol. of H_2O is taken away from 2 mols. of alcohol by the action of dehydrating agents,

$$C_2H_5\boxed{OH\quad H}OC_2H_5 = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O.$$

When represented by this formula, several facts concerning the behaviour of ether are brought to mind. Ether, unlike alcohol, contains no HO– group, and therefore it is not acted on by sodium or potassium, or by phosphorus pentachloride; and, not being a hydroxide, it does not interact with acids to form an ethereal salt and water. Ether may be regarded as the *anhydride* of alcohol, as it is formed from alcohol (2 mols.) by the removal of the elements of water, just in the same way as nitric anhydride is formed from nitric acid,

$$2C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2O \qquad 2NO_2{\cdot}OH = (NO_2)_2O + H_2O.$$

Ether may also be compared with the metallic oxides and regarded as *ethyl oxide*, since it is related to alcohol or ethyl hydroxide in the same way as the metallic oxides to the metallic hydroxides,

$$\begin{array}{llll} C_2H_5{\cdot}OH & C_2H_5{\cdot}O{\cdot}C_2H_5 & \text{or} & (C_2H_5)_2O \\ K{\cdot}OH & K{\cdot}O{\cdot}K & \text{or} & K_2O. \end{array}$$

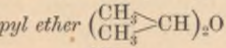
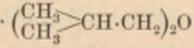
Finally, it may be regarded as a di-substitution product of water, the mono-substitution product being the corresponding alcohol,

$$H{\cdot}O{\cdot}H \qquad C_2H_5{\cdot}O{\cdot}H \qquad C_2H_5{\cdot}O{\cdot}C_2H_5.$$

The *homologues* of ether are very similar to ethyl ether in properties.

SUMMARY AND EXTENSION.

Some of the more important higher ethers are the following:

Dipropyl ether $(CH_3{\cdot}CH_2{\cdot}CH_2)_2O$	B.p.	90·7°
Di-isopropyl ether  $\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CH\right)_2O$	"	69°
Di-isobutyl ether  $\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CH{\cdot}CH_2\right)_2O$	"	122°
Di-isoamyl ether $(C_5H_{11})_2O$	"	170–175°

General Methods of Formation.—The ethers may be obtained by treating the sodium compounds of the alcohols with the alkyl halogen compounds,

$$CH_3{\cdot}ONa + CH_3I = CH_3{\cdot}O{\cdot}CH_3 + NaI;$$

but they are usually prepared by heating the alcohols with sulphuric acid. If a mixture of two alcohols be treated with sulphuric acid, *three* ethers are formed. A mixture of methyl and ethyl alcohols, for example, yields *methyl ether*, *ethyl ether*, and *methyl ethyl ether*, $CH_3{\cdot}O{\cdot}C_2H_5$. The formation of the two first-named compounds will be understood from the equations given above in the case of ethyl ether. Methyl ethyl ether is produced by the interaction (*a*) of methyl hydrogen sulphate, and ethyl alcohol, (*b*) of ethyl hydrogen sulphate and methyl alcohol,

$$CH_3{\cdot}HSO_4 + C_2H_5{\cdot}OH = CH_3{\cdot}O{\cdot}C_2H_5 + H_2SO_4$$
$$C_2H_5{\cdot}HSO_4 + CH_3{\cdot}OH = C_2H_5{\cdot}O{\cdot}CH_3 + H_2SO_4.$$

All ethers, such as methyl ethyl ether, $CH_3{\cdot}O{\cdot}C_2H_5$, which contain two different hydrocarbon groups, are termed *mixed ethers*, to distinguish them from *simple ethers*, such as ethyl ether, $C_2H_5{\cdot}O{\cdot}C_2H_5$, and those given in the above table, which contain two identical groups. Mixed ethers can also be obtained by treating the sodium compounds of the alcohols with alkyl halogen compounds,

$$CH_2{\cdot}ONa + C_3H_7I = CH_3{\cdot}O{\cdot}C_3H_7 + NaI.$$

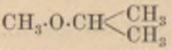
General Properties.—With the exception of methyl ether, which is a gas, the ethers are mobile, volatile, inflammable liquids, specifically lighter than water; they all boil at a much lower temperature than the corresponding alcohols. In chemical properties they closely resemble ethyl ether. They are not acted on by alkalies or alkali metals, and do not combine with dilute acids; but they are decomposed when heated with strong acids, yielding ethereal salts,

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + H_2O$$
$$CH_3{\cdot}O{\cdot}C_2H_5 + 2HBr = CH_3Br + C_2H_5Br + H_2O.$$

Chlorine and bromine act on ethers, forming substitution products such as

$$CH_2Cl{\cdot}O{\cdot}CH_3,\ CH_2Br{\cdot}O{\cdot}CH_2Br,\ C_2H_5{\cdot}O{\cdot}C_2H_4Cl,\ \&c.$$

Metamerism.—The ethers exist in isomeric forms. There are, for example, three compounds of the formula $C_4H_{10}O$,

$CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	 $CH_3{\cdot}O{\cdot}CH{<}\begin{matrix}CH_3\\CH_3\end{matrix}$	$CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3.$
Methyl Propyl Ether.	Methyl Isopropyl Ether.	Ethyl Ether.

Substances such as these, which have the same molecular formula, but in which *all* the carbon atoms in the molecule are not directly united, are called *metameric*; the phenomenon is called *metamerism*, and the several compounds, *metamers*. Metamerism is simply a particular form of isomerism, and there is no real distinction between the two, the different terms being used purely for the sake of convenience.

RADICLES.

On studying the equations which represent the interactions of alcohols, ethers, &c., it is evident that certain groups of atoms often remain unchanged during a whole series of double decompositions. Ethyl chloride, for example, may be converted into ethyl alcohol, the latter may be transformed into ethyl iodide, and this again may be converted into butane, but during all these interactions the group C_2H_5- remains unchanged, and behaves, in fact, as if it were a single atom,

$$C_2H_5{\cdot}Cl + H{\cdot}OH = C_2H_5{\cdot}OH + HCl$$
$$C_2H_5{\cdot}OH + HI = C_2H_5{\cdot}I + H_2O$$
$$2C_2H_5{\cdot}I + 2Na = C_2H_5{\cdot}C_2H_5 + 2NaI.$$

Numerous examples of a similar kind might be quoted; amongst others, the changes by which the five compounds, $CH_3{\cdot}Cl$, $CH_3{\cdot}OH$ $CH_3{\cdot}O{\cdot}CH_3$, $CH_3{\cdot}I$, and $CH_3{\cdot}CH_3$, may be successively transformed one into the other.

Groups of atoms, such as C_2H_5- and CH_3-, which act like *single atoms*, and which *enter unchanged* into a number of compounds, are termed **radicles**, or sometimes compound radicles.

Radicles may be monovalent, divalent, &c., according as they act like monad, dyad, &c., atoms; the radicles C_2H_5- and CH_3-, for example, are monad radicles, because they combine with one atom of hydrogen or its valency equivalent, as shown in the above equations.

The name **alkyl** or alcohol radicle is given to all the *monovalent* groups of atoms which are, theoretically, obtained on taking away one atom of hydrogen from the paraffins, methane, ethane, propane, butane, &c.; the distinctive names of these radicles are derived from those of the hydrocarbons by changing *ane* into *yl*, thus: *methyl*, CH_3-; *ethyl*, C_2H_5- or $CH_3{\cdot}CH_2-$; *propyl*, C_3H_7- or $CH_3{\cdot}CH_2{\cdot}CH_2-$; *isopropyl*, C_3H_7- or $(CH_3)_2CH-$; *butyl*, C_4H_9- or $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2-$; *isobutyl*, C_4H_9- or $(CH_3)_2CH{\cdot}CH_2-$, &c.

The compounds formed by the combination of these hypothetical alkyl radicles with hydrogen, as, for example, $CH_3{\cdot}H$, $C_2H_5{\cdot}H$, $C_3H_7{\cdot}H$, are named collectively the *alkyl hydrides*, and are identical with the paraffins; the corresponding chlorine compounds, such as $CH_3{\cdot}Cl$, $C_2H_5{\cdot}Cl$, $C_3H_7{\cdot}Cl$, are termed the *alkyl chlorides*, and so on. The letter R is frequently employed to represent an alkyl radicle, as, for example, in the formulæ $R{\cdot}OH$ (alcohols) and $R{\cdot}O{\cdot}R$ (simple ethers).

The name **alkylene** is given to the *divalent* radicles, which (except methylene) may be actually obtained by taking away two atoms of hydrogen from the paraffins. The alkylenes are *methylene*, $CH_2=$; *ethylene*, $C_2H_4=$; *propylene*, $C_3H_6=$; *butylene*, $C_4H_8=$, &c. ; and the compounds which they form, with chlorine, for example, such as $CH_2{:}Cl_2$, $C_2H_4{:}Cl_2$, are termed collectively the *alkylene chlorides*, &c.

Trivalent hydrocarbon radicles, such as *glyceryl*, $C_3H_5\equiv$, are seldom met with, and will be mentioned later.

Other radicles frequently met with are: hydroxyl, $-OH$; carbonyl, $=CO$; carboxyl, $-CO{\cdot}OH$; cyanogen, $-CN$; acetyl, $-CO{\cdot}CH_3$, &c. The true significance of the term radicle will be more easily understood when a greater number of organic compounds has been considered.

CHAPTER VIII.

ALDEHYDES AND KETONES.

The aldehydes form a homologous series of the general formula $C_nH_{2n}O$, or $C_nH_{2n+1}{\cdot}CHO$; they are derived from the primary alcohols $C_nH_{2n+1}{\cdot}CH_2{\cdot}OH$ by the removal of two atoms of hydrogen from the $-CH_2{\cdot}OH$ group,

Paraffins.	Alcohols.	Aldehydes.
$H{\cdot}CH_3$	$H{\cdot}CH_2{\cdot}OH$	$H{\cdot}CHO$
$CH_3{\cdot}CH_3$	$CH_3{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CHO$
$C_2H_5{\cdot}CH_3$	$C_2H_5{\cdot}CH_2{\cdot}OH$	$C_2H_5{\cdot}CHO$.

The word aldehyde is a contraction of *al*cohol *dehyd*rogenatum, this name having been originally given to acetaldehyde, because it is formed when hydrogen is taken from alcohol by a process of oxidation.

Formaldehyde, or methaldehyde, $H{\cdot}CHO$, is said to occur in those plant cells which contain the green colouring matter, chlorophyll, and is possibly an intermediate product in that wonderful process—the formation of starch and sugars from the carbon dioxide which the plant absorbs from the air.

Formaldehyde is produced when calcium formate is subjected to dry distillation,

$$(H{\cdot}COO)_2Ca = H{\cdot}CHO + CaCO_3,$$

and is prepared by passing a stream of air, saturated with the vapour of methyl alcohol, through a tube containing a copper spiral, or platinised asbestos, heated to dull redness;* the change is a process of oxidation,

$$CH_3{\cdot}OH + O = H{\cdot}CHO + H_2O.$$

The pungent-smelling liquid which collects in the receiver may contain, under favourable conditions, as much as 30–40 per cent. of formaldehyde, together with methyl alcohol and water. On evaporating the solution on a water-bath or even at ordinary temperatures, the formaldehyde gradually undergoes change (polymerisation), and is converted into paraformaldehyde, which remains as a white solid.

The formation of formaldehyde may be readily demonstrated by heating a spiral of platinum wire to dull redness and quickly suspending it over methyl alcohol contained in a beaker; the spiral begins to glow, and irritating vapours are rapidly evolved, a slight but harmless explosion usually taking place.

Formaldehyde is only known in dilute solution and in the state of a gas at high temperatures (see below). That it would probably be a gas at ordinary temperatures may be inferred by considering the boiling-points of the next higher members of the series. Since the difference between the boiling-points of two consecutive aldehydes such as

---

* Unless special precautions be taken, explosions frequently occur.

propaldehyde, $C_2H_5{\cdot}CHO$ (49°), and acetaldehyde, $CH_3{\cdot}CHO$ (20°·8), is about 28°, formaldehyde would probably boil at about $-7°$, or 28° lower than acetaldehyde.* Aqueous solutions of formaldehyde have a very penetrating, suffocating odour and a neutral reaction; they have also a powerful reducing action, since formaldehyde readily undergoes oxidation, yielding formic acid,

$$H{\cdot}CHO + O = H{\cdot}COOH.$$

When its aqueous solution is mixed with an ammoniacal solution of silver oxide, the latter is reduced, a silver mirror being obtained,

$$H{\cdot}CHO + Ag_2O = H{\cdot}COOH + 2Ag;$$

mercuric chloride is also reduced, first to mercurous chloride, then to mercury.

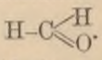
When formaldehyde is treated with reducing agents, it is converted into methyl alcohol,

$$H{\cdot}CHO + 2H = H{\cdot}CH_2{\cdot}OH.$$

When a concentrated aqueous solution of formaldehyde is mixed with a saturated solution of sodium hydrogen sulphite, direct combination takes place, a compound of the constitution $OH{\cdot}CH_2{\cdot}SO_3Na$ being formed. Formaldehyde interacts with hydroxylamine in aqueous solution, yielding *formaldoxime*,

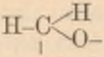
$$H{\cdot}CHO + NH_2{\cdot}OH = H{\cdot}CH:NOH + H_2O,$$

a substance which is only known in solution since it very readily undergoes polymerisation.

Constitution.—Since carbon is tetravalent, there is only one way of expressing graphically the constitution of formaldehyde, CH_2O, namely, by the formula  $H{-}C{<}^{H}_{O}$. In the formation of formaldehyde by the oxidation of methyl alcohol, $CH_3{-}O{-}H$, the hydrogen atom of the HO– group and one of the atoms combined directly with carbon are

---

* As a rule, the lowest member of a homologous series shows a somewhat abnormal behaviour, and its properties cannot be foretold with as much certainty as in the case of the higher members.

taken away. The carbon and oxygen atoms in formaldehyde are therefore represented in a state of combination different from that existing in methyl alcohol—namely, as joined by two lines instead of one. Formaldehyde behaves in some ways like an unsaturated compound, capable of forming additive products, because, under certain conditions, it may act as if it had the constitution  $\mathrm{H{-}\underset{|}{C}{<}^{H}_{O-}}$ In aqueous solution it probably exists to some extent as the hydrate $CH_2(OH)_2$.

Paraformaldehyde, $(CH_2O)_n$, is formed, as stated above, when an aqueous solution of formaldehyde is evaporated; it is a colourless, amorphous substance, sublimes readily, and melts at 171°. When strongly heated, it is completely decomposed into pure, *gaseous formaldehyde*, CH_2O, as is proved by vapour density determinations; but as the gas cools, paraformaldehyde is again produced. When paraformaldehyde is heated with a large quantity of water, it is reconverted into formaldehyde.

The relation between formaldehyde and paraformaldehyde is similar to that between yellow and red phosphorus, or between the allotropic modifications of elements in general. Just as yellow is converted into red phosphorus on heating, so formaldehyde is converted into paraformaldehyde; and just as red is changed into yellow phosphorus on heating more strongly, so paraformaldehyde is changed into formaldehyde. Here, however, the similarity in behaviour ends, since the gaseous formaldehyde changes into paraformaldehyde on cooling.

The different forms in which a definite compound may exist are termed **polymeric** forms or modifications, such forms being in many respects similar to the allotropic forms of the elements—that is to say, a polymeric form is simply an aggregate of the molecules of the original substance, and the change of the simple into a complex form is spoken of as **polymerisation**. Paraformaldehyde is a polymeric form or a **polymeride** or **polymer** of formaldehyde, and its molecule consists of two or more (n) molecules of formaldehyde united to form a complex molecule $(CH_2O)_n$.

Formaldehyde forms several polymeric modifications, and the readiness with which it undergoes polymerisation is one of its most characteristic properties. When its aqueous solution is treated with lime-water or other weak alkali, formaldehyde undergoes polymerisation into *formose*, a mixture of substances, some of which have the composition $(CH_2O)_6$ or $C_6H_{12}O_6$, and belong to the sugar group. This reaction is of great interest, since it shows that complex vegetable substances such as the sugars may be formed by very simple means.

Methylal, $CH_2(OCH_3)_2$, is an important derivative of formaldehyde. It may be obtained by boiling aqueous formaldehyde with methyl alcohol and a small quantity of sulphuric acid, but is usually prepared by oxidising methyl alcohol with manganese dioxide and sulphuric acid, the formaldehyde first produced combining with the unchanged methyl alcohol,

$$H{\cdot}CHO + 2CH_3{\cdot}OH = H{\cdot}CH(OCH_3)_2 + H_2O.$$

Methylal, a pleasant-smelling liquid, which boils at 42° and is readily soluble in water, is used in medicine as a soporific. When distilled with dilute sulphuric acid, it is resolved into methyl alcohol and formaldehyde, a reaction which may be conveniently employed for preparing the latter.

Acetaldehyde, or ethaldehyde, $CH_3{\cdot}CHO$, is contained in the 'first runnings' obtained in the rectification of refined spirit (p. 100), having been formed by the oxidation of the alcohol during the process of filtration through charcoal; it is formed when a mixture of calcium acetate and calcium formate is submitted to dry distillation,

$$(CH_3{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca = 2CH_3{\cdot}CHO + 2CaCO_3,$$

and is prepared by oxidising alcohol with potassium bichromate and sulphuric acid,

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O.$$

Coarsely powdered potassium bichromate (3 parts) and water (12 parts) are placed in a capacious flask fitted with a tap-funnel and attached to a condenser, and a mixture of alcohol (3 parts) and concentrated sulphuric acid (4 parts) is then run in moderately rapidly, the flask being gently heated on a water-bath during the operation. A vigorous action sets in, and a liquid, which consists of aldehyde, alcohol, water, and small quantities of acetal (see below), collects in the receiver. This liquid is now distilled from a water-bath, the temperature of which is not allowed to rise above 50°, when the aldehyde, being very volatile, passes over, most of the impurities remaining in the flask; the distillate is then mixed with ether, and the mixture saturated with dry ammonia, when a crystalline precipitate of *aldehyde ammonia* (see below) is obtained. This substance is transferred to a filter, washed with ether, and then decomposed by distillation with dilute sulphuric acid at as low a temperature as possible; the aldehyde is finally dehydrated by distillation with coarsely powdered anhydrous calcium chloride, the receiver being well cooled with ice in this and in the previous operations.

Acetaldehyde, or aldehyde, as it is usually called, is a colourless, mobile, very volatile liquid of sp. gr. 0·801 at 0°; it boils at 20·8°. It has a peculiar penetrating and suffocating odour, somewhat like that of sulphur dioxide, and when inhaled it produces cramp in the throat, and for some seconds takes away the power of respiration; it is very inflammable, and mixes with water, alcohol, and ether in all proportions. Aldehyde is slowly oxidised to acetic acid on exposure to the air, and, like formaldehyde, it has powerful reducing properties; it precipitates silver, in the form of a mirror, from ammoniacal solutions of silver oxide, being itself oxidised to acetic acid,

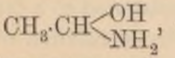
$$CH_3{\cdot}CHO + Ag_2O = CH_3{\cdot}COOH + 2Ag.$$

On treatment with reducing agents, it is converted into alcohol, just as formaldehyde is reduced to methyl alcohol,

$$CH_3{\cdot}CHO + 2H = CH_3{\cdot}CH_2{\cdot}OH$$
$$H{\cdot}CHO + 2H = H{\cdot}CH_2{\cdot}OH.$$

Aldehyde interacts readily with hydroxylamine in aqueous solution, yielding a crystalline compound, *acetaldoxime*,

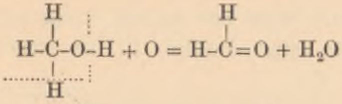
$$CH_3{\cdot}CHO + NH_2{\cdot}OH = CH_3{\cdot}CH{:}NOH + H_2O.$$

When aldehyde is shaken with a concentrated solution of sodium hydrogen sulphite (sodium bisulphite), direct combination occurs, and a colourless substance of the composition $CH_3{\cdot}CHO,NaHSO_3$ separates in crystals. This compound is readily decomposed by acids, alkalies, and alkali carbonates, aldehyde being liberated. Aldehyde also combines directly with dry ammonia, yielding a colourless, crystalline substance, *aldehyde ammonia*, $CH_3{\cdot}CHO,NH_3$, or  $CH_3{\cdot}CH{<}\begin{smallmatrix}OH\\ NH_2\end{smallmatrix}$, which is decomposed by acids, aldehyde being regenerated.

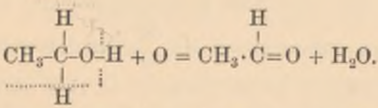
Aldehyde very readily undergoes polymerisation on treatment with acids, dehydrating agents, and other substances (see below). Its behaviour with alkalies is very characteristic; when it is warmed with potash or soda, a violent action sets in, and the aldehyde is converted into a brown substance called *aldehyde resin*.

Aldehyde may be detected by its smell, by its reducing action on silver oxide, and by the 'magenta' or 'rosaniline test' (Schiff's reaction), which is carried out as follows: Sulphurous acid is added to a dilute solution of rosaniline hydrochloride until the pink colour is just discharged; the solution to be tested is now added, when, if it contain a trace of aldehyde, a violet or pink colour immediately appears. This behaviour is not characteristic of acetaldehyde, as, with very few exceptions, all aldehydes give this reaction.

Constitution.—Aldehyde is formed by the oxidation of ethyl alcohol, just as formaldehyde is produced by the oxidation of methyl alcohol, two atoms of hydrogen being removed in both cases. Now, as regards formaldehyde, it must be assumed that the hydrogen atom of the HO– group takes part in the change; probably, therefore, this is also true in the case of acetaldehyde, because the two substances are so very similar in chemical properties that they must be similar in constitution. The two reactions may therefore be expressed in a similar manner,



$$H\text{–}\overset{H}{\underset{H}{C}}\text{–}O\text{–}H + O = H\text{–}\overset{H}{C}{=}O + H_2O$$

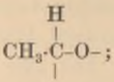


$$CH_3\text{–}\overset{H}{\underset{H}{C}}\text{–}O\text{–}H + O = CH_3\cdot\overset{H}{C}{=}O + H_2O.$$

Judging from analogy, then, the constitution of aldehyde is expressed by the formula $CH_3\cdot C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}$; this view accords very well with the whole chemical behaviour of the compound. Aldehyde, unlike alcohol, does not contain a hydrogen atom displaceable by sodium or potassium, and does not form salts with acids; these facts are expressed by the above formula, which shows that aldehyde does not contain an HO– group. When aldehyde is treated with phosphorus pentachloride, one atom of oxygen is displaced by *two* atoms of chlorine, a change which is very different from that which occurs when alcohol is acted on, and which affords further evidence that aldehyde is not a hydroxy-compound. This point is rendered very clear if the behaviour of aldehyde and alcohol respectively with phosphorus pentachloride be represented side by side,

$$CH_3\cdot CH\mathbf{O} + PCl_5 = CH_3\cdot CHCl_2 + POCl_3$$
$$CH_3\cdot CH_2\cdot\mathbf{OH} + PCl_5 = CH_3\cdot CH_2Cl + POCl_3 + HCl.$$

The fact that aldehyde has the power of combining directly with ammonia, sodium hydrogen sulphite, alcohol (see below), &c., is also indicated by the above constitutional formula. Under certain conditions the nature of the union between the carbon and oxygen atoms may undergo change, and the aldehyde may then act as if it had the constitution



$$CH_3{\cdot}\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}{-}O{-}\,;$$

in other words, it may behave like an unsaturated compound and combine directly with two monad atoms or groups, as in its reduction to ethyl alcohol, in its conversion into aldehyde ammonia, &c.

It will be seen that both formaldehyde and acetaldehyde contain the monovalent group $-C\Big\langle{}^{H}_{O}$, which is usually written $-CHO$ (not COH); it is the presence of this *aldehyde group* which determines their characteristic properties, and all aldehydes are assumed to contain a group of this kind.

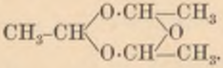
Polymerisation of Acetaldehyde.—Three well-defined polymerides of aldehyde are known—namely, aldol, paraldehyde, and metaldehyde.

Aldol, $(C_2H_4O)_2$, or $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$, is produced by the action of dilute hydrochloric acid, or of zinc chloride, on aldehyde at ordinary temperatures. It is a colourless, inodorous liquid, miscible with water, and shows all the ordinary properties of an aldehyde. It can be distilled under reduced pressure without decomposition, but when distilled under ordinary pressure, or when treated with dehydrating agents, it is converted into *crotonaldehyde* (p. 256) and water,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O.$$

Paraldehyde, $(C_2H_4O)_3$, is readily produced by adding a drop of concentrated sulphuric acid to aldehyde, an almost explosive action taking place. It is a colourless, pleasant-smelling liquid, boils at 124°, and solidifies in the cold. It is soluble in water, its cold saturated solution becoming turbid on warming, as it is less soluble in hot than in cold water; when distilled with dilute sulphuric acid, it is converted into aldehyde. Paraldehyde is used in medicine as a soporific.

Paraldehyde shows none of the ordinary properties of an aldehyde, and probably, therefore, does not contain the aldehyde or -CHO group; in other words, it is not a true aldehyde, and its constitution is usually represented by the formula



Metaldehyde, $(C_2H_4O)_n$, is produced by the action of acids on aldehyde at low temperatures. It crystallises in colourless needles, and is insoluble in water; it can be sublimed without decomposition, but on prolonged heating, it is converted into aldehyde, a change which is also readily brought about by distilling it with dilute sulphuric acid. Metaldehyde is probably isomeric with paraldehyde.

Derivatives of Aldehyde.—**Acetal**, $CH_3{\cdot}CH(OC_2H_5)_2$, is produced when a mixture of aldehyde and alcohol is heated at 100°, or when alcohol is oxidised with manganese dioxide and sulphuric acid (compare methylal, p. 120),

$$CH_3{\cdot}CHO + 2C_2H_5{\cdot}OH = CH_3{\cdot}CH(OC_2H_5)_2 + H_2O.$$

It is a colourless liquid, possessing an agreeable smell, and boiling at 104°; when distilled with dilute acids, it is decomposed into alcohol and aldehyde,

$$CH_3{\cdot}CH(OC_2H_5)_2 + H_2O = CH_3{\cdot}CHO + 2C_2H_5{\cdot}OH.$$

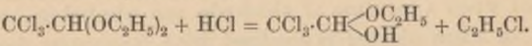
Chloral, or trichloraldehyde, $CCl_3{\cdot}CHO$, cannot be prepared by the direct action of chlorine on aldehyde; it is manufactured on a large scale by saturating alcohol with chlorine, first at ordinary temperatures, and then at the boiling-point, the operation taking some days. The crystalline product, which consists for the greater part of *chloral alcoholate*, $CCl_3{\cdot}CH{<}^{OC_2H_5}_{OH}$, is distilled with concentrated sulphuric acid, and the oily distillate of crude chloral converted into chloral hydrate (see below). After purifying the hydrate by recrystallisation from water, it is distilled with sulphuric acid, when pure chloral passes over.

The formation of chloral alcoholate may be represented by the equations

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O$$
$$CH_3{\cdot}CHO + C_2H_5{\cdot}OH = CH_3{\cdot}CH(OH){\cdot}OC_2H_5$$
$$CH_3{\cdot}CH(OH){\cdot}OC_2H_5 + 3Cl_2 = CCl_3{\cdot}CH(OH){\cdot}OC_2H_5 + 3HCl,$$

the aldehyde first produced by the oxidising action of the chlorine (p. 91), combining with alcohol, and being finally converted into chloral alcoholate by substitution.

It is, however, very doubtful whether the action is quite so simple. A more probable explanation is that acetal is first produced by the combination of the aldehyde with the unchanged alcohol, and then converted into trichloracetal, $CCl_3{\cdot}CH(OC_2H_5)_2$, by the further action of chlorine; this substance is finally decomposed by the hydrogen chloride produced during the reaction, giving chloral alcoholate and ethyl chloride,



$$CCl_3{\cdot}CH(OC_2H_5)_2 + HCl = CCl_3{\cdot}CH{<}^{OC_2H_5}_{OH} + C_2H_5Cl.$$

Chloral is an oily liquid of sp. gr. 1·512 at 20°, and boils at 97°. It has a penetrating and irritating smell, and in chemical properties closely resembles aldehyde, a fact which was only to be expected, since it is a simple substitution product of aldehyde, and contains the characteristic aldehyde group. It has reducing properties, combines directly with ammonia, sodium hydrogen sulphite, &c., and on oxidation it is converted into trichloracetic acid (p. 163), just as aldehyde is converted into acetic acid,

$$CCl_3{\cdot}CHO + O = CCl_3{\cdot}COOH.$$

On the addition of small quantities of acids, it readily undergoes polymerisation, being transformed into a white amorphous modification called *metachloral;* the same change takes place when chloral is kept for a considerable time. One of the most interesting reactions of chloral is its behaviour with boiling potash, by which it is quickly decomposed, giving chloroform (p. 172) and potassium formate,

$$CCl_3{\cdot}CHO + KOH = CHCl_3 + H{\cdot}COOK.$$

Pure chloroform is often prepared in this way.

Chloral Hydrate, $CCl_3{\cdot}CH(OH)_2$.—When chloral is poured into water, it sinks as an oil at first, but in a few seconds the oil changes to a mass of colourless crystals of chloral hydrate, a considerable rise in temperature taking place. Chloral hydrate melts at 57°, is readily soluble in water, and is decomposed on distillation with sulphuric acid, chloral passing over. In some respects it is a very stable substance; it does not polymerise, and does not give the rosaniline reaction of aldehydes. These facts point to the conclusion that chloral hydrate does not contain the aldehyde group, but that by combination with water the chloral has been converted into a substance of the constitution $CCl_3{\cdot}CH{<}^{OH}_{OH}$.

Chloral hydrate is extensively used in medicine as a soporific.

Homologues of Acetaldehyde.—The higher members of the homologous series of aldehydes, such as *propaldehyde*, $C_2H_5{\cdot}CHO$, *butaldehyde*, $C_3H_7{\cdot}CHO$, may be produced by the oxidation of the corresponding primary alcohols, or by the dry distillation of the calcium salts of the corresponding fatty acids with calcium formate; they resemble acetaldehyde in chemical properties.

Heptaldehyde, or **Œnanthol,** $C_6H_{13}{\cdot}CHO$, is of considerable interest because it is one of the products of the dry distillation of castor-oil. It is a colourless oil, boils at 154°, and has a penetrating, disagreeable odour; on oxidation it yields normal heptylic acid, $C_6H_{13}{\cdot}COOH$ (p. 158), and on reduction, normal heptyl alcohol, $C_6H_{13}{\cdot}CH_2{\cdot}OH$.

KETONES.

The ketones, of which the simplest, acetone, $CH_3{\cdot}CO{\cdot}CH_3$, may be taken as an example, are derived from the secondary alcohols, such as isopropyl alcohol, $CH_3{\cdot}CH(OH){\cdot}CH_3$, by the removal of two atoms of hydrogen from the $-CH(OH)$

group, the process being, in fact, strictly analogous to the formation of aldehydes from the primary alcohols. Ketones are characterised by containing the divalent group $>C=O$ united with two alkyl radicles, as in $CH_3{\cdot}CO{\cdot}C_2H_5$, $C_2H_5{\cdot}CO{\cdot}C_2H_5$, and their composition may be expressed by the general formula $C_nH_{2n}O$; they are isomeric with the aldehydes:

$$\left.\begin{array}{ll}\text{Propaldehyde,} & CH_3{\cdot}CH_2{\cdot}CHO \\ \text{Dimethyl ketone,} & CH_3{\cdot}CO{\cdot}CH_3\end{array}\right\} C_3H_6O$$

$$\left.\begin{array}{ll}\text{Butaldehyde,} & CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \\ \text{Ethylmethyl ketone,} & CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3\end{array}\right\} C_4H_8O.$$

Acetone, or dimethyl ketone, $CH_3{\cdot}CO{\cdot}CH_3$, occurs in small quantities in normal urine, and in cases of *diabetes mellitus* and *acetonuria* the quantity increases considerably. It also occurs in small quantities in the blood.

Acetone is formed when isopropyl alcohol is oxidised with potassium bichromate and sulphuric acid,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O,$$

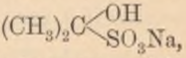
and is produced in considerable quantities during the dry distillation of wood and many other organic compounds, such as sugar, gum, &c. Crude wood-spirit, which has been freed from acetic acid (p. 89), consists in the main of a mixture of acetone and methyl alcohol. These two substances may be roughly separated by the addition of calcium chloride, which combines with the methyl alcohol; on subsequent distillation, crude acetone passes over, and may be purified by conversion into the bisulphite compound (see below).

Acetone is usually prepared by the dry distillation of crude calcium or barium acetate,

$$(CH_3{\cdot}COO)_2Ca = CH_3{\cdot}CO{\cdot}CH_3 + CaCO_3.$$

The distillate is fractionated, and the portion boiling between 50 and 60° mixed with a strong solution of sodium bisulphite. The crystalline cake of 'acetone sodium bisulphite,' which separates on standing, is well pressed, to free it from impurities, decomposed by distillation with dilute sodium carbonate, and the aqueous distillate of pure acetone dehydrated over calcium chloride.

Acetone is a colourless, mobile liquid of sp. gr. 0·792 at 20°; it boils at 56·5°, has a peculiar, pleasant, ethereal odour, and is miscible with water, alcohol, and ether in all proportions.

In chemical properties acetone resembles aldehyde in several important particulars. When shaken with a concentrated aqueous solution of sodium bisulphite, direct combination takes place with considerable development of heat, and a colourless, crystalline substance, *acetone sodium bisulphite*, $CH_3{\cdot}CO{\cdot}CH_3,NaHSO_3$, or  $(CH_3)_2C\begin{smallmatrix}\diagup OH\\ \diagdown SO_3Na\end{smallmatrix}$, separates. This compound is readily soluble in water, and is quickly decomposed by dilute acids and alkalies, acetone being regenerated. Acetone, like aldehyde, interacts with hydroxylamine in aqueous solution, forming acetoxime,

$$(CH_3)_2CO + NH_2{\cdot}OH = (CH_3)_2C{:}NOH + H_2O,$$

a crystalline substance, melting at 59°. When treated with phosphorus pentachloride, the oxygen atom in acetone is displaced by two atoms of chlorine, and β-dichloropropane is formed,

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3;$$

on reduction, acetone is converted into secondary propyl alcohol,

$$(CH_3)_2CO + 2H = (CH_3)_2CH{\cdot}OH.$$

At the same time acetone differs from aldehyde very widely in one or two important respects. It does not undergo polymerisation, and does not reduce ammoniacal solutions of silver oxide; it is oxidised only by moderately powerful agents, by which its molecule is broken up into acetic acid and carbon dioxide,

$$CH_3{\cdot}CO{\cdot}CH_3 + 4O = CH_3{\cdot}COOH + CO_2 + H_2O.$$

Acetone gives the iodoform reaction (p. 96), and is employed for the preparation of iodoform, chloroform, &c.; it is also used as a solvent.

Constitution.—Acetone is formed when isopropyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\text{–}OH$ (p. 104), loses two atoms of hydrogen by oxidation. It does not contain a hydroxyl-group, because, unlike the alcohols, it does not form salts with acids. That the oxygen atom is combined with carbon only—that is, that acetone contains a $\text{–}CO\text{–}$ group, is shown by the behaviour of acetone with phosphorus pentachloride, which is similar to that of aldehyde. Furthermore, the $\text{–}CO\text{–}$ group must be united with two methyl groups, as in the formula $CH_3\cdot CO\cdot CH_3$, because if it were not, acetone would be identical with propaldehyde, $CH_3\cdot CH_2\cdot C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown H\end{smallmatrix}$. These facts, and many others which might be mentioned, show that acetone has the constitution $CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_3$, or $(CH_3)_2CO$; its characteristic properties are determined by the presence of the divalent **carbonyl** or **ketonic** group $>\!C=O$, which is assumed to be contained in all ketones.

The similarity in chemical behaviour between acetone and aldehyde is at once brought to mind on considering their graphic formulæ; they both contain the carbonyl group,

Acetone, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C=O$ Aldehyde, $\begin{matrix}H\\CH_3\end{matrix}\!>\!C=O$;

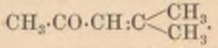
and therefore those changes, in which only this group takes part, are common to both substances. Such changes are, for example, interaction with hydroxylamine, behaviour with phosphorus pentachloride, and direct combination with sodium bisulphite, hydrogen, &c.; in the last two reactions, acetone acts as if it had the constitution $(CH_3)_2C\begin{smallmatrix}\diagup O-\\ \diagdown\end{smallmatrix}$. As regards oxidation, the difference between the two compounds is also readily understood; acetone does not contain the readily oxidisable hydrogen atom of the aldehyde group, and does not combine with oxygen without the molecule being broken up; it is therefore less readily acted on than aldehyde, and does not reduce silver oxide or give the rosaniline test, since both these reactions are the result of oxidation.

Condensation of Acetone.—When acetone is treated with certain dehydrating agents, it undergoes a peculiar change, two or more molecules combining together with elimination of one or more molecules of water,

$$2(CH_3)_2CO = \underset{\text{Mesityl Oxide.}}{C_6H_{10}O} + H_2O \quad 3(CH_3)_2CO = \underset{\text{Phorone.}}{C_9H_{14}O} + 2H_2O.$$

This, and similar changes, in which two or more molecules of the same or of different substances combine, with separation of water, are termed **condensations**, and the substances formed, **condensation products**; the process differs from polymerisation in this, that water is eliminated. Acetone yields three interesting condensation products. When it is saturated with dry hydrogen chloride, and the solution kept for some time, a mixture of *mesityl oxide* and *phorone* is formed, in accordance with the above equations; but when distilled with concentrated sulphuric acid, acetone yields a hydrocarbon, *mesitylene*, (part ii.), a derivative of benzene,

$$3(CH_3)_2CO = C_9H_{12} + 3H_2O.$$

Mesityl Oxide, $C_6H_{10}O$, is a colourless oil, boiling at 130°, and having a strong peppermint-like smell: when boiled with dilute sulphuric acid, it is decomposed with regeneration of acetone. Its constitution may be represented by the formula  $CH_3{\cdot}CO{\cdot}CH{:}C{<}^{CH_3}_{CH_3}$.

Phorone, $C_9H_{14}O$, crystallises in almost colourless prisms, melting at 28°; it boils at 196°, has a pleasant aromatic odour, and is decomposed by boiling dilute sulphuric acid with formation of acetone.

Substitution Products of Acetone.—Acetone is readily attacked by chlorine with formation of *monochloracetone*, $CH_3{\cdot}CO{\cdot}CH_2Cl$ (b.p. 119°), and *asymmetrical dichloracetone*, $CH_3{\cdot}CO{\cdot}CHCl_2$ (b.p. 120°). *Symmetrical dichloracetone*, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$, is produced by the oxidation of dichlorisopropyl alcohol, or dichlorohydrin (p. 252), $CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$; it is a colourless, crystalline solid (m.p. 45°; b.p. 172·5°). Higher substitution products of acetone have been obtained by indirect methods. The final product, *hexachloracetone*, or *perchloracetone*, $CCl_3{\cdot}CO{\cdot}CCl_3$, is a colourless liquid, boiling at 204°. Corresponding bromo-substitution products of acetone have also been prepared.

These halogen substitution products are characterised by their exceedingly irritating action on the eyes, the presence of a mere trace of these substances in the air being sufficient to cause a copious flow of tears; when dropped on the skin, they produce very painful blisters.

Homologues of Acetone may be obtained by the oxidation of the corresponding secondary alcohols and by the dry distillation of the calcium salts of the higher fatty acids; they resemble acetone in chemical properties.

Methylnonyl Ketone, $CH_3\cdot CO\cdot C_9H_{19}$, is the chief constituent of oil of rue, the essential oil obtained by distilling rue (*Ruta graveolens*) with steam. It is a colourless, crystalline substance, melts at 15°, boils at 224°, and possesses an odour resembling that of oranges.

Hydroximes and Hydrazones.—Aldehydes and ketones interact readily with hydroxylamine, $NH_2\cdot OH$, and with phenylhydrazine, $C_6H_5\cdot NH\cdot NH_2$ (part ii.), forming condensation products. This property is not only highly characteristic of all aldehydes and ketones, with one or two exceptions, but is also of the greatest value in the isolation and identification of the compounds in question.

The substances formed by the action of hydroxylamine on aldehydes are called *aldoximes*, those obtained from ketones, *ketoximes*, the term *oxime* or *hydroxime* being applied to both. Acetaldehyde, for example, yields acetaldoxime,

$$CH_3\cdot CHO + NH_2\cdot OH = CH_3\cdot CH{:}N\cdot OH + H_2O,$$

acetone giving acetoxime or dimethyl ketoxime,

$$(CH_3)_2CO + NH_2\cdot OH = (CH_3)_2C{:}N\cdot OH + H_2O,$$

the interactions being expressed by the general equation

$$>C\boxed{O + H_2}N\cdot OH = >C{:}N\cdot OH + H_2O.$$

The oximes are usually prepared by mixing an aqueous or alcoholic solution of the aldehyde or ketone (2 mols.) with an aqueous solution of hydroxylamine hydrochloride,

$NH_2 \cdot OH,HCl$ (2 mols.), and then adding sodium carbonate (1 mol.) in order to decompose the hydrochloride and set the base free,

$$2NH_2 \cdot OH,HCl + Na_2CO_3 = 2NH_2 \cdot OH + 2NaCl + CO_2 + H_2O.$$

The mixture is now heated gently, or kept at the ordinary temperature for some hours, and the oxime then extracted from the acidified solution by shaking with ether, or in some other suitable manner.

The lower aldoximes are mostly colourless, volatile, solid compounds, which distil without decomposition under reduced pressure, and mix with water in all proportions; the higher members are only sparingly soluble in water. The ketoximes have similar properties. Most oximes are decomposed, on treatment with boiling moderately strong hydrochloric acid, with formation of hydroxylamine hydrochloride, and regeneration of the aldehyde or ketone,

$$CH_3 \cdot CH{:}N \cdot OH + HCl + H_2O = CH_3 \cdot CHO + NH_2 \cdot OH,HCl.$$

They are usually readily soluble in caustic alkalies, with which they form compounds, such as

$$CH_3 \cdot CH{:}N \cdot ONa \text{ and } (CH_3)_2C{:}N \cdot OK;$$

but they are not decomposed by alkalies, even on boiling. One important difference between aldoximes and ketoximes is, that the former are decomposed by acetyl chloride, yielding cyanides or nitriles (p. 284),

$$CH_3 \cdot CH{:}N \cdot OH = CH_3 \cdot CN + H_2O,$$

whereas the latter are converted into acetyl derivatives,

$$(CH_3)_2C{:}N \cdot OH + CH_3 \cdot COCl = (CH_3)_2C{:}N \cdot O \cdot CO \cdot CH_3 + HCl.$$

The condensation products of aldehydes and ketones with phenylhydrazine are called *phenylhydrazones*, or simply *hydrazones.* They are formed according to the general equation,

$$>C\boxed{O + H_2}N \cdot NH \cdot C_6H_5 = >C{:}N \cdot NH \cdot C_6H_5,$$

as, for example, *acetaldehyde hydrazone*, $CH_3 \cdot CH{:}N \cdot NH \cdot C_6H_5$, and *acetone hydrazone*, $(CH_3)_2C{:}N{\cdot}NH{\cdot}C_6H_5$. The hydrazones are referred to later (part ii.), but it may be mentioned here that, like the hydroximes, they are usually decomposed by hot concentrated hydrochloric acid, with regeneration of the aldehyde or ketone.

SUMMARY AND EXTENSION.

The **Aldehydes** form a homologous series of the general formula $C_nH_{2n+1}{\cdot}CHO$, or $R{\cdot}CHO$, and are derived from the primary alcohols by the removal of two atoms of hydrogen from the $-CH_2{\cdot}OH$ group. The more important members of the series are—

			B.p.
Formaldehyde,	CH_2O	$H{\cdot}CHO$	—
Acetaldehyde,	C_2H_4O	$CH_3{\cdot}CHO$	20·8°
Propaldehyde,	C_3H_6O	$CH_3{\cdot}CH_2{\cdot}CHO$	49°
Butaldehyde,	C_4H_8O	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	74°
Isobutaldehyde,		$(CH_3)_2CH{\cdot}CHO$	63°
Valeraldehyde,	$C_5H_{10}O$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	102°
Isovaleraldehyde,		$(CH_3)_2CH{\cdot}CH_2{\cdot}CHO$	92°
Capraldehyde,	$C_6H_{12}O$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	128°
Heptaldehyde, or Œnanthol,	$C_7H_{14}O$	$CH_3{\cdot}[CH_2]_5{\cdot}CHO$*	155°

The **Ketones** are derived from the secondary alcohols by the removal of two atoms of hydrogen from the $>CH{\cdot}OH$ group, and have the general formula $R{\cdot}CO{\cdot}R'$, where R and R′ may be the same or different radicles; in the former case the substance is a *simple ketone*, but when R and R′ are different, it is a *mixed ketone* (compare ethers, p. 114). The more important ketones are—

Acetone, or dimethyl ketone	$(CH_3)_2CO$	B.p.	56·5°
Propione, or diethyl ketone	$(C_2H_5)_2CO$	„	103°
Butyrone, or dipropyl ketone	$(C_3H_7)_2CO$	„	144°
Isobutyrone, or di-isopropyl ketone		„	125°
Œnanthone, or dihexyl ketone	$(C_6H_{13})_2CO$	M.p.	30·5°
Laurone	$(C_{11}H_{23})_2CO$	„	69°
Palmitone	$(C_{15}H_{31})_2CO$	„	83°
Stearone	$(C_{17}H_{35})_2CO$	„	88°

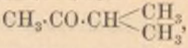
When the less important mixed ketones are also considered, the ketones form a homologous series,

$$C_3H_6O,\ C_4H_8O,\ C_5H_{10}O,\ C_6H_{12}O,\ \&c.,$$

---

* $[CH_2]_5$ is a convenient way of writing $-CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2-$.

in which numerous cases of isomerism occur. The first two members, acetone, $CH_3{\cdot}CO{\cdot}CH_3$, and methylethyl ketone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, exist in only one form, but there are three ketones of the composition $C_5H_{10}O$, namely,

Diethyl Ketone or Propione.	Methylpropyl Ketone.	Methylisopropyl Ketone.
$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	 $CH_3{\cdot}CO{\cdot}CH{<}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$,

and the number of possible isomerides rapidly increases on passing up the series.

Both aldehydes and ketones may be regarded as derived from the paraffins, by substituting one atom of oxygen for two atoms of hydrogen; they are, therefore, isomeric. In the case of aldehydes, two atoms of hydrogen of one of the CH_3– groups in the paraffin are displaced,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ giving } CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO;$$

but in the case of ketones, the oxygen atom is substituted for two hydrogen atoms of a –CH_2– group,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ giving } CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

Nomenclature.—The aldehydes (from *alcohol dehydrogenatum*) are conveniently named after the fatty acids which they yield on oxidation:

Formaldehyde, $H{\cdot}CHO$, giving formic acid, $H{\cdot}COOH$.
Acetaldehyde, $CH_3{\cdot}CHO$, " acetic acid, $CH_3{\cdot}COOH$.
Propaldehyde, $C_2H_5{\cdot}CHO$, " propionic acid, $C_2H_5{\cdot}COOH$.

Simple ketones, having been first obtained by the dry distillation of a salt of a fatty acid, are usually named after that acid from which they are in this way obtained; acetone, for example, from acetic acid, propione from propionic acid. Mixed ketones are named according to the alkyl groups which they contain, as exemplified above in the case of the isomerides of the composition $C_5H_{10}O$. Ketones in general may also be named after the hydrocarbons from which they are theoretically derived, employing the prefix 'keto' and a numeral, as, for example, 2-ketopropane, $\overset{1}{C}H_3{\cdot}\overset{2}{C}O{\cdot}\overset{3}{C}H_3$, and 3-ketohexane, $\overset{1}{C}H_3{\cdot}\overset{2}{C}H_2{\cdot}\overset{3}{C}O{\cdot}\overset{4}{C}H_2{\cdot}\overset{5}{C}H_2{\cdot}\overset{6}{C}H_3$.

Methods of Preparation.—*Aldehydes* are formed by the oxidation of primary alcohols,

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O;$$

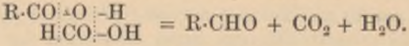
whereas *ketones* are produced from secondary alcohols by similar treatment,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.$$

Aldehydes may be prepared from the fatty acids by the dry distillation of their calcium salts with calcium formate:

$$(CH_3\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2CH_3\cdot CHO + 2CaCO_3,$$
$$(CH_3\cdot CH_2\cdot CH_2\cdot COO)_2Ca + (H\cdot COO)_2Ca$$
$$= 2CH_3\cdot CH_2\cdot CH_2\cdot CHO + 2CaCO_3.$$

In its simplest form this reaction may be considered as being due to the removal of water and carbon dioxide from one molecule of the fatty acid and one molecule of formic acid; thus,



$$\begin{array}{r:l:l} R\cdot CO & O & -H \\ H & CO & -OH \end{array} = R\cdot CHO + CO_2 + H_2O.$$

Ketones may be prepared by the distillation of the calcium salts of the fatty acids alone,

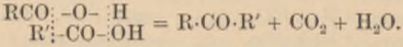
$$(CH_3\cdot COO)_2Ca = CH_3\cdot CO\cdot CH_3 + CaCO_3.$$

If a mixture of the calcium salts of two fatty acids (other than formic acid) be employed, a mixed ketone is formed,

$$\underset{\text{Calcium Acetate.}}{(CH_3\cdot COO)_2Ca} + \underset{\text{Calcium Propionate.}}{(C_2H_5\cdot COO)_2Ca} = \underset{\text{Methylethyl Ketone.}}{2CH_3\cdot CO\cdot C_2H_5} + 2CaCO_3;$$

at the same time two simple ketones (acetone and propione) are produced by the independent decomposition of the two salts.

This method of formation is readily understood if, for the sake of simplicity, the free acids instead of their calcium salts be considered,



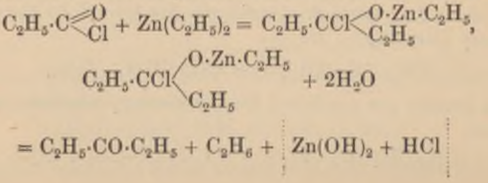
$$\begin{array}{r:l:l} RCO & -O- & H \\ R' & -CO- & OH \end{array} = R\cdot CO\cdot R' + CO_2 + H_2O.$$

Ketones may, in fact, be prepared by heating the higher fatty acids with phosphoric anhydride at about 200°,

$$\underset{\text{Stearic Acid.}}{2C_{17}H_{33}\cdot COOH} = \underset{\text{Stearone.}}{C_{17}H_{33}\cdot CO\cdot C_{17}H_{33}} + CO_2 + H_2O,$$

a method especially useful in the preparation of the higher ketones, such as laurone, palmitone, &c., which are obtained only with difficulty by any other method.

A very important synthetical method for the preparation of ketones consists in treating the acid chlorides (1 mol.) with the zinc alkyl compounds (1 mol.); in the first place, an additive product is formed, and this, on decomposition with water, yields the ketone,



$$C_2H_5\cdot C\begin{matrix}\nearrow O\\ \searrow Cl\end{matrix} + Zn(C_2H_5)_2 = C_2H_5\cdot CCl\begin{matrix}\nearrow O\cdot Zn\cdot C_2H_5\\ \searrow C_2H_5\end{matrix},$$

$$C_2H_5\cdot CCl\begin{matrix}\nearrow O\cdot Zn\cdot C_2H_5\\ \searrow C_2H_5\end{matrix} + 2H_2O$$

$$= C_2H_5\cdot CO\cdot C_2H_5 + C_2H_6 + \boxed{Zn(OH)_2 + HCl}$$

(Compare formation of tertiary alcohols by the action of *excess* of the zinc alkyl compound, p. 107).

Ketones may also be prepared by the hydrolysis of ethyl acetoacetate and its derivatives, a synthetical method of great practical importance (p. 193).

When hydrocarbons of the acetylene series are treated with 80 per cent. sulphuric acid (or with a solution of mercuric chloride or bromide), they combine directly with the elements of water, an aldehyde or a ketone being formed according to the constitution of the hydrocarbon (p. 87).

Physical Properties.—Excluding formaldehyde, the physical properties of which are unknown, the aldehydes and ketones up to about $C_{11}H_{22}O$ are colourless, mobile, neutral, volatile liquids. Aldehydes have usually a disagreeable, irritating smell, and their sp. gr. (at 20°) varies from about 0·780 in the case of acetaldehyde, to 0·834 in the case of caprylic aldehyde, $C_7H_{15}{\cdot}CHO$. Ketones have generally a not unpleasant odour, and their sp. gr. (at 20°) varies from 0·792 in the case of acetone, to 0·830 in the case of caprone, $(C_5H_{11})_2CO$. The boiling-point rises fairly regularly on passing up both series. The lowest members of both classes of compounds are readily soluble in water, but the solubility rapidly decreases as the number of carbon atoms in the molecule increases.

The higher aldehydes and ketones are usually colourless, waxy solids, insoluble or nearly so in water, but readily soluble in alcohol and ether.

Chemical Properties.—Aldehydes and ketones have many chemical properties in common, because they are similar in constitution, both classes of substances containing the carbonyl group $>CO$. Owing to the presence of this group, they have the power of combining directly under certain conditions with two monad atoms or their valency equivalent.

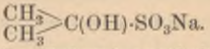
All the lower aldehydes and many* of the lower ketones form crystalline additive compounds when shaken with a concentrated aqueous solution of sodium bisulphite. This property is of great value in purifying aldehydes and ketones, and especially in separating them from substances which do not form 'bisulphite compounds,' as illustrated in the preparation of acetone from crude wood-spirit (p. 128). These 'bisulphite compounds' are soluble in water, but usually insoluble or nearly so in alcohol and ether. They may be regarded as salts of *hydroxy-sulphonic*

* With few exceptions, only those ketones containing the group $CH_3{\cdot}CO-$ combine readily with $NaHSO_3$.

acids,* the compounds formed by aldehyde and acetone respectively being

$CH_3\cdot CH(OH)\cdot SO_3Na$

Sodium Hydroxyethylsulphonate.



$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH)\cdot SO_3Na.$

Sodium Hydroxyisopropylsulphonate.

All these compounds are readily decomposed on warming with dilute alkalies or acids, the aldehydes or ketones being regenerated,

$$CH_3\cdot CH_2\cdot CH(OH)\cdot SO_3Na + HCl = CH_3\cdot CH_2\cdot CHO + NaCl + H_2O + SO_2.$$

The characteristic behaviour of aldehydes and ketones with hydroxylamine and with phenylhydrazine has been described above.

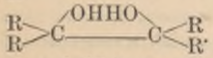
Aldehydes and ketones are readily acted on by reducing agents, such as sodium amalgam and water, zinc and hydrochloric acid, with formation of primary and secondary alcohols respectively,

$$CH_3\cdot CH_2\cdot CH_2\cdot CHO + 2H = CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$$
$$CH_3\cdot CO\cdot CH_2\cdot CH_3 + 2H = CH_3\cdot CH(OH)\cdot CH_2\cdot CH_3.$$

A secondary alcohol is not the sole product of the reduction of ketones, but is usually accompanied by varying quantities of interesting substances belonging to the class of *pinacones*. Acetone, for example, yields not only isopropyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$, but also *acetone pinacone*,

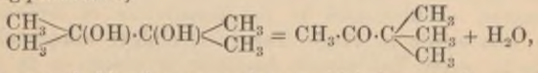
$$2(CH_3)_2CO + 2H = (CH_3)_2C(OH)\cdot C(OH)(CH_3)_2.$$

The formation of a pinacone may be accounted for by assuming that the first product of reduction of a ketone is a substance, $\begin{matrix}R\\R\end{matrix}{>}C{<}^{OH}$, produced by combination with one atom of hydrogen. This intermediate product may then combine with another atom of hydrogen to form a secondary alcohol, $\begin{matrix}R\\R\end{matrix}{>}C{<}\begin{matrix}OH\\H\end{matrix}$, or two molecules may unite to form a pinacone,



$\begin{matrix}R\\R\end{matrix}{>}\overset{OH\;HO}{C\text{———}C}{<}\begin{matrix}R\\R\end{matrix}.$ Similar products are formed in the reduction of aldehydes, but in smaller quantities.

Pinacone is decomposed on distillation with dilute sulphuric acid, yielding *pinacoline*,



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH)\cdot C(OH){<}\begin{matrix}CH_3\\CH_3\end{matrix} = CH_3\cdot CO\cdot C{\begin{matrix}\diagup CH_3\\ -CH_3\\ \diagdown CH_3\end{matrix}} + H_2O,$$

a very remarkable change, and one which has not been satisfactorily accounted for. Pinacoline is a colourless liquid, boils at 106°,

---

* A sulphonic acid is an organic acid containing the group $—SO_2\cdot OH$.

and has a very strong odour of peppermint. That it has the constitution given above, is shown by the facts that on oxidation with chromic acid, it yields trimethylacetic acid and carbon dioxide,

$$(CH_3)_3C\cdot CO\cdot CH_3 + 4O = (CH_3)_3C\cdot COOH + CO_2 + H_2O,$$

and that it is formed by the action of zinc methyl on trimethylacetyl chloride, $(CH_3)_3\cdot COCl$. (Compare preparation of ketones, p. 136).

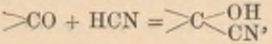
Aldehydes and ketones are readily acted on by phosphorus pentachloride with formation of dihalogen derivatives of the paraffins, the oxygen atom of the $>CO$ group being displaced by two atoms of chlorine. Aldehyde, for example, gives a *dichlorethane*, called *ethylidene chloride* (because it contains the ethylidene group $CH_3\cdot CH=$),

$$CH_3\cdot CHO + PCl_5 = CH_3\cdot CHCl_2 + POCl_3,$$

and acetone gives *β-dichloropropane* or *acetone dichloride*,

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3.$$

Aldehydes and ketones combine directly with hydrocyanic acid, forming additive products, termed *hydroxycyanides*. This reaction may be expressed by the general equation



$$>CO + HCN = >C<\begin{matrix}OH\\CN\end{matrix},$$

aldehyde, for example, giving *hydroxyethyl cyanide*,

$$CH_3\cdot CH(OH)\cdot CN,$$

and acetone, *hydroxyisopropyl cyanide*, $(CH_3)_2C(OH)\cdot CN$. These compounds are decomposed by hot concentrated alkalies and mineral acids, yielding *hydroxycarboxylic acids*, the $-CN$ group being transformed into $-COOH$ (compare p. 285),

$$CH_3\cdot CH(OH)\cdot CN + 2H_2O = CH_3\cdot CH(OH)\cdot COOH + NH_3.$$

Aldehydes *differ* from ketones in the following important respects: They usually undergo oxidation to a fatty acid on exposure to the air, and are readily oxidised by an ammoniacal solution of silver oxide, especially in presence of a little potash or soda, a silver mirror being formed. They also reduce alkaline solutions of copper (Fehling's solution, p. 263). Ketones, on the other hand, are only attacked by powerful oxidising agents, and the difference between their behaviour on oxidation and that of aldehydes is so characteristic that it may be made use of for determining whether a substance of doubtful constitution be an aldehyde or a ketone.

Aldehydes, on oxidation, are converted into fatty acids containing *the same number* of carbon atoms :

$$\underset{\text{Propaldehyde.}}{CH_3\cdot CH_2\cdot CHO} + O = \underset{\text{Propionic Acid.}}{CH_3\cdot CH_2\cdot COOH},$$

$$\underset{\text{Heptaldehyde.}}{CH_3\cdot[CH_2]_5\cdot CHO} + O = \underset{\text{Heptylic Acid.}}{CH_3\cdot[CH_2]_5\cdot COOH}.$$

Ketones, on oxidation, are decomposed with formation, usually, of a mixture of acids, each of which contains *a smaller number* of carbon atoms than the original ketone,

$$CH_3\cdot CO\cdot CH_3 + 4O = CH_3\cdot COOH + CO_2 + H_2O.$$

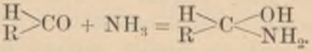
$$CH_3\cdot CO\cdot\vdots[CH_2]_4\cdot CH_3 + 3O = CH_3\cdot COOH + CH_3\cdot[CH_2]_3\cdot COOH.$$

In the case of mixed ketones, several acids may be formed. Methylamyl ketone, for example, might yield acetic acid, and valeric acid on oxidation, in which case the molecule would be decomposed as indicated by the dotted line in the above equation, or it might give carbon dioxide and caproic acid, the molecule being attacked in a different manner,

$$CH_3\vdots CO\cdot[CH_2]_4\cdot CH_3 + 4O = CH_3\cdot[CH_2]_4\cdot COOH + H_2O + CO_2.$$

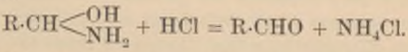
It frequently happens, therefore, that, in oxidising mixed ketones, several products are formed, the nature of which may afford important evidence as to the constitution of the ketone. Generally speaking, the oxidation of a mixed ketone follows the rule (Popoff's law) that the ketonic group –CO– remains united with the smaller alkyl group, in which case the decomposition represented in the above example by the first equation would take place almost entirely. Later experiments have shown, however, that Popoff's rule does not hold good in all cases, and must be considered as only approximately correct.

Aldehydes differ from ketones in combining readily with ammonia, forming additive products,



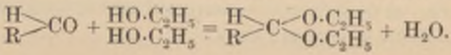
$$\genfrac{}{}{0pt}{}{H}{R}\!>CO + NH_3 = \genfrac{}{}{0pt}{}{H}{R}\!>C<\genfrac{}{}{0pt}{}{OH}{NH_2}.$$

These compounds, of which aldehyde ammonia is an example, are usually crystalline, and very readily soluble in water. They are decomposed on distillation with dilute acids, with regeneration of the aldehyde,



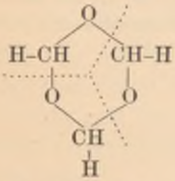
$$R\cdot CH<\genfrac{}{}{0pt}{}{OH}{NH_2} + HCl = R\cdot CHO + NH_4Cl.$$

Aldehydes differ again from ketones in combining with alcohols with elimination of water, to form substances called *acetals*,

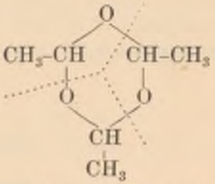


$$\genfrac{}{}{0pt}{}{H}{R}\!>CO + \genfrac{}{}{0pt}{}{HO\cdot C_2H_5}{HO\cdot C_2H_5} = \genfrac{}{}{0pt}{}{H}{R}\!>C<\genfrac{}{}{0pt}{}{O\cdot C_2H_5}{O\cdot C_2H_5} + H_2O.$$

Aldehydes, especially the lower members of the series, very readily undergo polymerisation, a property which distinguishes them from ketones in a very striking manner. Polymerisation may take place spontaneously, as in the case of formaldehyde, but usually only on addition of a small quantity of some mineral acid or of some substance, such as $ZnCl_2$, SO_2, &c., which acts in a manner as yet unexplained. The most common form of polymerisation is the combination of three molecules of the aldehyde to form substances called *paraldehydes*, such as paraformaldehyde, $(CH_2O)_3$, and paracetaldehyde $(C_2H_4O)_3$, the constitutions of which are usually represented by the formulæ



Paraformaldehyde.



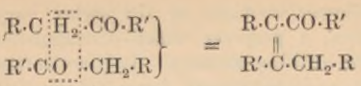
Paracetaldehyde, or Paraldehyde.

The method of combination of the three molecules to form a paraldehyde will be readily understood with the aid of the dotted lines. The paraldehydes are decomposed into the original aldehydes on distillation with dilute mineral acids. They do not show the characteristic reactions of aldehydes, consequently they are not true aldehydes, and do not contain the aldehyde group.

Aldehydes are generally very unstable in presence of alkalies, by which they are converted into brown resins of unknown nature.

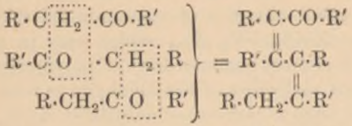
Ketones, as mentioned above, are much more stable than aldehydes; they do not reduce alkaline solutions of silver, copper, &c., or combine directly with ammonia or with alcohols, and they do not polymerise like the aldehydes.

When treated with dehydrating agents, both aldehydes and ketones readily undergo condensation, two or more molecules combining with loss of water, as illustrated in the case of aldehyde (p. 124) and acetone (p. 131). When condensations of this nature take place, the hydrogen atoms of one of the $-CH_2-$ or CH_3- groups, which is in direct combination with the $>CO$ group, are invariably eliminated, as shown in the following schemes, in which R, R′ may be either hydrogen atoms or similar or different alkyl groups:



$$\left.\begin{array}{l} R\cdot CH_2\cdot CO\cdot R' \\ R'\cdot CO\;\cdot CH_2\cdot R \end{array}\right\} = \begin{array}{l} R\cdot C\cdot CO\cdot R' \\ \quad\;\| \\ R'\cdot C\cdot CH_2\cdot R \end{array}$$

(Type of Mesityl Oxide).



$$\left.\begin{array}{l} R\cdot CH_2\cdot CO\cdot R' \\ R'\cdot CO\;\cdot CH_2\cdot R \\ \quad R\cdot CH_2\cdot CO\; R' \end{array}\right\} \begin{array}{l} \quad R\cdot C\cdot CO\cdot R' \\ \qquad\;\| \\ = R'\cdot C\cdot C\cdot R \\ \qquad\qquad\| \\ R\cdot CH_2\cdot C\cdot R' \end{array}$$

(Type of Phorone).

It is not necessary that the molecules undergoing condensation be identical; two different ketones, two different aldehydes, or an aldehyde and a ketone may condense together, always provided that the group $-CH_2-CO-$ be present in the molecule of one at least of the substances.

CHAPTER IX.

THE FATTY ACIDS.

The fatty acids form a homologous series of the general formula $C_nH_{2n+1}\cdot COOH$, or $C_nH_{2n}O_2$; they may be regarded as derivatives of the paraffins, the alcohols, or the aldehydes.

Paraffins.	Alcohols.	Aldehydes.	Fatty Acids.
$H\cdot CH_3$	$H\cdot CH_2\cdot OH$	$H\cdot CHO$	$H\cdot COOH$
$CH_3\cdot CH_3$	$CH_3\cdot CH_2\cdot OH$	$CH_3\cdot CHO$	$CH_3\cdot COOH$
$C_2H_5\cdot CH_3$	$C_2H_5\cdot CH_2\cdot OH$	$C_2H_5\cdot CHO$	$C_2H_5\cdot COOH$.

The term '*fatty*' was given to the acids of this series because many of the higher members occur in natural fats, and resemble fats in physical properties.

Formic Acid, CH_2O_2, or $H\cdot COOH$, occurs in nature in nettles, ants (*formicæ*), and other living organisms; the sting of ants and nettles owes part, at least, of its irritating effect to the presence of formic acid. When nettles or ants are macerated with water and the mixture distilled, weak aqueous formic acid collects in the receiver.

Formic acid can be obtained from its elements by simple methods. When carbon monoxide is passed over moistened potassium hydroxide heated at 100°, it is slowly absorbed, and potassium formate is produced,

$$CO + KOH = H{\cdot}COOK.$$

When moist carbon dioxide is passed over potassium, formate and carbonate of potassium are formed, the carbon dioxide being reduced by the nascent hydrogen evolved during the interaction of the potassium and water,

$$2H_2O + 2K = 2KOH + 2H, \text{ and } CO_2 + 2H + KOH = H{\cdot}COOK + H_2O,$$

$$\text{or } 3CO_2 + 4K + H_2O = 2H{\cdot}COOK + K_2CO_3.$$

The acid may be obtained from the potassium salt by distilling with dilute sulphuric acid.

Formic acid can also be obtained by oxidising methyl alcohol or formaldehyde with platinum black (precipitated platinum),

$$CH_3{\cdot}OH + 2O = H{\cdot}COOH + H_2O \qquad H{\cdot}CHO + O = H{\cdot}COOH,$$

and by heating hydrocyanic acid with alkalies or mineral acids,

$$HCN + 2H_2O = H{\cdot}COOH + NH_3.^*$$

Formic acid is prepared by heating oxalic acid with glycerol (glycerin); it can be obtained by heating oxalic acid alone,

$$C_2O_4H_2 = H{\cdot}COOH + CO_2,$$

but a large proportion of the acid sublimes without decomposition. Glycerol (about 50 c.c.) is placed in a retort connected with a condenser, crystallised oxalic acid (about 30 grams) added, and the mixture heated to about 100–110°; rather below this temperature, evolution of carbon dioxide commences, and dilute formic acid distils, but after keeping for some time at 100–110°, action ceases. A further quantity of oxalic acid is then added, and the heating continued, when carbon dioxide is again evolved, and a more concentrated solution of formic acid collects in the receiver. By adding

---

* If an alkali be used, ammonia is liberated, and a salt of formic acid obtained; whereas when a mineral acid is employed, free formic acid and an ammonium salt are produced.

more oxalic acid from time to time, a large quantity of formic acid can be obtained, the glycerol, like the sulphuric acid in the manufacture of ether, being able, theoretically, to convert an unlimited quantity of oxalic into formic acid.

When crystallised oxalic acid, $C_2O_4H_2 + 2H_2O$, is heated with glycerol, it loses its water of crystallisation; the anhydrous acid is then decomposed into carbon dioxide and formic acid; part of the latter distils with the water, part combining with the hydroxide, glycerol, to form the salt, glycerol formate, or monoformin,

$$C_2O_4H_2,2H_2O = H{\cdot}COOH + CO_2 + 2H_2O$$
$$C_3H_5(OH)_3 + H{\cdot}COOH = C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O.$$

On adding more crystallised oxalic acid, the monoformin is decomposed by part of the water expelled from the oxalic acid crystals, yielding glycerol and formic acid,

$$C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O = C_3H_5(OH)_3 + H{\cdot}COOH.$$

The regenerated glycerol and the anhydrous oxalic acid then interact as before, yielding monoformin, carbon dioxide, and water.

In order to prepare anhydrous formic acid, the aqueous distillate is gently warmed and excess of litharge added in small quantities at a time, the solution being gradually heated to boiling; as soon as the litharge ceases to be dissolved, the solution is filtered hot, and the filtrate evaporated to a small bulk, when colourless crystals of lead formate are obtained,

$$2H{\cdot}COOH + PbO = (H{\cdot}COO)_2Pb + H_2O.$$

This salt is carefully dried, and about $\frac{19}{20}$ths of it introduced in the form of coarse powder, between plugs of cotton wool, into the inner tube of an upright Liebig's condenser, which is connected above with an apparatus for generating hydrogen sulphide, and below with a suitable receiver closed with a calcium chloride drying tube; the lead formate is heated by passing steam through the outer tube of the condenser, and carefully dried hydrogen sulphide is led over it, when anhydrous formic acid collects in the receiver,

$$(H{\cdot}COO)_2Pb + SH_2 = 2H{\cdot}COOH + PbS.$$

The acid is now placed in a retort connected with a condenser, the remainder of the dried lead salt added, and, after warming gently for a short time, the acid is distilled, care being taken to prevent absorption of moisture; this rectification or distillation over lead formate is necessary in order to free the acid from hydrogen sulphide.

Formic acid is a colourless, mobile, hygroscopic liquid of sp. gr. 1·241 at 0°; it solidifies at low temperatures, melting again at 8°, and boiling at 101°. It has a pungent, irritating odour, recalling that of sulphur dioxide, and it blisters the skin like a nettle sting does; it is miscible with water and alcohol in all proportions. The anhydrous substance and its aqueous solution have an acid reaction, decompose carbonates, and dissolve certain metallic oxides; formic acid, in fact, behaves like a weak mineral acid. Like the aldehydes, it has reducing properties, and precipitates silver from warm solutions of ammoniacal silver nitrate, being itself oxidised to carbon dioxide,

$$H{\cdot}COOH + Ag_2O = 2Ag + CO_2 + H_2O.$$

When mixed with concentrated sulphuric acid, it is rapidly decomposed into carbon monoxide and water,

$$H{\cdot}COOH = CO + H_2O,$$

and when heated alone at 160° in closed vessels, it yields carbon dioxide and hydrogen,

$$H{\cdot}COOH = CO_2 + H_2.$$

The **Formates**, or salts of formic acid, are prepared by neutralising the acid with alkalies, hydroxides, &c., or by double decomposition; they are all soluble in water, but some, such as the lead and silver salts, only moderately easily; they are all decomposed by warm concentrated sulphuric acid, with evolution of carbon monoxide, and by dilute mineral acids, yielding formic acid. The *sodium* salt, $H{\cdot}COONa$, and the *potassium* salt, $H{\cdot}COOK$, are deliquescent; when heated at about 250°, they are converted into oxalates with evolution of hydrogen, a reaction which may be made use of for the preparation of pure hydrogen,

$$2H{\cdot}COONa = C_2O_4Na_2 + H_2.$$

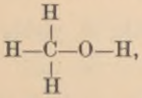
When *ammonium formate* is strongly heated, it is first converted into formamide (p. 162), then into hydrogen cyanide, water being eliminated in both stages,

$$H{\cdot}COONH_4 = H{\cdot}CO{\cdot}NH_2 + H_2O$$
$$H{\cdot}CO{\cdot}NH_2 = HCN + H_2O.$$

Silver formate, H·COOAg, is precipitated in colourless crystals on adding silver nitrate to a concentrated solution of an alkali formate, but it is unstable, and quickly darkens on exposure to light, very rapidly on boiling.

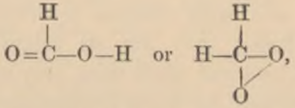
In order to test for formic acid or a formate, the solution, if acid, is neutralised with soda, and a portion warmed with an ammoniacal solution of silver nitrate; if a black precipitate of silver be produced, the presence of formic acid is confirmed by evaporating the rest of the neutral solution to dryness, and then warming the residue *very gently* with concentrated sulphuric acid, when carbon monoxide is evolved, and may be ignited at the mouth of the test tube.

Constitution.—Formic acid is produced from methyl alcohol,

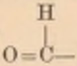


$$H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}O{-}H,$$

by the substitution of one atom of oxygen for two atoms of hydrogen, and must, therefore, have the constitution



$$O{=}\overset{\displaystyle H}{\overset{|}{C}}{-}O{-}H$$

because these are the only formulæ which can be constructed, assuming, as usual, that the atoms have the indicated valencies. But the second formula does not correctly indicate the behaviour of formic acid; it represents the two hydrogen atoms as being in the same state of combination, which is very improbable, since one of them is, the other is not, readily displaced by metals; it does not recall the fact that formic acid behaves in some respects like an aldehyde, which is indicated in the first formula by the presence of the aldehyde group  $\overset{\displaystyle H}{\underset{|}{}}\!\!\!\!\!\! O{=}C{-}$ For these and other reasons, which will be seen more clearly after considering the case of acetic acid (p. 152), the constitution of formic acid is represented by the first formula, which is usually written H·CO·OH, or simply H·COOH. From analogy with methyl alcohol and other compounds, it may be assumed that it is the hydrogen atom of the HO– group, and not that directly combined with carbon, which is displaced when the acid forms salts.

Acetic Acid, $C_2H_4O_2$, or $CH_3{\cdot}COOH$, occurs in nature in combination with alcohols in the essences or odoriferous oils of many plants, and is formed during the decay of many organic substances. It can be produced by gently heating sodium methoxide in a stream of carbon monoxide, just as formic acid may be obtained from sodium or potassium hydroxide under the same conditions,

$$CH_3{\cdot}ONa + CO = CH_3{\cdot}COONa;$$

also by boiling methyl cyanide (p. 285) with alkalies or mineral acids,

$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3;$$

and by exposing alcohol or aldehyde in contact with platinum black to the oxidising action of the air,

$$C_2H_6O + 2O = C_2H_4O_2 + H_2O \qquad 2C_2H_4O + 2O = 2C_2H_4O_2.$$

Acetic acid is manufactured on the large scale from the products of the dry distillation of wood. The brown aqueous portion of the distillate, obtained on heating wood in iron retorts (p. 89), contains a large quantity of acetic acid, and is called *pyroligneous acid;* it is first distilled with lime, as already described, to separate the methyl alcohol, acetone, and other volatile neutral substances, and the solution of calcium acetate is then evaporated in iron pans, when tarry or 'empyreumatic' matter rises as a scum and is skimmed off. The solution is finally evaporated to dryness, and the calcium salt distilled with concentrated hydrochloric acid from copper vessels, care being taken not to employ excess of acid,

$$(C_2H_3O_2)_2Ca + 2HCl = 2C_2H_4O_2 + CaCl_2.$$

The concentrated aqueous acetic acid which collects in the receiver is now mixed with a little potassium permanganate or bichromate, and again distilled, by which means most of the impurities are oxidised, and commercial acetic acid is obtained.

Vinegar.—When beer, or a weak wine such as claret, is left exposed to the air, it soon becomes sour, the alcohol which it contains being converted into acetic acid,

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

This change is not a simple oxidation, as represented by the equation, but a process of fermentation brought about by a living ferment, *mycoderma aceti.* This ferment, being in the atmosphere, soon finds its way into the solution, where it grows and multiplies and in some way causes the alcohol to combine with the oxygen of the air to form acetic acid. Strong wines, such as port and sherry, do not turn sour on exposure to the air, nor does an aqueous solution of pure alcohol, no matter how dilute, because the ferment is killed by strong alcohol, and cannot live in pure aqueous alcohol, since the latter does not contain nitrogenous substances, mineral salts, &c., which the ferment requires for food, and which are present in beers and wines.

Vinegar is simply a dilute solution of acetic acid, containing colouring matter and other substances, obtained by the acetous fermentation of poor wine or wine residues, of beer which has turned sour, and of other dilute alcoholic liquids; it is manufactured by one of the two following processes.

In the old *French* or *Orléans* process, a small quantity of wine is placed in large vats covered with perforated lids, the vats having been previously soaked inside with hot vinegar; the ferment soon gets into the wine, and vinegar is produced, the solution gradually becoming coated with a slimy film, known as 'mother-of-vinegar,' which is simply a mass of the living ferment. After some time more wine is added, the process being repeated at intervals until the vat is about half full; most of the vinegar is then drawn off, and the operations repeated with fresh quantities of wine.

In the modern *German* or '*quick vinegar process*,' large vats, provided with perforated sides, and fitted near the top and bottom with perforated discs, are employed, the space between the discs being filled with beech-wood shavings, which are first moistened with vinegar in order that they may become coated with a growth of the ferment; diluted 'raw-spirit,' containing 6–10 per cent. of alcohol, mixed with about 20 per cent. of vinegar, or with beer, or malt extract, to provide food for the ferment, is then poured in at the top, when it slowly trickles through the shavings in contact with the ferment, and provided with a free supply of air. The liquid which collects at the bottom is again poured over the shavings, the operations being continued until it is converted into vinegar—that is to say, until almost the whole of the alcohol has been oxidised to acetic acid. This process is much more rapid than the French method, since oxidation is hastened by the exposure of a large surface of the liquid; in both processes the fermenting liquid must be kept at a temperature of 25–40°.

Vinegar produced by the French process contains 6–10 per cent. of acetic acid; whereas that produced by the German process from diluted raw-spirit contains only 4–6 per cent. of acetic acid. Vinegar is used for table purposes and in the manufacture of white-lead and verdigris (see below); it is too dilute to be economically employed for the preparation of commercial acetic acid.

Pure acetic acid is prepared by distilling anhydrous sodium acetate with concentrated sulphuric acid; this salt is obtained by neutralising the impure commercial acid with sodium carbonate, recrystallising, and then fusing to expel the water of crystallisation. The distillate from this process contains only a small quantity of water, and solidifies, when cooled, to a mass of colourless crystals; it is then termed *glacial acetic acid* in contradistinction to the weaker acid, which does not crystallise so readily. The small quantity of water in glacial acetic acid can be got rid of by separating the crystals from the more dilute mother-liquors by pressure, melting them, and then cooling again, repeating the processes if necessary.

Anhydrous acetic acid is a colourless, crystalline, hygroscopic solid, melts at 16·5°, boils at 118°, and has the sp. gr. 1·080 at 0°; it has a pungent, penetrating smell, a burning action on the skin, and a sharp sour taste; it is inflammable when near its boiling-point, burning with a feebly luminous flame. It is miscible with water, alcohol, and ether in all proportions, and is an excellent solvent for most organic compounds, and for many inorganic substances, such as sulphur, iodine, &c., which are insoluble in water. It is a fairly strong acid, dissolves certain metals, and acts readily on metallic hydroxides; unlike formic acid, it has not reducing properties. The pure acid does not decolourise potassium permanganate; if impure, it will probably do so.

Acetic acid is largely used in medicine, in chemical laboratories, and in the manufacture of organic dyes, as well as for the preparation of many acetates of considerable commercial importance; the uses of vinegar have been mentioned.

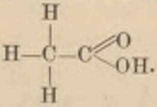
The **Acetates**, or salts of acetic acid, are prepared by neutralising the acid with carbonates, hydroxides, &c., or by double decomposition; they are crystalline compounds, soluble in water, and decomposed by mineral acids with liberation of acetic acid. *Sodium acetate*, $C_2H_3O_2Na + 3H_2O$, is extensively used in the laboratory; it melts in its water of crystallisation when heated, but as the water is expelled, it solidifies again. The anhydrous salt is hygroscopic, and is used as a dehydrating agent. *Potassium acetate*, $C_2H_3O_2K$, is deliquescent. *Ammonium acetate* is gradually decomposed into acetamide (p. 162) and water on dry distillation, $C_2H_3O_2 \cdot NH_4 = CH_3 \cdot CO \cdot NH_2 + H_2O$. *Silver acetate* is precipitated in colourless crystals on adding silver nitrate to a concentrated neutral solution of an acetate; it is moderately soluble in cold water, and does not darken on exposure to light. *Copper acetate*, $(C_2H_3O_2)_2Cu + H_2O$, is obtained by dissolving cupric oxide in acetic acid; it is a dark, greenish-blue substance. *Verdigris* is a blue, basic copper acetate, $(C_2H_3O_2)_2Cu + Cu(OH)_2$, containing water of crystallisation, and is manufactured by leaving sheet-copper in contact with vinegar, or with grape-skins, the sugars in which have undergone fermentation first into alcohol, then into acetic acid. When washed with water, part of the salt dissolves and green verdigris is obtained; both these basic acetates are used as pigments. Copper acetate and copper arsenite unite to form a beautiful emerald green, insoluble double salt, $(C_2H_3O_2)_2Cu + (AsO_3)_2Cu_3$, known as *Schweinfurth's green.* This substance was formerly employed in large quantities in colouring wall-papers, carpets, blinds, &c.; but as its dust is poisonous, and as it is liable to decompose in presence of decaying starch or other organic matter, with evolution of hydrogen arsenide, its use is now almost abandoned. *Lead acetate*, or 'sugar of lead,' $(C_2H_3O_2)_2Pb + 3H_2O$, prepared by dissolving litharge in commercial acetic acid, has a sweet (sugary) astringent taste, and is very poisonous; when its solution is boiled with litharge, a soluble basic lead acetate is formed. *Ferric acetate* is prepared on the large scale by dissolving scrap iron in pyroligneous acid, the greenish ferrous salt first produced being rapidly oxidised in contact with the air and excess of acetic acid to the deep reddish-brown ferric salt; the solution is known in commerce as 'iron liquor,' or 'black liquor.' When a solution of ferric acetate containing traces of other salts is heated, an insoluble basic iron salt is precipitated, the solution becoming clear; this property is made use of in separating the metals of the iron group, also in dyeing and 'printing' cotton, for which purpose 'iron liquor' is used as a mordant. *Aluminium acetate* is prepared by precipitating a solution of aluminium sulphate with sugar of lead, or by dissolving precipitated aluminium hydroxide in acetic acid; its solution is known as 'red liquor,' and is used as a mordant, as, when heated, it loses acetic acid, an insoluble basic salt being formed. *Chromic acetate* is prepared by similar methods, and is also used as a mordant.

If a solution is to be tested for acetic acid or an acetate, it is boiled with a few drops of strong sulphuric acid, when the characteristic smell of acetic acid is observed. A fresh portion of the solution is then neutralised with soda, if necessary, evaporated to dryness, and the residue warmed with a few drops of alcohol and a little strong sulphuric acid, when ethyl acetate (p. 185) is formed; this substance is recognised by its pleasant fruity odour (which should be compared with that of alcohol and of ether).

Constitution.—The formation of acetic acid by the oxidation of ethyl alcohol is clearly a process similar to that by which formic acid is produced from methyl alcohol; if, therefore, the two changes be represented in a similar manner,

$$\begin{aligned} H{\cdot}CH_2{\cdot}OH + 2O &= H{\cdot}CO{\cdot}OH + H_2O \\ CH_3{\cdot}CH_2{\cdot}OH + 2O &= CH_3{\cdot}CO{\cdot}OH + H_2O, \end{aligned}$$

the constitution of acetic acid will be expressed by the formula $CH_3{\cdot}CO{\cdot}OH$, or



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-C\begin{matrix}\nearrow O \\ \searrow OH.\end{matrix}$$

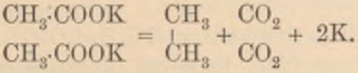
Again, formic acid is produced when hydrogen cyanide is boiled with mineral acids (p. 143), whilst acetic acid is formed from methyl cyanide under the same conditions. Expressing these two changes in a similar manner,

$$\begin{aligned} H{\cdot}CN + 2H_2O &= H{\cdot}CO{\cdot}OH + NH_3 \\ CH_3{\cdot}CN + 2H_2O &= CH_3{\cdot}CO{\cdot}OH + NH_3, \end{aligned}$$

the constitution of acetic acid will be represented by the same formula as before.

If now the properties of acetic acid be considered, it will be evident that the constitutional formula arrived at in this manner indicates the chemical behaviour of the acid, and accounts for its methods of formation, decompositions, and relations to other compounds better than any other formula.

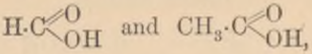
From the numerous arguments which might be advanced in support of this statement, the following only will be quoted: (1) Acetic acid contains an HO– group, because its behaviour with phosphorus pentachloride is similar to that of alcohols (p. 95). (2) It contains a methyl or CH_3– group—that is to say, three of the four atoms of hydrogen in acetic acid are *directly* combined with carbon. This is shown by the fact that three of the four hydrogen atoms behave like those in CH_4, C_2H_6, &c., and are displaceable by free chlorine (p. 162); also by the production of ethane by the electrolysis of potassium acetate, a change which can be formulated in a simple manner, only by assuming the presence of a CH_3– group,



$$\begin{matrix} CH_3{\cdot}COOK \\ CH_3{\cdot}COOK \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + \begin{matrix} CO_2 \\ CO_2 \end{matrix} + 2K.$$

Since, then, judging by its chemical behaviour, acetic acid contains a CH_3– and an HO– group, it must have the constitution $CH_3{\cdot}C{<}^{O}_{OH}$, which confirms the conclusion previously arrived at.

The relation between formic and acetic acids, and their similarity in certain chemical properties, are satisfactorily accounted for by the constitutional formulæ



$$H\cdot C\Big<^{O}_{OH} \quad \text{and} \quad CH_3\cdot C\Big<^{O}_{OH},$$

which thus confirm one another. The acids are both represented as containing the monovalent group of atoms $-C\Big<^{O}_{OH}$, which has not been met with in any of the *neutral* compounds yet considered; it may be concluded, therefore, that their characteristic *acid* properties are due to the presence of this group. As, moreover, aldehydes contain the group $-C\Big<^{O}_{H}$, but do not contain hydrogen displaceable by metals, it must be the hydrogen atom of the HO– group which is displaced when the acids form salts. The particular monovalent group of atoms common to formic and acetic acids is named the *carboxyl*-group, and is usually written $-CO\cdot OH$, or simply, for convenience, $-COOH$.

Homologues of Acetic Acid.—As all the higher members of the series of fatty acids resemble formic and acetic acids in chemical properties, may be produced by similar methods, and undergo similar changes, it is assumed that they all contain a carboxyl-group. With the exception of formic acid, they may, in fact, be regarded as derived from the paraffins, by the substitution of the monovalent carboxyl-group for one atom of hydrogen; acetic acid, $CH_3\cdot COOH$, from methane, CH_4; propionic acid, $C_2H_5\cdot COOH$, from ethane; and so on. They form, therefore, a homologous series of the general formula $C_nH_{2n+1}\cdot COOH$, or $C_nH_{2n}O_2$, and are all monobasic or *monocarboxylic* acids.

As in other homologous series, the higher members exist in isomeric forms, the number of isomerides theoretically possible in any given case being the same as that of the corresponding primary alcohols. The two isomeric acids, butyric acid,

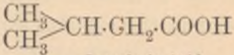
$CH_3\cdot CH_2\cdot CH_2\cdot COOH$, and isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot COOH$, for example, correspond with the two primary alcohols, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot OH$, respectively.

Those isomerides which are derived from the normal paraffins, by substituting $-COOH$ for one atom of hydrogen in the CH_3- group, are termed *normal* or primary acids, as normal butyric acid, $CH_3\cdot CH_2\cdot CH_2\cdot COOH$, normal heptylic acid, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$; those which contain the group $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH-$ are usually termed *iso*-acids, as, for example, isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot COOH$, isovaleric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot COOH$, but the term is not used very systematically.

With the exception of the normal acids and one or two well-known iso-acids, such as those just quoted, it is usual, to avoid confusion, to name the fatty acids as if they were derived from acetic acid, just as the alcohols are regarded as derivatives of carbinol; the four isomerides of the molecular formula $C_5H_{10}O_2$, for example, are named as follows:

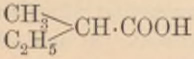
$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$

Normal Valeric Acid
(Propylacetic Acid).



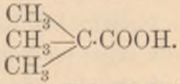
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot COOH$

Isovaleric Acid
(Isopropylacetic Acid).



$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH\cdot COOH$

Methylethylacetic Acid.



$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!C\cdot COOH.$

Trimethylacetic Acid.

Propionic acid, $C_3H_6O_2$, or $CH_3\cdot CH_2\cdot COOH$, exists in only one form, and occurs in crude pyroligneous acid; it is formed when acrylic acid (p. 257) is reduced with sodium amalgam,

$$C_3H_4O_2 + 2H = C_3H_6O_2,$$

and when lactic acid (p. 225) is heated with concentrated hydriodic acid, which, at a high temperature, is a powerful reducing agent,*

$$CH_3{\cdot}CH(OH){\cdot}COOH + 2HI = CH_3{\cdot}CH_2{\cdot}COOH + H_2O + I_2.$$

It is prepared by oxidising propyl alcohol with chromic acid,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + 2O = CH_3{\cdot}CH_2{\cdot}COOH + H_2O.$$

Propionic acid is a colourless liquid, boils at 141°, and has a pungent sour smell; it is miscible with water in all proportions, but on adding a little calcium chloride to the solution, part of the acid separates at the surface, forming an oily layer. This property is characteristic of all fatty acids, which are readily soluble in water, except formic and acetic acids. Propionic acid is a mono-carboxylic acid, and closely resembles acetic acid in chemical properties; its salts, the **propionates**, are soluble in water, and of little importance.

There are two acids of the molecular formula $C_4H_8O_2$. **Normal butyric acid**, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, occurs in the vegetable and animal kingdoms, both in the free state and in combination with glycerol; it is an important constituent of butter. It is formed during the decay of nitrogenous animal matter, and during the butyric fermentation of lactic acid. When milk is left exposed to the air, it turns sour, the milk sugar which it contains being converted into lactic acid by a minute organism, the *lactic ferment*, which is present in the air, and finds its way into the milk,

$$\underset{\text{Milk Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Lactic Acid.}}{4C_3H_6O_3}.$$

The lactic ferment has the power of converting other sugars besides milk sugar (or lactose) into lactic acid. If now a little decaying cheese be added to the sour milk, and the solu-

---

* In the reduction of lactic acid the following changes occur:

$$CH_3{\cdot}CH(OH){\cdot}COOH + HI = CH_3{\cdot}CHI{\cdot}COOH + H_2O$$

$$CH_3{\cdot}CHI{\cdot}COOH + H\vdots I = CH_3{\cdot}CH_2{\cdot}COOH + I_2.$$

In such reductions it is usual to add a pinch of amorphous phosphorus to the mixture, in order that the iodine may be reconverted into hydriodic acid ($3I + P + 3H_2O = H_3PO_3 + 3HI$).

tion be kept neutral by adding some chalk,* *butyric fermentation* sets in, the lactic acid being converted into butyric acid by the action of another organism, the *butyric ferment,* which is present in the decomposing cheese,

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Butyric acid is usually prepared by a combination of these two processes of fermentation.

Butyric acid is a thick sour liquid, boiling at 163°. It has a very disagreeable odour, like that of rancid butter and stale perspiration, in which it occurs; it is miscible with water in all proportions, but separates on adding calcium chloride.

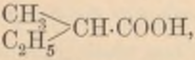
The **butyrates,** or salts of butyric acid, are soluble in water; the *calcium salt* $(C_4H_7O_2)_2Ca + H_2O$ is more soluble in cold than in hot water, so that when a cold saturated solution is heated, part of the salt separates in crystals, and the solution becomes turbid.

Isobutyric acid, or dimethylacetic acid, $(CH_3)_2CH{\cdot}COOH$, may be prepared by the oxidation of isobutyl alcohol,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}OH + 2O = (CH_3)_2CH{\cdot}COOH + H_2O.$$

It boils at 155°, and resembles the normal acid very closely, but is not miscible with water in all proportions, one part of the acid requiring about five parts of water for solution. The *calcium salt* $(C_4H_7O_2)_2Ca + 5H_2O$, unlike that of butyric acid, is more soluble in hot than in cold water.

Of the four isomerides of the molecular formula $C_5H_{10}O_2$, **isovaleric acid,** or isopropylacetic acid, $(CH_3)_2CH{\cdot}CH_2{\cdot}COOH$, and **active valeric acid,** or methylethylacetic acid,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH{\cdot}COOH,$$

are the most important. These acids occur together in the plant all-heal, or valerian, and in angelica root; the mixture of acids obtained by distilling the macerated plants with water is known as valeric or valerianic acid, and is an oily liquid, boiling at about 174°. A mixture of these two acids may

---

* The ferment ceases to act if the solution become too strongly acid.

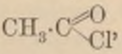
be prepared by oxidising commercial amyl alcohol (p. 105) with chromic acid.

The **hexylic acids**, $C_6H_{12}O_2$, are of little importance; seven of the eight isomerides theoretically possible are known, including normal hexylic acid (caproic acid).

Normal heptylic acid, $C_7H_{14}O_2$, or $C_6H_{13}\cdot COOH$, one of the seventeen theoretically possible isomerides, of which only nine are known, is prepared by oxidising castor-oil or œnanthaldehyde (p. 127) with nitric acid; it is an oily, rather unpleasant smelling liquid, sparingly soluble in water; it boils at 223°, and, like all the lower members of the series, is readily volatile in steam.

Palmitic acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}\cdot COOH$, and **stearic acid**, $C_{18}H_{36}O_2$, or $C_{17}H_{35}\cdot COOH$, occur in large quantities in animal and vegetable fats and oils (p. 166), from which they are prepared on the large scale principally for the manufacture of stearin candles; they are colourless, waxy substances, melting at 62° and 69° respectively, and insoluble in water, but soluble in alcohol, ether, &c. Their sodium and potassium salts are soluble in pure water, and are the principal constituents of soaps (p. 168), but their calcium, magnesium, and other salts are insoluble. A mixture of these two acids was at one time thought to be a definite compound, and named *margaric acid;* this name is now given to an artificially prepared acid, $C_{17}H_{34}O_2$, or $C_{16}H_{33}\cdot COOH$, which stands between palmitic and stearic acids in the series, and which seems not to occur in nature.

Derivatives of the Fatty Acids.

Acid Chlorides.—When phosphorus pentachloride is added to anhydrous acetic acid, an energetic action takes place, and **acetyl chloride**,  $CH_3\cdot C\begin{array}{l}\nearrow\!\!\!\!\!\!= O\\ \searrow Cl\end{array}$, is formed, with evolution of hydrogen chloride; this change is analogous to that which occurs when an alcohol is treated with phosphorus pentachloride,

$$CH_3{\cdot}CO{\cdot}OH + PCl_5 = CH_3{\cdot}COCl + POCl_3 + HCl$$
$$CH_3{\cdot}CH_2{\cdot}OH + PCl_5 = CH_3{\cdot}CH_2Cl + POCl_3 + HCl.$$

Phosphorus trichloride and oxychloride also convert acetic acid into acetyl chloride.

Acetyl chloride is best prepared by adding phosphorus trichloride, or oxychloride, from a tap funnel to anhydrous sodium or potassium acetate contained in a retort connected with a condenser, and then distilling from a water-bath; a phosphite, or a mixture of metaphosphate and chloride, is left in the retort,

$$3CH_3{\cdot}COONa + PCl_3 = 3CH_3{\cdot}COCl + Na_3PO_3$$
$$2CH_3{\cdot}COOK + POCl_3 = 2CH_3{\cdot}COCl + KPO_3 + KCl.$$

It is a colourless, pungent-smelling liquid, boils at 55°, and fumes in moist air; when poured into water, it is rapidly decomposed, with formation of acetic acid,

$$CH_3{\cdot}COCl + H_2O = CH_3{\cdot}COOH + HCl.$$

Acetyl chloride bears the same relation to acetic acid as ethyl chloride to alcohol; it may, in fact, be produced by passing hydrogen chloride into anhydrous acetic acid containing phosphorus pentoxide, which combines with the water formed, and thus prevents the reverse change (compare ethereal salts, p. 187),

$$CH_3{\cdot}COOH + HCl = CH_3{\cdot}COCl + H_2O.$$

Acetyl chloride is not only quickly decomposed by alkalies and by water, but also, more or less rapidly, by all compounds containing one or more hydroxyl-groups; the interaction always takes place in such a way that hydrogen chloride is produced, the monovalent *acetyl*-group $CH_3{\cdot}C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\end{smallmatrix}$ displacing the hydrogen of the hydroxyl-group,

$$C_2H_5{\cdot}OH + CH_3{\cdot}COCl = C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3 + HCl$$
$$C_3H_7{\cdot}OH + CH_3{\cdot}COCl = C_3H_7{\cdot}O{\cdot}CO{\cdot}CH_3 + HCl.$$

Acetyl chloride may therefore be employed as a reagent for determining the presence of a hydroxyl-group. All that is necessary is to add the dry substance, in the state of a fine powder, if a solid, to excess of acetyl chloride, and then heat the mixture or solution for some time. The substance may be recovered unchanged, indicating that it is not a hydroxy-compound, or it may be converted into a new substance, an *acetyl* derivative, by the substitution of the acetyl-group for hydrogen; in the latter case, a combustion of the substance is usually made, in order to ascertain its composition, from which the number of times the acetyl-group has displaced hydrogen is determined;[*] or, since acetyl derivatives are decomposed by boiling acids and alkalies, the percentage of acetic acid obtained from the substance may be directly estimated,

$$C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3 + KOH = C_2H_5{\cdot}OH + CH_3{\cdot}COOK.$$

All the fatty acids except formic acid may be converted into *acid chlorides*, such as *propionyl chloride*, $CH_3{\cdot}CH_2{\cdot}COCl$, by the methods described above; the products resemble acetyl chloride in chemical properties, and may be employed for the detection of hydroxyl-groups. *Acid bromides*, such as $CH_3{\cdot}COBr$, can be obtained in a similar manner.

Anhydrides.—The hydrogen atom in a carboxyl-group $-COOH$ is not, as a rule, displaced by the acetyl-group on treatment with acetyl chloride, but, when an alkali salt of a fatty acid is heated with acetyl chloride, an acetyl derivative of the acid is formed,

$$CH_3{\cdot}COOK + CH_3{\cdot}COCl = CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + KCl.$$

The compound obtained from an acetate in this way may be regarded as acetyl oxide, $(CH_3{\cdot}CO)_2O$, or as an **anhydride** of acetic acid, derived from 2 mols. of the acid by loss of 1 mol. of water, just as ethers are derived from alcohols, and inorganic anhydrides from the corresponding acids,

---

[*] Except when the acetyl derivative has the same, or nearly the same percentage composition as the original substance, in which case the number of acetyl groups in the molecule is determined by boiling with standard alkali or acid, and then estimating by titration the amount of acetic acid which has been formed.

$$\begin{matrix}CH_3\cdot CO\vdots OH\\ CH_3\cdot COO\vdots H\end{matrix} = \left.\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\right> O + H_2O$$

$$\begin{matrix}C_2H_5\cdot OH\\ C_2H_5\cdot OH\end{matrix} = \left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right> O + H_2O \qquad \begin{matrix}NO_2\cdot OH\\ NO_2\cdot OH\end{matrix} = \left.\begin{matrix}NO_2\\ NO_2\end{matrix}\right> O + H_2O.$$

Acetic anhydride, $(CH_3\cdot CO)_2O$, may be prepared by heating the anhydrous alkali acetates (4 mols.) with phosphorus oxychloride (1 mol.); the salt is first acted on by the oxychloride yielding acetyl chloride (see above), which interacts with more salt, forming acetic anhydride, or, expressed in one equation,

$$4CH_3\cdot COONa + POCl_3 = 2(CH_3\cdot CO)_2O + NaPO_3 + 3NaCl.$$

Acetic anhydride is a mobile liquid, boils at 137°, and has an unpleasant, irritating odour; it is decomposed by alkalies, by water, and by nearly all substances (except acids) which contain the hydroxyl-group, acetyl derivatives being formed,

$$(CH_3\cdot CO)_2O + H_2O = 2CH_3\cdot COOH$$

$$(CH_3\cdot CO)_2O + C_2H_5\cdot OH = CH_3\cdot CO\cdot O\cdot C_2H_5 + CH_3\cdot COOH.$$

Acetic anhydride may therefore be employed in ascertaining whether a substance contains a hydroxyl-group just as well as acetyl chloride, the operations being carried out as already described.

All the fatty acids, except formic acid, may be converted into anhydrides by treating the acid chloride with an alkali salt, or by heating excess of an alkali salt with phosphorus oxychloride. If an acid chloride be treated with a salt of a different acid, *mixed anhydrides*, corresponding with the mixed ethers, are obtained. All these anhydrides resemble acetic anhydride in chemical properties.

Amides.—Acetyl chloride and acetic anhydride interact not only with compounds containing a hydroxyl-group, but also with anhydrous ammonia; the compound obtained in this way may be regarded as derived from ammonia by the substitution of the acetyl-group for one atom of hydrogen, and is named acetamide.

$$CH_3{\cdot}COCl + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + NH_4Cl$$
$$(CH_3{\cdot}CO)_2O + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}CO{\cdot}ONH_4.$$

Acetamide, $CH_3{\cdot}CO{\cdot}NH_2$, may also be produced by heating ethyl acetate (p. 185) with concentrated ammonia under pressure,

$$CH_3{\cdot}CO{\cdot}OC_2H_5 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH,$$

but it is best prepared by slowly distilling ammonium acetate in a stream of dry ammonia,

$$CH_3{\cdot}CO{\cdot}ONH_4 = CH_3{\cdot}CO{\cdot}NH_2 + H_2O.$$

As one distillation is not sufficient to insure complete decomposition, that portion of the distillate boiling above 140° is collected separately and redistilled, these operations being repeated three or four times.

Acetamide crystallises in colourless needles, melts at 80–82°, and boils at 222°. When pure, it has only a faint odour, but as usually prepared, it has a strong smell of mice, owing to the presence of traces of impurity; it is readily soluble in water and alcohol. When heated with mineral acids or alkalies, it is decomposed into acetic acid and ammonia, or their salts (compare foot-note, p. 143),

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2O = CH_3{\cdot}COOH + NH_3;$$

on distillation with phosphoric anhydride, it loses 1 mol. of water, and is converted into methyl cyanide or acetonitrile,

$$CH_3{\cdot}CO{\cdot}NH_2 = CH_3{\cdot}CN + H_2O.$$

Formic acid and all the higher fatty acids may be converted into amides by methods similar to those given above; *formamide*, $H{\cdot}CO{\cdot}NH_2$, for example, may be prepared by distilling ammonium formate. These amides closely resemble acetamide in chemical and physical properties, but their solubility in water rapidly diminishes on passing up the series. It is a remarkable fact that the melting-points of the amides of the fatty acids lie very close together, most of them melting between 95° and 110°, and all within the limits of 79° and 129°.

Substitution Products of Acetic Acid.—Since acetic acid, like methyl chloride, is a mono-substitution product of marsh-gas, and contains three atoms of hydrogen combined with carbon, it might be expected to give halogen substitution products, just as does methyl chloride. As a matter of fact, acetic acid yields three substitution products on treatment with chlorine in sunlight,

$$CH_3{\cdot}COOH + Cl_2 = CH_2Cl{\cdot}COOH + HCl$$
$$CH_3{\cdot}COOH + 2Cl_2 = CHCl_2{\cdot}COOH + 2HCl$$
$$CH_3{\cdot}COOH + 3Cl_2 = CCl_3{\cdot}COOH + 3HCl.$$

If the constitutions of acetic acid and of these three compounds be correctly represented by these formulæ, it would be expected that, as the chloro-substitution products still contain the carboxyl-group, they would behave like monocarboxylic acids, and, like acetic acid, form salts, acid chlorides, anhydrides, &c. This again is the fact; the three substitution products are monobasic acids, similar to acetic acid and to one another in chemical properties.

The three chloracetic acids may be prepared by passing chlorine into boiling acetic acid, to which a little iodine has been added. When iodine is present, the process can be carried out in absence of sunlight, because the iodine is converted into iodine trichloride, which acts on the acetic acid even in the dark,

$$CH_3{\cdot}COOH + ICl_3 = CH_2Cl{\cdot}COOH + HCl + ICl.$$

The iodine chloride is again converted into trichloride by direct combination with chlorine, and so the process continues, a very small quantity of iodine being sufficient to insure chlorination. The iodine, or rather the iodine chloride, is spoken of as a chlorine *carrier*.

Chloracetic acid, $CH_2Cl{\cdot}COOH$, is a crystalline substance; it melts at 62°, and boils at 185–187°.

Dichloracetic acid, $CHCl_2{\cdot}COOH$, is a liquid, and boils at 190–191°; it is best prepared by treating chloral hydrate with potassium cyanide in aqueous solution,

$$KCN + CCl_3{\cdot}CH(OH)_2 = CHCl_2{\cdot}COOH + HCN + KCl.$$

Trichloracetic acid, $CCl_3{\cdot}COOH$, is best prepared by oxidising the corresponding aldehyde, chloral, with concentrated nitric acid,

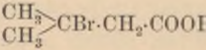
$$CCl_3\cdot CHO + O = CCl_3\cdot COOH.$$

It melts at 52°, boils at 195°, and is decomposed by hot alkalies into chloroform and a carbonate,

$$CCl_3\cdot COOH + KOH = CHCl_3 + KHCO_3.$$

The three bromacetic and iodacetic acids are similar in properties. On treating any of these halogen substitution products with nascent hydrogen, they are reconverted into acetic acid by inverse substitution. The higher fatty acids may be converted into halogen substitution products, which, however, unlike those of acetic acid, exist in isomeric forms. Propionic acid, for example, gives two monochloro-propionic acids—namely, *α*-chloro-propionic acid, $CH_3\cdot CHCl\cdot COOH$, and *β*-chloro-propionic acid, $CH_2Cl\cdot CH_2\cdot COOH$. For the purpose of distinguishing between these substitution products, the carbon atoms are lettered *α*, *β*, *γ*, *δ*, &c., commencing always with that which is combined with the carboxyl-group

$$\underset{\delta}{CH_3}\cdot\underset{\gamma}{CH_2}\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CH_2}\cdot COOH\,;$$

the acid of the constitution  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CBr\cdot CH_2\cdot COOH$, for example, is named *β*-bromisopropylacetic acid.

SUMMARY AND EXTENSION.

The Fatty Acids.—Carboxy-derivatives of the paraffins of the general formula $C_nH_{2n+1}\cdot COOH$, or $C_nH_{2n}O_2$. The more important members of this homologous series are the following, the number of *known* isomerides being given by the figures in brackets:

		M.p.	B.p.	Sp. gr.	
Formic acid, $H\cdot COOH$ (1)		8·3°	101°	1·241	at 0°
Acetic acid, $CH_3\cdot COOH$ (1)		16·5°	118°	1·080	″
Propionic acid, $C_2H_5\cdot COOH$ (1)		-24°	141°	1·013	″
Butyric acid, $C_3H_7\cdot COOH$ (2)	Normal	-4°	163°	0·978	″
	Iso-	—	155°	0·965	″
Valeric acid, $C_4H_9\cdot COOH$ (4)	Normal	—	186°	0·957	″
	Iso-	—	174°	0·947	″
Heptylic acid, $C_6H_{13}\cdot COOH$ (8)		—	223°	0·945	″
Lauric acid, $C_{11}H_{23}\cdot COOH$ (3)		43·6°	—	0·875	At the melting-point.
Myristic acid, $C_{13}H_{27}\cdot COOH$ (2)		54°	—	0·862	
Palmitic acid, $C_{15}H_{31}\cdot COOH$ (2)		62°	—	0·853	
Stearic acid, $C_{17}H_{33}\cdot COOH$ (3)		69°	—	0·845	

Heptylic acid and all the higher members named in this table are normal acids; they occur in nature in fats and oils, and contain an even number of carbon atoms. The higher normal acids containing an odd number of carbon atoms, $C_8H_{17}{\cdot}COOH$, $C_{10}H_{21}{\cdot}COOH$, &c., are known, but they do not occur in nature.

Formic acid is prepared by heating oxalic acid with glycerol, acetic acid from pyroligneous acid, and by the acetous fermentation of alcohol, butyric acid by the butyric fermentation of lactic acid, and palmitic and stearic acids by the hydrolysis of glycerides occurring in fats and oils.

Methods of Preparation.—By the oxidation of primary alcohols and of aldehydes,

$$C_2H_5{\cdot}CH_2{\cdot}OH + 2O = C_2H_5{\cdot}COOH + H_2O$$
$$C_6H_{13}{\cdot}CHO + O = C_6H_{13}{\cdot}COOH.$$

By boiling alkyl cyanides with alkalies or mineral acids,

$$C_2H_5{\cdot}CN + 2H_2O = C_2H_5{\cdot}COOH + NH_3.$$

By heating those dicarboxylic acids in which the two carboxyl-groups are combined with one and the same carbon atom (p. 234),

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2.$$

By the hydrolysis of derivatives of ethyl acetoacetate (p. 189),

$$CH_3{\cdot}CO{\cdot}CH(C_3H_7){\cdot}COOC_2H_5 + 2KOH = C_3H_7{\cdot}CH_2{\cdot}COOK$$
$$+ CH_3{\cdot}COOK + C_2H_5{\cdot}OH.$$

Physical Properties.—At ordinary temperatures, the lower members are colourless liquids (except acetic acid), miscible with water, alcohol, and ether in all proportions. On passing up the series, they become more oily in character, gradually lose their pungent smell, and become less readily soluble in water. The higher members, from $C_{10}H_{20}O_2$, are solid, waxy, or fatty substances, have only a faint smell, and are insoluble in water, but soluble in alcohol and ether. They are all volatile in steam except the highest members, which, however, may be distilled in super-heated steam. The first three members are specifically heavier than water, but the sp. gr. decreases as the series is ascended (see table). With the exception of the highest members, they boil without decomposition under ordinary atmospheric pressure, the boiling-point rising about 19° for every addition of $-CH_2-$ to the molecule; the melting-point also rises, but not continuously, acids containing an odd number of carbon atoms melting at a lower temperature than the preceding members containing an even number of carbon atoms,

$C_{12}H_{24}O_2$	$C_{13}H_{26}O_2$	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$.
43·6°	40·5°	54°	51°	62°	60°

Chemical Properties.—The fatty acids are very stable, and are only with difficulty oxidised and broken up; nevertheless, owing to the presence of the carboxyl-group, they readily undergo a variety of double decompositions. They are all monobasic acids, but the acid character becomes less and less pronounced on passing up the series; whereas formic and acetic acids readily decompose carbonates, and dissolve metals and metallic hydroxides, the higher members, such as palmitic and stearic acids, are with difficulty recognised as acids by ordinary tests. The metallic salts of the lower members are soluble in water; but on passing up the series, the solubility decreases, until, in the case of the higher acids, only the alkali salts (soaps) are soluble.

Fatty acids interact with alcohols, especially in presence of dehydrating agents, forming ethereal salts and water,

$$CH_3{\cdot}COOH + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + H_2O.$$

When treated with phosphorus pentachloride, &c., they are converted into acid chlorides,

$$C_2H_5{\cdot}COOH + PCl_5 = C_2H_5{\cdot}COCl + POCl_3 + HCl.$$

These acid chlorides interact readily with hydroxy-compounds, giving ethereal salts,

$$C_2H_5{\cdot}COCl + CH_3{\cdot}OH = C_2H_5{\cdot}CO{\cdot}OCH_3 + HCl;$$

on distillation with an alkali salt of a fatty acid, they yield anhydrides of the acids,

$$C_2H_5{\cdot}COCl + C_2H_5{\cdot}COOK = (C_2H_5{\cdot}CO)_2O + KCl;$$

and when treated with ammonia, they give amides,

$$CH_3{\cdot}COCl + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + HCl.$$

The fatty acids yield halogen substitution products under suitable conditions. From the alkali salts of the fatty acids, ketones, aldehydes, and paraffins can be prepared without difficulty, and, as the aldehydes and ketones are easily reduced to alcohols, which again are readily converted into ethers and olefines, all these compounds may be obtained from the fatty acids.

Fats, Oils, Soaps, Stearin, and Butter.

Composition of Fats and Oils.—When beef or mutton suet is kneaded in a muslin bag in a basin of hot water, the fat melts and passes out, leaving the membrane or tissue in the bag; the melted fat solidifies on cooling, and is known as *tallow.* The fat obtained from pigs, in a similar manner, is much softer, and is called *lard*

When tallow is heated with water in closed vessels at about 200°, or treated with superheated steam (steam which has been passed through tubes heated at about 200°), it is decomposed into glycerol (p. 248) and fatty acids; if the mixture be now distilled in superheated steam, these products pass over, the distillate being an aqueous solution of glycerol, at the surface of which floats the mixture of fatty acids. A similar decomposition takes place when tallow is heated with dilute sulphuric acid, but in this case it is not necessary to heat so strongly.

All animal fats, such as lard, goose-fat, bone-fat, butter, &c., and the fatty oils, such as olive-, linseed-, rape-, palm-, and cotton-seed oils, which are obtained by pressing the seeds or fruit of certain plants, behave in a similar manner, and when heated with dilute sulphuric acid, or with water under pressure, are decomposed into glycerol and a mixture of fatty acids. The occurrence of these acids in natural fats and oils, and the fact that the higher members of the series resemble fats in physical properties, led to the use of the term 'fatty acid,' which is now applied to all the members of the series.

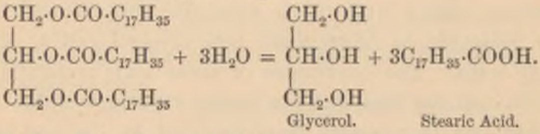
The chemical compounds of which these fats are composed are called *glycerides;* they are ethereal salts (p. 171), formed, together with water, by the combination of the fatty acids with the alcohol, glycerol, which acts as a hydroxide or weak base. Glycerol is a *tri-acid* base, and can combine with and neutralise three molecules of a monobasic or monocarboxylic acid, forming neutral salts, just as can the tri-acid bismuth hydroxide,

$$C_3H_5(OH)_3 + 3CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_3 + 3H_2O$$
$$Bi(OH)_3 + 3HCl = BiCl_3 + 3H_2O.$$

These glycerides or salts are named after the acids from which they are formed. The salt formed from acetic acid is called *triacetin;* that from palmitic acid, *tripalmitin;* and that from stearic acid, *tristearin,* and so on.

Now the chief constituents of fats and oils are tristearin and tripalmitin, which are solid at ordinary temperatures, and a liquid glyceride, *trioleïn*, which is formed by the combination of glycerol with *oleïc acid*.* When a fat contains a relatively large proportion of tristearin and tripalmitin, it is solid and comparatively hard (tallow) at ordinary temperatures; when, however, it contains a relatively large proportion of trioleïn, it is soft and pasty (lard), or liquid (olive-oil).

These glycerides, like other salts formed from weak acids and weak bases, are not very stable, and at moderately high temperatures they are decomposed by water and by dilute mineral acids, being converted into glycerol and an acid; in the case of tristearin, for example,



$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \end{array} + 3H_2O = \begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array} + 3C_{17}H_{35}{\cdot}COOH.$$

Since fats and oils are mixtures of glycerides, they yield mixtures of fatty acids.

Soaps.—On treatment with alkalies the glycerides are decomposed much more readily than by water, yielding alkali salts, the weak base, glycerol, being liberated, just as ammonia or methyl alcohol is liberated from its salts on adding a stronger base. In manufacturing soaps, a fat or oil, such as tallow or cotton-seed oil, is heated in an iron pan with a small but sufficient quantity of caustic soda, when it is converted after some time into a thick, homogeneous, frothy solution, which contains glycerol and the sodium salts of the various acids which were present in the glycerides—that is to say, the sodium salts of stearic, palmitic, and oleïc acids. Some common salt is now added, whereupon the sodium

---

* *Oleïc acid*, $C_{17}H_{33}{\cdot}COOH$ (p. 258), is a liquid at ordinary temperatures. It contains two atoms of hydrogen less than stearic acid, $C_{17}H_{35}{\cdot}COOH$, and is, therefore, an *unsaturated* acid, belonging to a different series; its lead salt is soluble in ether, a property very rarely met with in other lead salts.

salts separate from the solution of glycerol and salt as a curd, because they are insoluble in salt water. The curd, after having been drained off, and allowed to cool, slowly solidifies, and is then known as *hard soap*, which is simply a mixture of the sodium salts of palmitic, stearic, and oleïc acids with water and alkali. When fats or oils are boiled with potash, instead of with soda, similar chemical changes take place, and the potassium salts of the acids are formed; if common salt be now added to the solution, the potassium are partially converted into sodium salts, and a hard soap is finally obtained; if, however, without adding salt, the homogeneous solution be allowed to cool, it sets to a jelly-like mass of *soft soap*, which is a mixture of the potassium salts of the above-named acids, containing glycerol and a large percentage of water.

The decomposition of fats and oils in this way in the process of soap-making originally received the name *saponification*, and the fats and oils were said to be *saponified*. The term saponification was then applied generally to the analogous decomposition of other ethereal salts by alkalies, in spite of the fact that the products were not soaps, but the word *hydrolysis* has now to a great extent taken its place. Hydrolysis may be roughly defined as the decomposition of one compound into two or more, with fixation of the elements of water or of some hydroxide. The decomposition of glycerides by water, acids, and alkalies, and the changes expressed by the following equations, are examples of hydrolysis,

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
$$C_2H_3O_2{\cdot}C_2H_5 + H_2O = C_2H_4O_2 + C_2H_5{\cdot}OH$$
$$C_2H_5Cl + KOH = C_2H_5{\cdot}OH + KCl.$$

Stearin and Glycerol.—Stearin consists principally of a mixture of stearic and palmitic acids, and is manufactured by decomposing tallow with water, superheated steam, dilute sulphuric acid, or milk of lime under pressure (see above). After distilling the products in a current of superheated steam — first acidifying with sulphuric acid, if lime has been used—the pasty mixture of fatty acids is separated from the aqueous solution of glycerol, and pressed, in order to squeeze out as much of the liquid oleïc acid as possible. The pressed mass is then gently warmed, and pressed again between warm plates, when a further quantity of oleïc acid is squeezed out, together with some palmitic and stearic acids. The hard mass that remains is called *stearin;* it is mixed with a little paraffin to make it less brittle, and employed in large quantities in the manufacture of stearin candles. The pasty mass of oleïc, palmitic, and stearic acids, separated from the stearin, is known as *oleomargarine* (from oleïc and 'margaric' acids), and is employed for the preparation of artificial butter. Glycerol (p. 248) is obtained from the aqueous distillate, after separating the fatty acids; the solution is decolourised by filtration through charcoal, and evaporated to a syrup.

Butter and Margarine.—Butter, prepared from cream, is a mixture of fat (about 87 per cent.), water (about 12 per cent.), and small quantities of caseïn, milk-sugar, and salts. Pure butter-fat contains about 92 per cent. of a mixture of tristearin, tripalmitin, and trioleïn, about 7·7 per cent. of tributyrin, and traces of other glycerides, and substances which impart flavour; it differs from all other fats and oils, in containing a large proportion of *tributyrin*, the glyceride of butyric acid.

Artificial butter, or *margarine*, is prepared from oleomargarine (see above), which has been carefully manufactured from the best ox-suet; the oleomargarine is flavoured and coloured by churning it with milk, sometimes also by the addition of artificial colouring and flavouring substances. When carefully prepared, it is a wholesome substitute for butter, and probably just as nutritious, although perhaps not quite so easily digested.

CHAPTER X.

ETHEREAL SALTS.

It has been pointed out that the alcohols behave in some respects like metallic hydroxides, and combine with acids, forming salts and water,

$$C_2H_5{\cdot}OH + HCl = C_2H_5Cl + H_2O$$
$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O$$
$$CH_3{\cdot}OH + CH_3{\cdot}COOH = CH_3{\cdot}COOCH_3 + H_2O.$$

These compounds are called **ethereal salts** or **esters**, in contradistinction to the metallic salts.

Halogen Ethereal Salts and Halogen Derivatives of the Paraffins.

The ethereal salts of the halogen acids are identical with the *halogen mono-substitution products of the paraffins*, and may be obtained either from the alcohols or from the paraffins; they form homologous series of the general formula $C_nH_{2n+1}{\cdot}X$ where X = Cl, Br, or I.

Methyl chloride,	CH_3Cl	Methyl bromide,	CH_3Br	Methyl iodide,	CH_3I
Ethyl "	C_2H_5Cl	Ethyl "	C_2H_5Br	Ethyl "	C_2H_5I
Propyl "	C_3H_7Cl	Propyl "	C_3H_7Br	Propyl "	C_3H_7I

The di-, tri-, &c. halogen substitution products of the paraffins, such as methylene dichloride, CH_2Cl_2, chloroform, $CHCl_3$, iodoform, CHI_3, and carbon tetrachloride, CCl_4, cannot be regarded as ethereal salts, but, being closely related to the halogen ethereal salts, are conveniently considered in this chapter.

Methyl chloride, or chloromethane, CH_3Cl, is one of the four substitution products obtained on treating methane with chlorine in sunlight, and is formed in small quantities when methyl alcohol is heated with *concentrated* hydrochloric acid,

$$CH_3{\cdot}OH + HCl = CH_3Cl + H_2O.$$

It is prepared by passing hydrogen chloride into methyl alcohol containing anhydrous zinc chloride (Groves' process), as described in the case of ethyl chloride (p. 175); also by heating methyl alcohol with sodium chloride and concentrated sulphuric acid.

It is a colourless gas, and liquefies at very low temperatures, boiling at –24°; it burns with a green-edged flame, is moderately easily soluble in water, and when heated with water or dilute potash under pressure, it is converted into methyl alcohol,

$$CH_3Cl + H_2O = CH_3{\cdot}OH + HCl.$$

Methyl chloride is employed on the large scale in the preparation of organic dyes, the compressed gas being also used for the artificial production of a low temperature; for these purposes it is manufactured by heating trimethylamine hydrochloride (p. 207) with hydrochloric acid,

$$N(CH_3)_3,HCl + 3HCl = 3CH_3Cl + NH_4Cl.$$

Methylene (or methene) **dichloride,** CH_2Cl_2, is prepared by reducing chloroform with zinc and hydrochloric acid in alcoholic solution,

$$CHCl_3 + 2H = CH_2Cl_2 + HCl;$$

it is a colourless, heavy liquid, boiling at 41°.

Chloroform, or trichloromethane, $CHCl_3$, is formed when methane, methyl chloride, or methylene dichloride, is treated with chlorine in sunlight, and when many simple organic substances containing oxygen, such as ethyl alcohol, acetone, &c., are heated with bleaching powder, which acts as an oxidising as well as a chlorinating agent (see below).

Chloroform may be prepared by distilling alcohol or acetone with bleaching powder: Some strong bleaching powder (about 450 grams) is made into a cream with about 1½ litres of water contained in a large flask, and alcohol, methylated spirit, or acetone (about 100 c.c.) is gradually added; the flask is then connected with a condenser, and slowly heated on a water-bath, when a mixture of chloroform, water, and alcohol or acetone distils. If the operation has been successful, the chloroform collects as a heavy oil at the bottom of the receiver; but if too much alcohol or acetone be present, the chloroform must be precipitated by adding water. It is then separated with the aid of a funnel, washed with water, shaken once or twice with a little concentrated sulphuric acid, which frees it from water, alcohol, &c., and redistilled from a water-bath.

The chloroform prepared in this way is not quite pure; the pure substance is best prepared by distilling chloral or chloral hydrate (p. 125) with caustic soda, the product being separated in the manner just described,

$$CCl_3{\cdot}CHO + NaOH = CHCl_3 + H{\cdot}COONa.$$

The changes which occur in the preparation of chloroform from alcohol are complex; it is probable that aldehyde is first formed by oxidation, and then converted into chloral, which is decomposed by the calcium hydroxide which is always produced during the reaction, yielding chloroform and calcium formate. When acetone is employed, trichloracetone is probably formed in the first place; this compound is then decomposed by the calcium hydroxide, giving chloroform and calcium acetate,

$$2CH_3{\cdot}CO{\cdot}CCl_3 + Ca(OH)_2 = 2CHCl_3 + (CH_3{\cdot}COO)_2Ca.$$

Chloroform is a heavy, pleasant-smelling liquid of sp. gr. 1·498 at 15°, and boils at 61°; when strongly heated, it burns with a green-edged flame, but it is not inflammable at ordinary temperatures. It is readily decomposed by warm alcoholic potash, yielding potassium formate and chloride,

$$CHCl_3 + 4KOH = H{\cdot}COOK + 3KCl + 2H_2O.$$

If a drop of chloroform be added to a mixture of aniline (part ii.) and alcoholic potash, an intensely nauseous smell is observed on warming gently, owing to the formation of *phenylcarbylamine* or *phenylisocyanide*,*

$$CHCl_3 + 3KOH + C_6H_5{\cdot}NH_2 = C_6H_5{\cdot}NC + 3KCl + 3H_2O, \text{ or}$$
$$C_6H_5{\cdot}NH_2 + H{\cdot}COOH = C_6H_5{\cdot}NC + 2H_2O.$$

---

* The experiment should be performed in a test tube, only one drop of aniline being employed, and the contents of the test tube should afterwards be carefully poured into the sink-pipe, in a draught closet if possible.

This reaction affords a very delicate test for chloroform and for aniline, and is spoken of as the **carbylamine reaction** (p. 202).

Chloroform is extensively employed in surgery as an anæsthetic, its vapour when inhaled causing unconsciousness. For this purpose pure chloroform must be employed, as the impure substance is dangerous, and produces bad after-effects.* Pure chloroform gives no precipitate with silver nitrate, and does not darken when shaken with concentrated sulphuric acid or with strong potash.

Carbon tetrachloride, or tetrachloromethane, CCl_4, the final product of the action of chlorine on CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$, is prepared by passing chlorine into boiling chloroform in sunlight, or by passing chlorine into carbon bisulphide in presence of antimony pentachloride, which acts as a chlorine carrier (p. 163),

$$CS_2 + 3SbCl_5 = CCl_4 + S_2Cl_2 + 3SbCl_3,$$
$$SbCl_3 + Cl_2 = SbCl_5;$$

in the latter case the sulphur dichloride is got rid of, after a preliminary distillation, by shaking the product with potash, the carbon tetrachloride being purified by redistillation. Carbon tetrachloride is a very heavy, pleasant-smelling liquid, boiling at 76–77°; on treatment with nascent hydrogen, it is converted into $CHCl_3$, CH_2Cl_2, CH_3Cl, and CH_4 successively, by inverse substitution. It is decomposed by hot alcoholic potash,

$$CCl_4 + 4KOH = 4KCl + CO_2 + 2H_2O.$$

The halogen ethereal salts, *methyl bromide*, CH_3Br (b.p. 4·5°), and *methyl iodide*, CH_3I (b.p. 44°), are prepared by methods similar to those employed in the case of the corresponding

---

* In the presence of air, chloroform gradually undergoes decomposition, especially under the influence of light, carbonyl chloride (phosgene gas, $COCl_2$) and hydrochloric acid being produced, $CHCl_3 + O = COCl_2 + HCl$. As carbonyl chloride is very poisonous, it is necessary to keep all chloroform required for anæsthetic purposes in the dark, the bottle being kept as full as possible, so as to exclude air.

ethyl salts (see below), which they closely resemble in chemical properties.

Iodoform, or triiodomethane, CHI_3, a halogen tri-substitution product of methane, is closely related to chloroform, and may be considered here. It is formed when ethyl alcohol (but *not* methyl alcohol), acetone, aldehyde, and other simple organic substances containing oxygen united with a $CH_3{\cdot}C\equiv$ group are warmed with iodine and an alkali or alkali carbonate; the changes which occur are doubtless similar to those which take place in the preparation of chloroform.

Iodoform is prepared by gradually adding iodine to an aqueous solution of sodium carbonate containing a little alcohol and heated at 60–80°; the precipitated iodoform is separated by filtration, and purified by recrystallisation from dilute alcohol. It crystallises in lustrous, yellow, six-sided plates, melts at 119°, and has a peculiar, very characteristic odour; it sublimes readily, and is volatile in steam. It is used in medicine and surgery as an antiseptic.

Ethyl chloride, or chlorethane, C_2H_5Cl, is formed when ethane is treated with chlorine in sunlight, and when alcohol is heated with concentrated hydrochloric acid, or treated with phosphorus pentachloride, or trichloride, at ordinary temperatures,

$$C_2H_5{\cdot}OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

Ethyl chloride is prepared by Groves' process: Hydrogen chloride, carefully dried with concentrated sulphuric acid, is passed into a flask containing absolute alcohol, to which about half its weight of coarsely powdered anhydrous zinc chloride has been added; the flask is connected with a reflux condenser (p. 186), and is provided with a safety tube. As soon as the solution is saturated with hydrogen chloride, it is gently warmed on the water-bath, when ethyl chloride and alcohol pass off; the alcohol vapour is cooled in passing through the condenser, the liquid running back into the flask. The gaseous ethyl chloride now passes through three wash-bottles containing water, dilute potash, and concentrated sulphuric acid respectively, by which means it is freed from hydrogen chloride, alcohol, and moisture; the pure ethyl chloride is then collected in a U-tube immersed in a freezing mixture.

Zinc chloride is a powerful dehydrating agent, and combines with the water produced during the interaction,

$$C_2H_5 \cdot OH + HCl = C_2H_5Cl + H_2O.$$

Unless some dehydrating agent be present, very little ethyl chloride is formed, because it is decomposed by water, or rather its formation cannot take place in presence of much water.

Ethyl chloride may also be prepared by warming a mixture of absolute alcohol, concentrated sulphuric acid, and sodium chloride, the gas being purified and condensed in the same way as before; the sulphuric acid not only interacts with the salt, forming hydrogen chloride, but also acts as a dehydrating agent.

Ethyl chloride is a colourless, very volatile liquid, boiling at 12·5°; it burns with a greenish, smoky flame, and is only sparingly soluble in water, but miscible with alcohol, ether, &c. When heated with water or potash under pressure, it yields ethyl alcohol,

$$C_2H_5Cl + H_2O = C_2H_5 \cdot OH + HCl;$$

on treatment with chlorine in sunlight, it gives di-, tri-, &c. substitution products of ethane. It gives no immediate precipitate with aqueous silver nitrate, but when warmed with an *alcoholic* solution of silver nitrate, silver chloride is quickly precipitated, ethyl nitrate remaining in solution,

$$C_2H_5Cl + AgNO_3 = C_2H_5 \cdot NO_3 + AgCl.$$

Ethyl bromide, or bromethane, C_2H_5Br, is formed when alcohol is heated with concentrated hydrobromic acid, or treated with phosphorus tribromide or pentabromide, at ordinary temperatures,

$$C_2H_5 \cdot OH + PBr_5 = C_2H_5Br + POBr_3 + HBr.$$

It is prepared by dropping bromine from a stoppered funnel into a mixture of alcohol (60 grams) and amorphous phosphorus (10 grams) contained in a distilling-flask, connected with a condenser and immersed in cold water; after adding the whole of the bromine, the mixture is distilled. The distillate is shaken with dilute potash to free it from bromine, hydrobromic acid, and alcohol, and then washed by shaking with water; after drying with calcium chloride, the ethyl bromide is purified by fractional distillation,

$$3C_2H_5{\cdot}OH + P + 3Br = 3C_2H_5Br + H_3PO_3.$$

It may also be prepared by distilling a mixture of alcohol, concentrated sulphuric acid, and potassium bromide.

Ethyl bromide is a colourless, pleasant-smelling, heavy liquid, and boils at 39°; it resembles ethyl chloride in its behaviour with water, potash, and silver nitrate.

Ethyl iodide, or iodethane, C_2H_5I, is formed when alcohol is heated with concentrated hydriodic acid; it is prepared by gradually adding iodine (100 grams), in small quantities at a time, to a mixture of alcohol (50 grams) and amorphous phosphorus (10 grams), and then distilling from a water-bath, the product being purified exactly as described in the case of ethyl bromide,

$$3C_2H_5{\cdot}OH + P + 3I = 3C_2H_5I + H_3PO_3.$$

Ethyl iodide is a colourless, pleasant-smelling, highly refractive, very heavy liquid, boiling at 72°; on exposure to light, it turns yellowish-brown, owing to the separation of traces of iodine, this phenomenon being observed in the case of nearly all organic compounds containing iodine. In chemical properties it closely resembles ethyl chloride and ethyl bromide.

Other halogen ethereal salts or halogen mono-substitution products of the paraffins, such as **propyl bromide,** C_3H_7Br, **butyl iodide,** C_4H_9I, &c., may be prepared by methods similar to those given above; they are all colourless, neutral, pleasant-smelling liquids, as a rule specifically heavier than water, in which they are insoluble, or nearly so. They are slowly decomposed, or hydrolysed (p. 188), by boiling water and by aqueous alkalies, yielding the alcohols,

$$C_3H_7Br + KOH = C_3H_7{\cdot}OH + KBr;$$

when boiled with *alcoholic* potash, they are converted into olefines,

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

They do not give an immediate precipitate with silver nitrate in aqueous solution; but in alcoholic solution, especially on warming, a halogen silver salt is quickly precipitated, and an organic *nitrate* remains in solution,

$$C_2H_5I + AgNO_3 = C_2H_5{\cdot}NO_3 + AgI.$$

Although these compounds closely resemble one another in chemical properties, their physical properties depend to a considerable extent on the halogen which they contain, the sp. gr. and boiling-point rising on displacing chlorine by bromine, or bromine by iodine:

	Sp. gr. at 0°	B.p.		Sp. gr. at 0°	B.p.
Methyl chloride, CH_3Cl	—	−22°	Ethyl chloride, C_2H_5Cl	0·921	12·5°
Methyl bromide, CH_3Br	1·73	+4·5°	Ethyl bromide, C_2H_5Br	1·47	39°
Methyl iodide, CH_3I	2·33	45°	Ethyl iodide, C_2H_5I	1·975	72°

Although the monohalogen derivatives of methane and ethane exist in only one form, those of propane and the higher paraffins show isomerism. There are, for example, two compounds of the molecular formula, C_3H_7I, corresponding with the two alcohols, $C_3H_7{\cdot}OH$, namely, *normal propyl iodide*, $CH_3{\cdot}CH_2{\cdot}CH_2I$ (b.p. 102°), and *isopropyl iodide*, $CH_3{\cdot}CHI{\cdot}CH_3$ (b.p. 89·9°). The monohalogen derivatives of butane exist theoretically in four isomeric forms, two of which, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$, and $CH_3{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$, are derived from normal butane; the other two, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{\cdot}CH_2X$, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CX{\cdot}CH_3$, from isobutane.

Tertiary butyl iodide, $(CH_3)_3CI$, has been previously mentioned. It may be obtained by treating isobutyl alcohol with zinc chloride or sulphuric acid, and then dissolving the isobutylene formed in this way in concentrated hydriodic acid,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}OH = (CH_3)_2C:CH_2 + H_2O$$
$$(CH_3)_2C:CH_2 + HI = (CH_3)_2CI{\cdot}CH_3;$$

also by heating trimethylcarbinol with hydriodic acid,

$$(CH_3)_3C{\cdot}OH + HI = (CH_3)_3I + H_2O.$$

It is a colourless oil, boils at 100° with slight decomposition, and is readily acted on by alkalies, being converted into isobutylene.

Ethereal Salts of Nitric Acid.

The ethereal salts of nitric acid are formed when the halogen ethereal salts are warmed with silver nitrate in alcoholic solution,

$$CH_3I + AgNO_3 = CH_3{\cdot}NO_3 + AgI;$$

they are also produced, together with nitrites (see below), when the alcohols are treated with concentrated nitric acid,

$$C_3H_7{\cdot}OH + HNO_3 = C_3H_7{\cdot}NO_3 + H_2O.$$

Ethyl nitrate, $C_2H_5{\cdot}NO_3$, is formed when alcohol is treated with ordinary concentrated nitric acid,

$$C_2H_5{\cdot}OH + HNO_3 = C_2H_5{\cdot}NO_3 + H_2O,$$

but so much heat is developed that, unless care be taken, the reaction becomes almost explosive in violence; even when the mixture is cooled, only a comparatively small quantity of ethyl nitrate is produced, owing to the acid oxidising some of the alcohol, and being itself reduced to nitrous acid, which then interacts with the alcohol, forming ethyl nitrite. If, however, the nitric acid be mixed with a little urea (p. 289), a substance which decomposes nitrous acid,

$$CO(NH_2)_2 + 2NO{\cdot}OH = CO_2 + 3H_2O + 2N_2,$$

the reaction takes place with much less violence, and ethyl nitrate is the sole product.

For these reasons ethyl nitrate is prepared by gradually adding alcohol (not more than 30 grams) to half its volume of nitric acid (sp. gr. 1·4), to which about 5 grams of urea have been added; the mixture is then *very slowly* heated on a water-bath in a large retort provided with a condenser. The mixture of ethyl nitrate, alcohol, and acid which collects in the receiver is shaken with water in a separating funnel, the heavy oil dried with calcium chloride, and distilled from a water-bath.

Ethyl nitrate is a colourless liquid of sp. gr. 1·11 at 20°, and boils at 87°; it has a pleasant fruity odour, and is almost insoluble in water, but readily soluble in alcohol, &c. It burns with a luminous flame, and when dropped on to a hot surface it sometimes explodes. It is slowly decomposed by boiling water, quickly by hot alkalies, yielding alcohol and nitric acid or a nitrate,

$$C_2H_5{\cdot}NO_3 + H_2O = C_2H_5{\cdot}OH + HNO_3.$$

On reduction with tin and hydrochloric acid it yields *hydroxylamine*,

$$C_2H_5{\cdot}NO_3 + 6H = C_2H_5{\cdot}OH + NH_2{\cdot}OH + H_2O.$$

Methyl nitrate, $CH_3{\cdot}NO_3$ (b.p. 66°), and the higher homologues closely resemble ethyl nitrate in properties.

Ethereal Salts of Nitrous Acid.

The ethereal salts of nitrous acid are produced by the action of nitrous acid on the alcohols,

$$C_2H_5{\cdot}OH + HNO_2 = C_2H_5{\cdot}NO_2 + H_2O.$$

They may be prepared by saturating the alcohols with the fumes evolved by the interaction of arsenic trioxide and nitric acid,* or by distilling alcohol with sodium nitrite and sulphuric acid, or with copper and nitric acid.†

Ethyl nitrite, $C_2H_5{\cdot}NO_2$, is usually prepared by slowly dropping concentrated nitric acid (3 c.c.) into a cold mixture of alcohol (20 c.c.) and concentrated sulphuric acid (2 c.c.), then adding copper turnings (about 4 grams), and distilling carefully from a water-bath.

The distillate consists of a mixture of ethyl nitrite, alcohol, and its oxidation products; when mixed with alcohol, it is employed in medicine as 'sweet spirits of nitre.' In order to prepare pure ethyl nitrite, the distillate is shaken with water, the oil dried over calcium chloride, and redistilled.

Ethyl nitrite is a colourless liquid of sp. gr. 0·900 at 15·5°; it boils at 17°, and has a pleasant fruity odour like that of apples; it is insoluble in water, and is readily hydrolysed by boiling water or dilute alkalies,

$$C_2H_5{\cdot}NO_2 + KOH = C_2H_5{\cdot}OH + KNO_2.$$

---

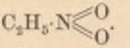
* $As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$.

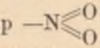
† $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + 2H_2O + 2HNO_2$.

Methyl nitrite, $CH_3{\cdot}NO_2$, is a gas; the higher homologues resemble ethyl nitrite.

Nitro-paraffins.—When ethyl iodide is heated with silver nitrite, very interesting changes occur: part of the ethyl iodide interacts with the silver nitrite, yielding *ethyl nitrite*, the rest being converted into *nitro-ethane*, both changes being expressed by the equation

$$C_2H_5I + AgNO_2 = C_2H_5{\cdot}NO_2 + AgI.$$

Ethyl nitrite and nitro-ethane are isomeric; the former is simply a salt of nitrous acid, $HO{\cdot}N{:}O$, and has the constitution $C_2H_5{\cdot}O{\cdot}N{:}O$, whereas the latter contains pentavalent nitrogen, and has the constitution  $C_2H_5{\cdot}N\begin{smallmatrix}\leqslant O\\ \leqslant O\end{smallmatrix}$.

Compounds, similar to nitro-ethane in constitution and isomeric with the corresponding nitrites, may be obtained from other halogen ethereal salts in the above manner; they are termed *nitro-paraffins*, because they are derived from the paraffins by the substitution of the nitro group  $—N\begin{smallmatrix}\leqslant O\\ \leqslant O\end{smallmatrix}$ for one atom of hydrogen.

The nitro-paraffins are colourless, pleasant-smelling liquids, and distil without decomposition, but their boiling-points are much higher than those of the corresponding nitrites; nitro-ethane, for example, boils at 114°, ethyl nitrite at 17°. They differ from the nitrites in certain important particulars: the nitro-paraffins are soluble in, but are not decomposed by caustic alkalies, whereas the nitrites, like all other ethereal salts, undergo hydrolysis, yielding an alcohol and a nitrite. The nitro-paraffins are converted into amines on reduction,

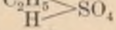
$$C_2H_5{\cdot}NO_2 + 6H = C_2H_5{\cdot}NH_2 + 2H_2O,$$

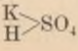
whilst the nitrites yield hydroxylamine, or ammonia, and an alcohol,

$$C_5H_{11}{\cdot}O{\cdot}N{:}O + 6H = C_5H_{11}{\cdot}OH + NH_3 + H_2O.$$

Ethereal Salts of Sulphuric Acid.

Dibasic acids, such as sulphuric acid, form two classes of salts with alcohols—namely, acid salts, corresponding with the acid sulphates, and normal or neutral salts, corresponding with the neutral sulphates,

Ethyl hydrogen sulphate,  $\begin{smallmatrix}C_2H_5\\ H\end{smallmatrix}{>}SO_4$ Ethyl sulphate, $(C_2H_5)_2SO_4$.

Potassium hydrogen sulphate,  $\begin{smallmatrix}K\\ H\end{smallmatrix}{>}SO_4$ Potassium sulphate, K_2SO_4.

Ethyl hydrogen sulphate, ethylsulphuric acid, or *sulphovinic acid* (from sulphuric acid and spirits of wine), $C_2H_5{\cdot}HSO_4$, is formed when ethylene is passed into fuming sulphuric acid, or heated with ordinary sulphuric acid,

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4.$$

It is prepared in the following manner: A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated at 100° for about an hour, when part of the alcohol is converted into ethyl hydrogen sulphate,

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O.$$

The solution is cooled, diluted with water, and treated with a slight excess of barium carbonate, when barium sulphate and barium ethylsulphate are formed,

$$2C_2H_5{\cdot}HSO_4 + BaCO_3 = (C_2H_5{\cdot}SO_4)_2Ba + CO_2 + H_2O.$$

After filtering from the barium sulphate and excess of barium carbonate, the cold solution of barium ethylsulphate is treated with dilute sulphuric acid as long as a precipitate is produced, and filtered again to separate the barium sulphate,

$$(C_2H_5{\cdot}SO_4)_2Ba + H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + BaSO_4.$$

The filtrate is now free from sulphuric acid; it is evaporated at ordinary temperature under reduced pressure over sulphuric acid, when alcohol and water pass off and are absorbed by the sulphuric acid, and ethyl hydrogen sulphate remains as a thick sour liquid.

Ethyl hydrogen sulphate has an acid reaction, decomposes carbonates, and is, in fact, like potassium hydrogen sulphate, a monobasic acid, since it contains one atom of hydrogen displaceable by metals. The *potassium* salt, $C_2H_5{\cdot}KSO_4$, may be prepared by neutralising the acid with potassium carbonate, or by treating a solution of the barium salt with potassium carbonate, and, after filtering, evaporating to dryness; it is a colourless, crystalline, neutral compound, readily soluble in water. The *barium* salt, $(C_2H_5{\cdot}SO_4)_2Ba$, is also readily soluble in water, so that ethylsulphuric acid does not give a precipitate with barium chloride.

Ethyl hydrogen sulphate is a very interesting substance, as it is an intermediate product in the conversion of alcohol into ethylene and ether, and of ethylene into alcohol. When boiled with water it yields alcohol, so that it cannot be obtained from its aqueous solution by evaporating at 100°,

$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4;$$

when heated with alcohol it gives ether,

$$C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2SO_4;$$

and when heated alone, or with concentrated sulphuric acid, it yields ethylene,

$$C_2H_5{\cdot}HSO_4 = C_2H_4 + H_2SO_4.$$

Other alcohols combine with sulphuric acid, yielding acid salts corresponding with ethyl hydrogen sulphate; these compounds, the *alkyl hydrogen sulphates*, closely resemble ethyl hydrogen sulphate in properties, and undergo similar decompositions.

Ethyl sulphate, $(C_2H_5)_2SO_4$, the normal or neutral salt, is of comparatively little importance; it may be prepared by warming silver sulphate with ethyl iodide, when double decomposition takes place, just as when silver sulphate is treated with potassium iodide,

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI.$$

It is a colourless liquid, boiling at 208°, with decomposition.

MERCAPTANS AND SULPHIDES.

Alcohols form two classes of compounds with hydrogen sulphide—namely, the hydrosulphides and the sulphides; the former bear the same relation to the metallic hydrosulphides as the alcohols to the metallic hydroxides, whereas the sulphides are related to the metallic sulphides just as the ethers to the metallic oxides,

Ethyl hydrosulphide,	$C_2H_5{\cdot}SH$	Ethyl sulphide,	$(C_2H_5)_2S$
Potassium hydrosulphide,	$K{\cdot}SH$	Potassium sulphide,	K_2S
Ethyl hydroxide,	$C_2H_5{\cdot}OH$	Ethyl oxide,	$(C_2H_5)_2O$
Potassium hydroxide,	$K{\cdot}OH$	Potassium oxide,	K_2O

The organic hydrosulphides or sulphhydrates are usually called **mercaptans** (*mercurium captans*) on account of their property of combining readily with mercuric oxide, forming crystalline compounds; they may be regarded as *sulphur-* or *thio-alcohols*, and the organic sulphides, as *thio-ethers*.

Ethyl mercaptan, $C_2H_5{\cdot}SH$, may be obtained by treating alcohol with phosphorus pentasulphide,

$$5C_2H_5{\cdot}OH + P_2S_5 = 5C_2H_5{\cdot}SH + P_2O_5;$$

it is prepared by distilling a concentrated solution of ethyl potassium sulphate with potassium hydrosulphide,

$$C_2H_5{\cdot}KSO_4 + KSH = C_2H_5{\cdot}SH + K_2SO_4.$$

It is a colourless, very unpleasant-smelling liquid, boiling at 36°. The hydrogen atom in the HS– group is displaceable by metals more readily than that in the HO– group of the alcohols; when ethyl mercaptan is treated with sodium or potassium, it yields *sodium* or *potassium mercaptide*, $C_2H_5{\cdot}SNa$, or $C_2H_5{\cdot}SK$, with evolution of hydrogen; when shaken with mercuric oxide, it yields *mercuric mercaptide*,

$$2C_2H_5{\cdot}SH + HgO = (C_2H_5{\cdot}S)_2Hg + H_2O,$$

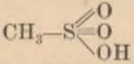
a crystalline compound, which is decomposed by hydrogen sulphide, giving ethyl mercaptan,

$$(C_2H_5{\cdot}S)_2Hg + SH_2 = 2C_2H_5{\cdot}SH + HgS.$$

Other mercaptans can be obtained by similar reactions; they are characterised by having a highly unpleasant, garlic-like smell, and in chemical properties they resemble ethyl mercaptan; on oxidation with nitric acid they are converted into *sulphonic acids*,

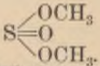
$$\underset{\text{Ethylsulphonic Acid.}}{C_2H_5{\cdot}SH + 3O = C_2H_5{\cdot}SO_2{\cdot}OH.}$$

Sulphonic acids contain the group $—SO_2{\cdot}OH$, the alkyl group being attached to the sulphur atom, and not to oxygen, as in the alkyl sulphites,



$$CH_3{—}S\begin{cases}{=}O\\{=}O\\{—}OH\end{cases}$$

Methylsulphonic Acid.



$$S\begin{cases}{—}OCH_3\\{=}O\\{—}OCH_3.\end{cases}$$

Methyl Sulphite.

They are powerful acids, forming salts, such as potassium ethylsulphonate, $C_2H_5{\cdot}SO_2{\cdot}OK$; and they differ from the sulphites in not being hydrolysed when boiled with dilute aqueous potash. They stand, therefore, in much the same relationship to the sulphites as the nitro-paraffins to the nitrites (p. 181).

Ethyl sulphide, $(C_2H_5)_2S$, may be obtained by treating ether with phosphorus pentasulphide,

$$5(C_2H_5)_2O + P_2S_5 = 5(C_2H_5)_2S + P_2O_5,$$

and by distilling a concentrated aqueous solution of ethyl potassium sulphate with potassium sulphide,

$$2C_2H_5{\cdot}KSO_4 + K_2S = (C_2H_5)_2S + 2K_2SO_4.$$

It is a colourless, neutral, unpleasant-smelling liquid, and boils at 91°; like the ethers, it does not contain hydrogen displaceable by metals, and is a comparatively inert substance.

Other sulphides can be obtained by similar methods, and have similar properties.

Ethereal Salts of Organic Acids.

Ethyl acetate, acetic ether,

$$C_2H_3O_2{\cdot}C_2H_5, \text{ or } CH_3{\cdot}CO{\cdot}OC_2H_5,$$

is formed when acetyl chloride or acetic anhydride is treated with alcohol,

$$CH_3{\cdot}COCl + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + HCl$$
$$(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + CH_3{\cdot}COOH;$$

also when a metallic salt of acetic acid is heated with a halogen salt of ethyl alcohol,

$$CH_3{\cdot}COOK + C_2H_5Br = CH_3{\cdot}COOC_2H_5 + KBr,$$

and when alcohol is heated with glacial acetic acid,

$$CH_3{\cdot}COOH + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + H_2O.$$

It is prepared by gradually adding a mixture of equal volumes of alcohol and acetic acid to a mixture of equal volumes of alcohol and concentrated sulphuric acid, heated at about 140° in a retort connected with a condenser; this process, like that by which ether is prepared, is theoretically continuous, the alcohol and sulphuric acid combining to form ethyl hydrogen sulphate, which then interacts with acetic acid, forming ethyl acetate and sulphuric acid,

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O$$
$$C_2H_5{\cdot}HSO_4 + C_2H_4O_2 = C_2H_3O_2{\cdot}C_2H_5 + H_2SO_4.$$

The distillate is shaken with a concentrated solution of sodium chloride, when the alcohol dissolves, the ethyl acetate separating as an oil; it is dried with calcium chloride, and purified by fractional distillation.

Ethyl acetate is a colourless, mobile liquid, having a pleasant fruity odour, and boiling at 77°; it is specifically lighter than water, in which it is moderately easily soluble. It is readily hydrolysed (see below) by hot alkalies, more slowly by hot mineral acids, and by water,

$$CH_3{\cdot}COOC_2H_5 + H_2O = CH_3{\cdot}COOH + C_2H_5{\cdot}OH.$$

When treated with concentrated ammonia it yields acetamide and alcohol,

$$CH_3{\cdot}COOC_2H_5 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH.$$

Sodium acts readily on ethyl acetate, with formation of ethyl acetoacetate (p. 189).

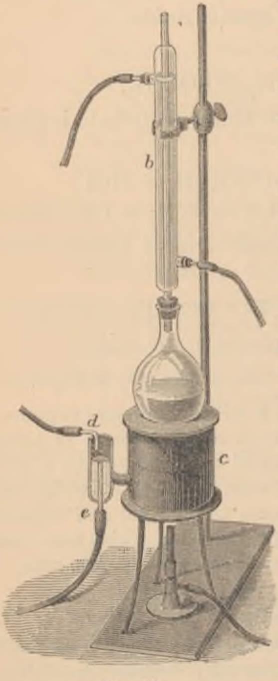


Fig. 18.

Since ethyl acetate has a rather characteristic smell, and is formed when acetic acid or any of its salts is warmed with alcohol and concentrated sulphuric acid, the presence of acetic acid or an acetate may be readily detected by this reaction, the so-called 'acetic-ether' test.

In hydrolysing ethereal salts, and in many other operations, as, for example, in the preparation of ethylene from ethyl bromide, it is often necessary to boil the aqueous, alcoholic, ethereal, or other solution for a long time; in order, therefore, to avoid loss of solvent, or of the substances present in solution, the flask or other vessel is connected with a *reflux* condenser (*b*, fig. 18), so that the vapours, which would otherwise pass away, are condensed, the liquid running back into the flask. The latter may be heated over a piece of wire-gauze or on a sand-bath, but when alcohol, ether, or other substances of low-boiling point are being used, a water-bath is usually employed. A very convenient form of water-bath (*c*) is that shown in the figure. During use, water slowly but continuously runs from the tube (*d*), which is connected with the water-supply; the water in the bath is thus kept at a constant level, the surplus running away through (*e*). With apparatus similar to that shown, a liquid may be kept constantly boiling for days without requiring any attention.

SUMMARY AND EXTENSION.

Although the ethereal salts of mineral acids are, on the whole, very similar in chemical properties, they are derived from acids of such diverse characters that slight differences in behaviour are only to be expected. The ethereal salts of organic acids, on the other hand, being derived from acids of similar nature, resemble one another in chemical properties so very closely that they may be described in a general manner.

The ethereal salts of organic acids may all be produced by treating an alcohol with the chloride or anhydride of the acid,

$$C_3H_7{\cdot}COCl + CH_3{\cdot}OH = C_3H_7{\cdot}COOCH_3 + HCl,$$

and by heating a metallic salt of the acid with a halogen salt of an alcohol,

$$C_2H_5{\cdot}COOAg + CH_3I = C_2H_5{\cdot}COOCH_3 + AgI.$$

They are all formed when an alcohol is treated with an acid, but the change is never complete, because, after the interaction has proceeded for some time, the quantity of ethereal salt decomposed by the water produced is the same as that formed by the combination of the acid with the alcohol; in other words, a condition of equilibrium is established when the two changes represented by the equations

$$CH_3{\cdot}OH + C_2H_4O_2 = C_2H_3O_2{\cdot}CH_3 + H_2O$$
$$C_2H_3O_2{\cdot}CH_3 + H_2O = CH_3{\cdot}OH + C_2H_4O_2$$

balance one another; this is usually expressed by writing the equations thus,

$$CH_3{\cdot}OH + C_2H_4O_2 \quad \rightleftarrows \quad C_2H_3O_2{\cdot}CH_3 + H_2O,$$

which indicates that the change takes place in either direction.

The proportion of ethereal salt produced depends on the nature of the alcohol and acid, and on their relative quantities; it is independent of the temperature, but the higher the temperature the sooner the condition of equilibrium is established. If the water produced during the interaction be prevented in some way from decomposing the ethereal salt, the desired change is far more complete; when, for example, methyl alcohol is heated with excess of anhydrous oxalic acid, it is almost completely converted into methyl oxalate, because the anhydrous oxalic acid combines with the water as fast as it is formed, and thus the inverse change is prevented,

$$C_2O_4H_2 + 2CH_3{\cdot}OH = C_2O_4(CH_3)_2 + 2H_2O.$$

In order, then, to prepare an ethereal salt from an acid and an alcohol, some dehydrating agent, such as hydrogen chloride, sulphuric acid, zinc chloride, &c., should be present. Based on these considerations, the two methods usually employed in preparing ethereal salts of organic acids are (*a*) by passing hydrogen chloride into a mixture of the acid and alcohol, and then warming the saturated solution; (*b*) by warming a mixture of the acid and alcohol with concentrated sulphuric acid. In both cases the mineral acids act as dehydrating agents. If the ethereal salt be readily volatile (ethyl acetate), the mixture is now distilled; if not, it is poured into water and the ethereal salt isolated by filtration, if a solid, by extraction with ether, if a liquid, or if it be soluble in water.

When only a small quantity of acid is at disposal, and it is desired to prepare one of its ethereal salts, it is converted into the silver salt, and the latter is warmed with a halogen ethereal salt (see above).

Normal ethereal salts are usually colourless, neutral, pleasant-smelling liquids, which distil unchanged under atmospheric pressure, and are volatile in steam; a few, such as *cetyl palmitate*, $C_{16}H_{31}O_2{\cdot}C_{16}H_{33}$, which occurs in spermaceti, are solid at ordinary temperatures, and distil with decomposition. They are all comparatively inert substances, and resemble the ethers perhaps more closely than any other class of compounds, although, at the same time, they differ from them in several important respects. The acid ethereal salts are usually non-volatile, and act like feeble acids.

All ethereal salts are decomposed by water, mineral acids, and alkalies, the change which they undergo being spoken of as hydrolysis (or saponification, p. 169),

$$CH_3{\cdot}COOC_3H_7 + KOH = CH_3{\cdot}COOK + C_3H_7{\cdot}OH$$

$$2H{\cdot}COOCH_3 + Ba(OH)_2 = (H{\cdot}COO)_2Ba + 2CH_3{\cdot}OH.$$

The rapidity with which hydrolysis takes place depends on the temperature and concentration of the solution, as well as on the nature of the ethereal salt and of the hydrolysing agent; as a rule, potash, soda, and barium hydroxide are the most powerful hydrolysing agents. Since ethereal salts are generally insoluble in water, if they be boiled with aqueous alkalies or mineral acids they are not attacked very quickly; it is usual, therefore, to employ *alcoholic* potash, &c., in which the ethereal salts are soluble.

All ethereal salts of organic acids yield amides on treatment with concentrated aqueous or alcoholic ammonia,

$$C_3H_7{\cdot}COOCH_3 + NH_3 = C_3H_7{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}OH,$$

whereas the halogen ethereal salts give amines with alcoholic ammonia (p. 200),

$$C_2H_5I + NH_3 = C_2H_5{\cdot}NH_2, HI.$$

The ethereal salts of organic acids afford an excellent example of the special form of isomerism known as metamerism; ethyl formate, $H{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$, for example, is metameric with methyl acetate, $CH_3{\cdot}CO{\cdot}O{\cdot}CH_3$; propyl formate, $H{\cdot}COOC_3H_7$, is metameric with ethyl acetate, $CH_3{\cdot}COOC_2H_5$, and with methyl propionate, $C_2H_5{\cdot}COOCH_3$.

Many ethereal salts occur in the fruit, flower, and other parts of plants, and it is to their presence in many cases that the scent of the part is due; many are prepared artificially for flavouring sweets, pastry, perfumes, &c.: amyl acetate, $CH_3{\cdot}COOC_5H_{11}$, for example, prepared from commercial amyl alcohol, has a strong smell of pears, and is known as 'pear-oil;' methyl butyrate, $C_3H_7{\cdot}COOCH_3$, is sold as 'pine-apple oil,' isoamyl isovalerate as 'apple-oil,' and so on.

CHAPTER XI.

SYNTHESIS OF KETONES AND FATTY ACIDS WITH THE AID OF ETHYL ACETOACETATE AND ETHYL MALONATE.

In the whole domain of organic chemistry probably no compounds have been more extensively used for synthetical purposes than ethyl acetoacetate and ethyl malonate, and certainly one of the most important uses to which these substances have been put is the synthesis of a great variety of ketones and fatty acids, many of which could have been prepared only with great difficulty by other methods.

Ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$, the ethyl salt of **acetoacetic acid,** is formed when ethyl acetate is treated with sodium, and the product decomposed with dilute acids. The final result is that 2 molecules of ethyl acetate combine with loss of 1 molecule of alcohol, the following equation representing the reaction in its simplest form,

$$CH_3{\cdot}CO\boxed{OC_2H_5 + H}CH_2{\cdot}COOC_2H_5 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + C_2H_5{\cdot}OH.$$

In reality, however, the interaction is a complex one; the *sodium derivative* of ethyl acetoacetate is first formed,

$$2CH_3{\cdot}COOC_2H_5 + 2Na = CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_5{\cdot}ONa + H_2,$$

and this sodium derivative, when decomposed with dilute acids, yields ethyl acetoacetate,

$$CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + HCl = CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + NaCl.$$

Preparation.—Sodium (30 grams), in the form of thin wire or shavings, is added to pure dry ethyl acetate (300 grams) contained in a flask connected with a reflux condenser. As soon as the vigorous action which sets in has subsided, the flask is heated on a water-bath, until bright particles of sodium are no longer visible on shaking.

The thick brownish semi-solid product, which consists of the sodium derivative of ethyl acetoacetate, is allowed to cool, and then treated with dilute (1 : 4) hydrochloric acid, until the solution is distinctly acid to test-paper. An equal volume of a saturated solution of salt is now added, and the oily layer separated from the aqueous solution, dried over calcium chloride, and fractionated. At first a quantity of unchanged ethyl acetate passes over; the thermometer then rises rapidly to about 160°, the fraction 170–185° consisting of nearly pure ethyl acetoacetate, and weighing 40–50 grams.

Ethyl acetoacetate is a colourless liquid, boiling at 180°, and having an agreeable fruity odour; it is sparingly soluble in water, but readily in alcohol and ether. The alcoholic solution assumes a beautiful violet colour on the addition of ferric chloride.

It is remarkable that, although neutral to test-paper, ethyl acetoacetate possesses acid properties. It dissolves in dilute potash or soda, and is reprecipitated on the addition of acids, but it is insoluble in alkali carbonates.

The **sodium derivative,** $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$, which is so largely used for synthetical purposes, may be prepared by adding sodium to a solution of ethyl acetoacetate in ether or benzene,

$$2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + 2Na = 2CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + H_2,$$

or by mixing ethyl acetoacetate with an alcoholic solution of sodium ethoxide,

$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + NaO\cdot C_2H_5 = CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + C_2H_5\cdot OH.$$

On evaporating the solvent in a current of hydrogen, the sodium derivative is obtained as a white crystalline mass, which is readily soluble in water, alcohol, and ether; it rapidly deliquesces in contact with moist air, and undergoes decomposition when its aqueous solution is boiled.

When shaken with a saturated solution of copper acetate, ethyl acetoacetate forms a green crystalline *copper derivative*, $(C_6H_9O_3)_2Cu$.

This property of forming metallic derivatives is due to the presence of the group $-CO-CH_2-CO-$; all substances which contain this, or the group $-CO-\underset{|}{CH}-CO-$, yield derivatives with sodium, frequently also with other metals.

The sodium derivative of ethyl acetoacetate interacts readily with alkyl halogen compounds with formation of a sodium halogen salt and a *mono-substitution derivative* of ethyl acetoacetate, the alkyl group taking the place previously occupied by the metal. Thus methyl iodide interacts with the sodium derivative of ethyl acetoacetate, forming ethyl *methyl*acetoacetate,

$$CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + CH_3I = CH_3\cdot CO\cdot CH(CH_3)\cdot COOC_2H_5 + NaI,$$

whereas when propyl bromide is employed, ethyl *propyl*acetoacetate, $CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5$, results, and so on.

All the alkyl mono-substitution derivatives of ethyl acetoacetate contain the group $-CO-\underset{|}{CH}-CO-$, and are therefore capable of forming sodium derivatives such as

$CH_3\cdot CO\cdot CNa(CH_3)\cdot COOC_2H_5$, $CH_3\cdot CO\cdot CNa(C_3H_7)\cdot COOC_2H_5$, &c., on treatment with sodium or sodium ethoxide, the metal taking the place of the hydrogen atom in the $-\underset{|}{CH}-$ group.

From these sodium derivatives, by the action of alkyl halogen compounds, *di-substitution derivatives* of ethyl acetoacetate are produced thus:

$$CH_3{\cdot}CO{\cdot}CNa(CH_3){\cdot}COOC_2H_5 + C_2H_5Br = CH_3{\cdot}CO{\cdot}C(C_2H_5)(CH_3){\cdot}COOC_2H_5 + NaBr.$$

Ethyl *Ethylmethyl*acetoacetate.

$$CH_3{\cdot}CO{\cdot}CNa(C_3H_7){\cdot}COOC_2H_5 + C_3H_7I = CH_3{\cdot}CO{\cdot}C(C_3H_7)_2{\cdot}COOC_2H_5 + NaI.$$

Ethyl *Dipropyl*acetoacetate.

In order, then, to obtain a di-substituted ethyl acetoacetate, the mono-substitution derivative is first prepared and then treated with sodium ethoxide and the alkyl halogen compound; the introduction of both alkyl groups cannot be carried out in one operation, because ethyl acetoacetate is not sufficiently acid in properties to form a disodium derivative of the constitution $CH_3{\cdot}CO{\cdot}CNa_2{\cdot}COOC_2H_5$.

The synthesis of the alkyl substitution products of ethyl acetoacetate is usually carried out as follows: The theoretical quantity of sodium (1 atom) is dissolved in 10–12 times its weight of absolute alcohol, and the solution of sodium ethoxide is thoroughly cooled. The ethyl acetoacetate, or the mono-substituted ethyl acetoacetate, (1 mol.), and a slight excess of the alkyl halogen compound (1 mol.) are now gradually added, the whole being well cooled during the operation; the flask is then connected with a reflux condenser (p. 186), and the mixture heated to boiling until neutral to test-paper. In order to isolate the product, the alcohol is distilled from a water-bath, the residue mixed with water to dissolve the precipitated sodium salt, and the whole extracted with ether; the ethereal solution is dried with calcium chloride, the ether distilled off, and the residual oil purified by fractional distillation.

The following are some of the more important mono- and di-substitution products of ethyl acetoacetate, with their boiling-points:

		B.p.
Ethyl *methyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}COOC_2H_5$	187°
Ethyl *dimethyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}C(CH_3)_2{\cdot}COOC_2H_5$	184°
Ethyl *ethyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5$	198°
Ethyl *diethyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}C(C_2H_5)_2{\cdot}COOC_2H_5$	218°
Ethyl *propyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}CH(C_3H_7){\cdot}COOC_2H_5$	209°
Ethyl *isopropyl*acetoacetate,	$CH_3{\cdot}CO{\cdot}CH(C_3H_7){\cdot}COOC_2H_5$	201°

The *mono*-substituted ethyl acetoacetates differ from ethyl acetoacetate in that they are insoluble in alkalies, and do not give copper derivatives, although they readily form sodium derivatives. The *di*-substituted ethyl acetoacetates do not contain a hydrogen atom displaceable by metals: both classes of compounds give a characteristic bluish-violet colouration with ferric chloride.

One of the most important reactions of ethyl acetoacetate and its derivatives is the decomposition which these substances undergo when treated with alkalies or mineral acids. Alkalies at ordinary temperatures simply hydrolyse the ethereal salts with formation of the alkali salts of the corresponding acids,

$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + KOH = \underset{\text{Potassium Acetoacetate.}}{CH_3\cdot CO\cdot CH_2\cdot COOK} + C_2H_5\cdot OH.$$

On acidifying the solution and extracting with ether, the free acids are obtained; these ketonic acids are, however, very unstable, decomposing in many cases at ordinary temperatures, and always very readily on warming, yielding carbon dioxide and a ketone,

$$CH_3\cdot CO\cdot CH_2\cdot COOH = CH_3\cdot CO\cdot CH_3 + CO_2$$
$$CH_3\cdot CO\cdot C(C_2H_5)_2\cdot COOH = CH_3\cdot CO\cdot CH(C_2H_5)_2 + CO_2.$$

When heated with alkalies, ethyl acetoacetate and its derivatives are decomposed in two ways, the course of the decomposition depending to a great extent on the strength of the alkali used.

Boiling *dilute* alcoholic potash converts these substances into *ketones*, with separation of potassium carbonate (**ketonic hydrolysis**),

$$CH_3\cdot CO\cdot CH_2\vdots COOC_2H_5 + 2KOH = CH_3\cdot CO\cdot CH_3 + K_2CO_3 + C_2H_5\cdot OH$$

$$CH_3\cdot CO\cdot C(C_2H_5)_2\vdots COOC_2H_5 + 2KOH = CH_3\cdot CO\cdot CH(C_2H_5)_2 + K_2CO_3 + C_2H_5\cdot OH.$$

Ketonic hydrolysis is also brought about by boiling with dilute mineral acids. If, however, *strong* alcoholic potash be employed, the decomposition takes place in quite a different manner, the potassium salt of a fatty acid being the principal product **(acid hydrolysis)**,

$$CH_3{\cdot}CO \vdots CH_2{\cdot}COOC_2H_5 + 2KOH = 2CH_3{\cdot}COOK + C_2H_5{\cdot}OH$$

$$\begin{aligned}CH_3{\cdot}CO \vdots C(C_2H_5)_2{\cdot}COOC_2H_5 + 2KOH &= CH_3{\cdot}COOK \\ &+ \underset{\text{Potassium Diethylacetate.}}{(C_2H_5)_2CH{\cdot}COOK} + C_2H_5{\cdot}OH.\end{aligned}$$

Ethyl acetoacetate is therefore a very important compound, as with its aid any fatty acid, or any ketone (containing the group $CH_3{\cdot}CO-$) can be synthetically prepared, provided the requisite alkyl halogen compound can be obtained.

Example.—If an acid of the constitution $(C_2H_5)(C_3H_7)CH{\cdot}COOH$—namely, ethylpropylacetic acid—be required, ethyl *ethyl*acetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5$, might be first prepared; on treating the sodium derivative of this substance with propyl iodide, ethyl *ethylpropyl*acetoacetate, $CH_3{\cdot}CO{\cdot}C(C_2H_5)(C_3H_7){\cdot}COOC_2H_5$, would be formed, and the latter, when heated with *strong* alcoholic potash, would yield the potassium salt of the acid required,

$$\begin{aligned}&CH_3{\cdot}CO{\cdot}C(C_2H_5)(C_3H_7){\cdot}COOC_2H_5 + 2KOH = \\ &\qquad CH_3{\cdot}COOK + CH(C_2H_5)(C_3H_7){\cdot}COOK + C_2H_5{\cdot}OH.\end{aligned}$$

Example.—If a ketone of the constitution $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9$—namely, butyl acetone—be required, ethyl butylacetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5$, would be prepared, by treating the sodium compound of ethyl acetoacetate with butyl iodide, and then decomposed by boiling with *dilute* alcoholic potash or dilute sulphuric acid,

$$\begin{aligned}&CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5 + 2KOH = \\ &\qquad CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9 + K_2CO_3 + C_2H_5{\cdot}OH.\end{aligned}$$

The acid and the ketonic hydrolysis of ethyl acetoacetate and its derivatives always take place to some extent side by side, whether weak or strong alkali be used. It is not possible, for instance, to decompose an ethyl acetoacetate derivative with strong alkali, without a small amount of ketone being formed, and when dilute alkali is used, a certain quantity of the salt of a fatty acid is invariably produced; nevertheless the relative quantities of the products depend very largely on the strength of the alkali employed.

Constitution of Ethyl Acetoacetate.—On hydrolysis, ethyl acetoacetate is converted into acetoacetic acid, which when gently warmed is decomposed into acetone and carbon dioxide; this acid is therefore evidently the carboxylic acid of acetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$, and its ethereal salt, ethyl acetoacetate, must be represented by the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$.

That ethyl acetoacetate contains a ketonic group $-CO-$ is shown by the fact that it combines with sodium bisulphite, hydroxylamine, phenylhydrazine, and hydrogen cyanide, and that on reduction it is converted into β-hydroxybutyric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, or its ethyl salt. In some of its reactions, however, ethyl acetoacetate behaves as if it contained a hydroxyl-group, and had the constitution represented by the formula $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$, and there are reasons for believing that other substances which contain the group $-CO-CH_2-$ or $-CO-\underset{|}{C}H-$ are also capable of existing in two forms; at all events, their behaviour is such that in some cases the assumption must be made that these groups, by intramolecular change (p. 290), are converted into $-C(OH){:}CH-$ and $-C(OH){:}\underset{|}{C}-$ respectively.

The constitution of the sodium derivative of ethyl acetoacetate may be expressed by the formula $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$; the sodium atom is represented as directly combined with carbon, because when the sodium derivative is treated with alkyl halogen compounds, substitution products of ethyl acetoacetate are formed in which the alkyl group is certainly directly united with carbon, as is shown by their behaviour on hydrolysis.

Other Ketonic Acids.

Pyruvic acid, or acetylformic acid, $CH_3{\cdot}CO{\cdot}COOH$, is formed by the dry distillation of tartaric acid (p. 241),

$$\begin{array}{l} CH(OH){\cdot}COOH \\ | \\ CH(OH){\cdot}COOH \end{array} = CH_3{\cdot}CO{\cdot}COOH + CO_2 + H_2O.$$

It is an oily, sour-smelling liquid, distils at 165–170°, and is soluble in water in all proportions. It combines with hydroxylamine, and gives with phenylhydrazine in aqueous solution a very sparingly soluble phenylhydrazone, $CH_3{\cdot}C(N_2HC_6H_5){\cdot}COOH$, the formation of which serves as a ready means of detecting the acid, even when present in small quantity. When treated with sodium amalgam, pyruvic acid is reduced to lactic acid (p. 225),

$$CH_3{\cdot}CO{\cdot}COOH + 2H = CH_3{\cdot}CH(OH){\cdot}COOH.$$

Levulinic acid (β-acetylpropionic acid), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is produced when starch, cane-sugar, dextrose, levulose, and other carbohydrates containing 6, or a multiple of 6, carbon atoms are boiled with dilute hydrochloric acid.

Preparation.—Starch (3 kilos) is gradually added to hot hydrochloric acid of sp. gr. 1·1 (3 litres), and the thin syrup is then heated in a reflux apparatus for twenty hours on a water-bath. The solution is separated from the humus matter by pressure between cloths, and after concentration to a syrup, extracted with ether; the ethereal solution is evaporated, and the residual crude levulinic acid purified by distillation under reduced pressure.

Levulinic acid melts at 33·5° and distils at 250°; it is very soluble in water, combines readily with hydroxylamine and phenylhydrazine, and when reduced with sodium amalgam it yields γ-hydroxyvaleric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. Levulinic acid is isomeric with methylacetoacetic acid or α-acetylpropionic acid, $CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}COOH$.

Ethyl malonate, $CH_2(COOC_2H_5)_2$, does not belong to the same class of substances as ethyl acetoacetate, although, like the latter, it contains the group $-CO{\cdot}CH_2{\cdot}CO-$; it is, however, conveniently considered in this chapter on account of its employment in the synthesis of fatty acids.

When potassium chloracetate is digested with potassium cyanide in aqueous solution, potassium cyanacetate is produced,

$$CH_2Cl{\cdot}COOK + KCN = CH_2(CN){\cdot}COOK + KCl.$$

This salt, on hydrolysis with hydrochloric acid, yields malonic acid (p. 234),

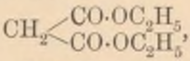
$$CH_2(CN){\cdot}COOK + 2HCl + 2H_2O = CH_2(COOH)_2 + KCl + NH_4Cl,$$

but if the dry potassium cyanacetate be mixed with alcohol and the mixture saturated with hydrogen chloride, ethyl malonate is produced,

$$CH_2(CN){\cdot}COOK + 2HCl + 2C_2H_5{\cdot}OH = CH_2(COOC_2H_5)_2 + KCl + NH_4Cl.$$

Preparation.—Chloracetic acid (100 grams) is dissolved in water (200 c.c.) and neutralised with potassium carbonate (76 grams);

potassium cyanide (75–80 grams) is then added, and the whole heated in a large porcelain basin until a vigorous reaction commences. As soon as this has subsided, the solution is evaporated on a sand-bath, the thick semi-solid residue being constantly stirred with a thermometer until the temperature reaches 135°; the solid cake of potassium chloride and cyanacetate is powdered, transferred to a flask, an equal weight of alsolute alcohol added, and the boiling mixture saturated with dry hydrogen chloride (compare p. 187–8). When cold, the solution is poured into twice or thrice its volume of ice-water; the product is then extracted with ether, the ethereal solution washed with water, dried with calcium chloride, and the ether distilled off. The crude oil is purified by fractional distillation; the portion boiling at 195–200°, after two or three distillations, consists of practically pure ethyl malonate.

Ethyl malonate,  $CH_2<\begin{matrix}CO{\cdot}OC_2H_5\\CO{\cdot}OC_2H_5\end{matrix}$, like ethyl acetoacetate, contains the group $-CO{\cdot}CH_2{\cdot}CO-$, and is capable of forming a sodium derivative when treated with the metal or with sodium ethoxide,

$$2CH_2(COOC_2H_5)_2 + 2Na = 2CHNa(COOC_2H_5)_2 + H_2$$

$$CH_2(COOC_2H_5)_2 + NaO{\cdot}C_2H_5 = CHNa(COOC_2H_5)_2 + C_2H_5{\cdot}OH.$$

Unlike ethyl acetoacetate, it does not dissolve in aqueous alkalies, because its alkali derivatives are decomposed by water, and it does not give a colouration with ferric chloride. The sodium derivative of ethyl malonate interacts readily with alkyl halogen compounds, yielding homologues of ethyl malonate,

$$CHNa(COOC_2H_5)_2 + C_2H_5I = \underset{\text{Ethyl Ethylmalonate.}}{CH(C_2H_5)(COOC_2H_5)_2} + NaI;$$

these mono-substitution derivatives, like those of ethyl acetoacetate, are again capable of forming sodium derivatives, which, by further treatment with alkyl halogen compounds, yield di-substitution derivatives of ethyl malonate,

$$CH(C_2H_5)(COOC_2H_5)_2 + NaO{\cdot}C_2H_5 = CNa(C_2H_5)(COOC_2H_5)_2 + C_2H_5{\cdot}OH$$

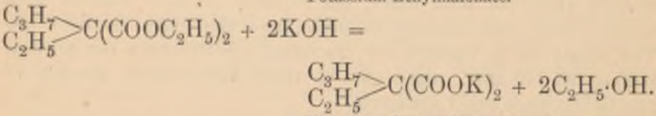
$$CNa(C_2H_5)(COOC_2H_5)_2 + C_3H_7I = \underset{\text{Ethyl Propylethylmalonate.}}{C(C_3H_7)(C_2H_5)(COOC_2H_5)_2} + NaI.$$

In this way a great variety of derivatives may be obtained, the syntheses being carried out exactly as described in the case of the substitution products of ethyl acetoacetate.

Ethyl malonate and its derivatives are readily hydrolysed by boiling alcoholic potash with formation of the potassium salts of the corresponding acids,

$$C_2H_5{\cdot}CH(COOC_2H_5)_2 + 2KOH = C_2H_5{\cdot}CH(COOK)_2 + 2C_2H_5{\cdot}OH$$

Potassium Ethylmalonate.

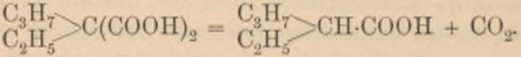


$$\genfrac{}{}{0pt}{}{C_3H_7}{C_2H_5}{>}C(COOC_2H_5)_2 + 2KOH = \genfrac{}{}{0pt}{}{C_3H_7}{C_2H_5}{>}C(COOK)_2 + 2C_2H_5{\cdot}OH.$$

Potassium Propylethylmalonate.

Malonic acid and the dicarboxylic acids derived from it are rapidly and quantitatively decomposed at about 200° with evolution of carbon dioxide and formation of fatty acids. This behaviour is shown by all acids which contain two carboxyl-groups directly combined with the *same* carbon atom (p. 234),

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2$$



$$\genfrac{}{}{0pt}{}{C_3H_7}{C_2H_5}{>}C(COOH)_2 = \genfrac{}{}{0pt}{}{C_3H_7}{C_2H_5}{>}CH{\cdot}COOH + CO_2.$$

Propylethylmalonic Acid. Propylethylacetic Acid.

Ethyl malonate is, therefore, of the utmost service in the synthesis of fatty acids, and is indeed more used for this purpose than ethyl acetoacetate, because in the case of the latter, ketones are always formed on hydrolysis as bye-products. The value of both synthetical methods is also much enhanced by the fact that the constitution of the acid (or ketone) obtained is always known, which is very often not the case when other methods are employed.

Example.—Normal valeric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is to be prepared synthetically. In the first place the sodium derivative of ethyl malonate would be heated with propyl iodide, and the resulting ethyl propylmalonate, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2$, hydrolysed with boiling alcoholic potash. The propylmalonic acid obtained from the potassium salt is heated at about 200° or distilled, when it decomposes into normal valeric acid and carbon dioxide,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(COOH)_2 = CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH + CO_2.$$

CHAPTER XII.

ALKYL COMPOUNDS OF NITROGEN, PHOSPHORUS, ARSENIC, SILICON, ZINC, MERCURY, AND OTHER ELEMENTS.

Amines.

Many of the compounds described in the preceding pages may be conveniently considered as having been derived from the hydrogen compounds of certain non-metals; the alcohols and ethers, for example, may be regarded as derivatives of water, the mercaptans and sulphides as derivatives of sulphuretted hydrogen,

$$\begin{array}{lll} H \cdot O \cdot H & C_2H_5 \cdot OH & C_2H_5 \cdot O \cdot C_2H_5 \\ H \cdot S \cdot H & C_2H_5 \cdot SH & C_2H_5 \cdot S \cdot C_2H_5. \end{array}$$

In a similar manner the hydrides of many other elements may be directly or indirectly converted into organic compounds by the substitution of one or more alkyl groups for an equivalent quantity of hydrogen; from ammonia, for example, a very important class of strongly basic substances, termed **amines,** may be obtained, these compounds being classed as *primary*, *secondary*, or *tertiary* amines, according as 1, 2, or 3 atoms of hydrogen in ammonia have been displaced by alkyl groups.

Primary.		*Secondary.*	
Methylamine,	$NH_2 \cdot CH_3$	Dimethylamine,	$NH(CH_3)_2$
Ethylamine,	$NH_2 \cdot C_2H_5$	Diethylamine,	$NH(C_2H_5)_2$
Propylamine,	$NH_2 \cdot C_3H_7$	Dipropylamine,	$NH(C_3H_7)_2$

Tertiary.	
Trimethylamine,	$N(CH_3)_3$
Triethylamine,	$N(C_2H_5)_3$
Tripropylamine,	$N(C_3H_7)_3$.

The methods of formation and general character of the amines will, perhaps, be best understood from a description of the ethyl compounds.

Ethylamine, $NH_2{\cdot}C_2H_5$, was first obtained by Würtz, by distilling ethyl isocyanate (p. 287), with potash, the change being analogous to that which occurs in the case of hydrogen isocyanate (p. 286),

$$CO{:}N{\cdot}C_2H_5 + 2KOH = NH_2{\cdot}C_2H_5 + K_2CO_3$$
$$CO{:}NH + 2KOH = NH_3 + K_2CO_3.$$

It is formed when methyl cyanide (acetonitrile) is treated with nascent hydrogen, generated from zinc and sulphuric acid (Mendius' reaction), or from alcohol and sodium,

$$CH_3{\cdot}CN + 4H = CH_3{\cdot}CH_2{\cdot}NH_2.$$

It is also produced when ethyl chloride, bromide, or iodide is heated at about 100° in closed vessels with alcohol which has been saturated with ammonia (Hofmann); the halogen acid produced during the interaction combines with the amine, forming a salt,

$$C_2H_5I + NH_3 = NH_2{\cdot}C_2H_5, HI.$$

Ethylamine is prepared by mixing propionamide (1 mol.) with bromine (1 mol.), and then adding a 10 per cent. solution of potash until the colour of the bromine disappears: the solution of the bromamide which is thus produced,

$$C_2H_5{\cdot}CO{\cdot}NH_2 + Br_2 + KOH = C_2H_5{\cdot}CO{\cdot}NHBr + KBr + H_2O,$$

is now gently warmed with excess of potash, when the bromamide is converted into ethylamine,

$$C_2H_5{\cdot}CO{\cdot}NHBr + 3KOH = C_2H_5{\cdot}NH_2 + KBr + K_2CO_3 + H_2O.$$

In the conversion of propionamide into ethylamine one atom of carbon and one atom of oxygen are taken away, and a derivative of propionic acid is converted into what may be regarded as a derivative of acetic acid, since ethylamine is readily converted into ethyl alcohol and the latter into acetic acid; it is possible, therefore, to transform propionic into acetic acid,

$CH_3{\cdot}CH_2{\cdot}COOH$	$CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2$	$CH_3{\cdot}CH_2{\cdot}NH_2$	$CH_3{\cdot}CH_2{\cdot}OH$
Propionic Acid.	Propionamide.	Ethylamine.	Ethyl Alcohol.

$CH_3{\cdot}COOH.$
Acetic Acid.

As, moreover, the amides of other fatty acids behave in this respect like propionamide, it is clear that a given fatty acid may be converted into the next lower homologue, and so on down the series.

Conversely, a given fatty acid may be transformed into the next higher homologue in the following manner: The calcium salt of the acid is distilled with calcium formate and the resulting aldehyde converted into the corresponding alcohol by reduction; the alcohol is then transformed into the chloride, the latter treated with potassium cyanide, and the resulting cyanide hydrolysed with alkalies or mineral acids,

$$\underset{\text{Acetic Acid.}}{CH_3\cdot COOH} \quad \underset{\text{Acetaldehyde.}}{CH_3\cdot CHO} \quad \underset{\text{Ethyl Alcohol.}}{CH_3\cdot CH_2\cdot OH} \quad \underset{\text{Ethyl Chloride.}}{CH_3\cdot CH_2Cl} \quad \underset{\text{Ethyl Cyanide.}}{CH_3\cdot CH_2\cdot CN}$$

$$\underset{\text{Propionic Acid.}}{CH_3\cdot CH_2\cdot COOH.}$$

The cyanide may be converted into the acid in another way; it is first reduced with sodium and alcohol, yielding an amine, from which the fatty acid is obtained in the manner already stated.

Primary amines may also be obtained by reducing the nitroparaffins,

$$CH_3\cdot NO_2 + 6H = CH_3\cdot NH_2 + 2H_2O,$$

and by heating the alkyl nitrates with alcoholic ammonia,

$$C_3H_7\cdot O\cdot NO_2 + NH_3 = C_3H_7\cdot NH_2,\ HNO_3.$$

Ethylamine is a colourless, mobile, inflammable liquid of sp. gr. 0·689 at 15°, and boils at 18·7°; it is soluble in water in all proportions, and the solution, like the liquid itself, has a pungent, slightly fish-like odour, distinguishable from that of ammonia only with difficulty. An aqueous solution of ethylamine might, in fact, be easily mistaken for a solution of ammonia, so closely do they resemble one another in properties; the former, like the latter, has a strongly alkaline reaction, and gives, especially on warming, a pungent-smelling gas, which fumes when brought into proximity with concentrated hydrochloric acid. It precipitates metallic hydroxides from solutions of their salts, and neutralises even the most powerful acids, forming salts, which are readily soluble in water. Ethylamine, therefore, is an organic *base*, and its basic properties are even more pronounced than those of ammonia, since it liberates ammonia from ammonium salts; the salts of ethylamine are, however, decomposed by the hydroxides and carbonates of sodium and potassium. In spite of the fact that ethylamine is so readily soluble in water, it separates from the solutions as an oil on the addition of a large quantity of solid potash or potassium carbonate; it is very hygroscopic, and readily absorbs carbon dioxide from the air, forming with it a salt.*

Although, speaking generally, ethylamine is very stable, it is rapidly converted into ethyl alcohol on treatment with nitrous acid in aqueous solution, nitrogen being liberated,

$$C_2H_5{\cdot}NH_2 + HO{\cdot}NO = C_2H_5{\cdot}OH + H_2O + N_2;$$

this reaction is exactly analogous to that which occurs when ammonia and nitrous acid (ammonium nitrite) are heated together,

$$NH_4NO_2 \text{ or } NH_3 + HO{\cdot}NO = 2H{\cdot}OH + N_2.$$

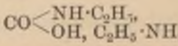
Ethylamine is also quickly changed when it is warmed with chloroform and alcoholic potash. The intensely disagreeable smell of the product (ethylcarbylamine, compare p. 285) is at once recognisable, and affords a sure indication of the presence of a primary amine (Hofmann's carbylamine reaction),

$$C_2H_5{\cdot}NH_2 + CHCl_3 + 3KOH = C_2H_5{\cdot}NC + 3KCl + 3H_2O.$$

The two reactions just mentioned are characteristic of *all primary amines*, and are of considerable practical importance; the first is employed for the conversion of the primary amines into hydroxy-compounds, the second for their detection.

Ethylamine is a monacid base, and, like ammonia, forms salts by direct combination, in virtue of the possible pentavalency of the nitrogen atom; these salts are all soluble in water, and some of them, like those of ammonia, readily sublime, even at ordinary temperatures; they usually differ from ammonium salts in being soluble in alcohol, a property which is frequently made use of in isolating the amine.

---

* Probably not a carbonate, but a carbamate (p. 291), 
$CO{<}\begin{smallmatrix}NH{\cdot}C_2H_5,\\ OH,\ C_2H_5{\cdot}NH_2.\end{smallmatrix}$

Ethylamine hydrochloride, $C_2H_5{\cdot}NH_3Cl$, or $C_2H_5{\cdot}NH_2$, HCl, as usually written, crystallises in large plates, melts at about 80°, and is deliquescent. The *sulphate*, $2C_2H_5{\cdot}NH_2$, H_2SO_4, has similar properties. The halogen salts, like those of ammonia, form double salts with many other metallic halogen salts; of these compounds the *platinochlorides* and the *aurochlorides* are the most important; they correspond with the ammonium double salts of similar composition,

Ethylamine platinochloride,	$(C_2H_5{\cdot}NH_2)_2$, H_2PtCl_6
Ammonium platinochloride,	$(NH_3)_2$, H_2PtCl_6
Ethylamine aurochloride,	$C_2H_5{\cdot}NH_2$, $HAuCl_4$
Ammonium aurochloride,	NH_3, $HAuCl_4$.

These organic platinum and gold salts are usually yellow, orange, or red, and are generally much more sparingly soluble in water than the simple salts; for the latter reason they are very serviceable in detecting and isolating the amines; on ignition they give a residue of pure metal.

Diethylamine, $NH(C_2H_5)_2$, is formed when ethyl iodide is heated with alcoholic ammonia, just as described in the case of ethylamine; one molecule of the hydrogen iodide produced combines with the base to form a salt, the other uniting with the excess of ammonia,

$$2C_2H_5I + NH_3 = NH(C_2H_5)_2, HI + HI.$$

Diethylamine is a colourless, inflammable liquid, boiling at 56°; it is a stronger base than ethylamine, which it resembles very closely in smell, solubility, &c., and also in forming simple and double salts. It is readily distinguished from ethylamine inasmuch as it does not give the carbylamine reaction; its behaviour with nitrous acid is also totally different from that of ethylamine, since, instead of being converted into an alcohol, it yields *ethylnitrosamine*,

$$(C_2H_5)_2NH + HO{\cdot}NO = (C_2H_5)_2N{\cdot}NO + H_2O.$$

All secondary amines behave in this way; that is to say, on treatment with nitrous acid, they are converted into *nitrosamines* by the substitution of the monovalent nitroso-group

–NO for the atom of hydrogen which is directly united with nitrogen.

When a nitrosamine is mixed with phenol (part ii.) and concentrated sulphuric acid, it gives a dark-green solution which, after diluting with water, becomes red, and on adding excess of alkali, assumes a beautiful and intense blue or green colour; this reaction (Liebermann's, or the nitroso-reaction) affords a means, not only of detecting a nitrosamine, but also a secondary amine, as the latter is convertible into the former.

Diethylamine hydrochloride, $(C_2H_5)_2NH, HCl$, is colourless, and readily soluble in water; its *platinochloride*, $[(C_2H_5)_2NH]_2, H_2PtCl_6$, and *aurochloride*, $(C_2H_5)_2NH, HAuCl_4$, are orange, and less readily soluble.

Triethylamine, $N(C_2H_5)_3$, like the primary and secondary amines, is produced when ethyl iodide is heated with alcoholic ammonia,

$$3C_2H_5I + NH_3 = N(C_2H_5)_3, HI + 2HI.$$

It is a pleasant-smelling liquid, boiling at 89°, and except that it is more sparingly soluble in water, and is a stronger base even than diethylamine, it resembles the primary and secondary compounds in most ordinary properties. It does not give the carbylamine reaction, and is not acted on by nitrous acid at ordinary temperatures, so that it is readily distinguished from the primary and secondary amines; *other tertiary amines* resemble triethylamine in these respects. The salts of triethylamine correspond with those of the other bases.

Triethylamine, and other tertiary amines, combine directly with one molecule of the alkyl halogen compounds, yielding salts corresponding with those of ammonia,

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I; \quad NH_3 + HI = NH_4I.$$

These salts are more stable than those of the amines, and are either not acted on, or only very slowly attacked by potash or soda, even on boiling; when, however, their aqueous solutions are shaken with freshly precipitated silver oxide (which acts like a hydroxide), double decomposition results, and hydroxy-compounds, corresponding with ammonium hydroxide, are formed,

$$N(C_2H_5)_4I + Ag{\cdot}OH = N(C_2H_5)_4{\cdot}OH + AgI$$
$$NH_4I + Ag{\cdot}OH = NH_4{\cdot}OH + AgI.$$

The hydroxides obtained in this way are termed *quaternary ammonium bases*, or *tetralkylammonium hydroxides*; although, in constitution, they are similar to ammonium hydroxide, they differ from the latter in several important respects, and resemble rather the hydroxides of sodium and potassium.

Tetrethylammonium hydroxide, $N(C_2H_5)_4{\cdot}OH$, for example, is a crystalline, deliquescent substance, and has only a faint smell, like that of potash; it has a powerful alkaline reaction, absorbs carbon dioxide from the air, and is a stronger base even than potash or soda; when strongly heated, it is resolved into triethylamine and ethyl alcohol, or its decomposition products,

$$N(C_2H_5)_4{\cdot}OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

The salts of tetrethylammonium hydroxide, such as the iodide (see above), may also be obtained by treating the hydroxide with acids; they are mostly crystalline.

The tetralkylammonium halogen salts undergo decomposition or dissociation on dry distillation, yielding a tertiary amine and an alkyl halogen salt, just as ammonium chloride is resolved into ammonia and hydrogen chloride,

$$N(C_2H_5)_4Cl = N(C_2H_5)_3 + C_2H_5Cl \qquad NH_4Cl = NH_3 + HCl.$$

Under ordinary circumstances the halogen ethereal salt, being much more volatile than the tertiary amine, can be separated from the latter before re-combination takes place.

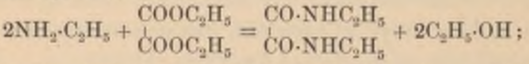
In a similar manner the halogen salts of *some* tertiary amines may be converted into secondary, and those of secondary into primary, amines,

$$N(CH_3)_3, HCl = N(CH_3)_2H + CH_3Cl$$
$$N(CH_3)_2H, HCl = N(CH_3)H_2 + CH_3Cl.$$

Separation of Amines.—Three of the general methods for the preparation of amines—namely, the decomposition of alkyl isocyanates, the reduction of nitriles, and the decomposition of amides of the fatty acids with bromine and potash, give the primary compounds only; when, however, an alkyl halogen compound is heated with alcoholic ammonia, not only are primary, secondary, and tertiary amines all produced at the same time, but the tertiary amine combines with the alkyl halogen compound to form a quaternary ammonium derivative; the product consists, therefore, of a mixture of four organic salts, and contains also ammonium salts. In order to separate and isolate the several compounds, the mixture is first evaporated to expel ammonia, alcohol, and any unchanged alkyl salt, and then distilled with excess of potash; the primary, secondary, and tertiary amines, which, together with ammonia, are thus liberated from their salts, collect in the receiver, and may be absorbed with hydrochloric acid, whilst the residue contains the stable salt of the tetralkylammonium base; the latter may usually be isolated by neutralising the solution with hydrochloric acid, evaporating to dryness, and extracting the powdered residue with alcohol.

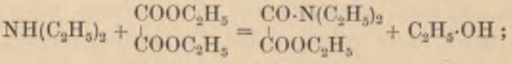
The acid solution of the three amine salts is evaporated almost to dryness and treated with solid potash, when a mixture of the bases rises to the surface as an oil and is separated with the aid of a funnel; the oil is dried by distilling it with lumps of potash and then treated with ethyl oxalate, when, in the case of the ethyl bases, for example, the following changes occur:

The primary amine is converted into ethyloxamide, a derivative of oxamide (p. 233),



$$2NH_2\cdot C_2H_5 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CO\cdot NHC_2H_5 \\ | \\ CO\cdot NHC_2H_5 \end{array} + 2C_2H_5\cdot OH;$$

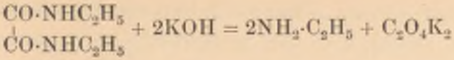
the secondary amine gives ethyl diethyloxamate, a derivative of oxamic acid (p. 234),



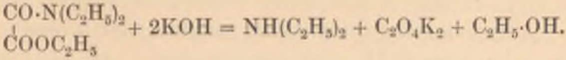
$$NH(C_2H_5)_2 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CO\cdot N(C_2H_5)_2 \\ | \\ COOC_2H_5 \end{array} + C_2H_5\cdot OH;$$

the tertiary amine is not acted on, and is easily separated from the two less volatile products by heating the mixture as long as oil passes over.

The residue is allowed to cool, and the crystalline ethyloxamide separated from the liquid ethyl diethyloxamate by filtration or by treatment with water, in which the former alone is soluble; the two compounds are then separately distilled with potash, the bases being collected and isolated as described in the case of the mixture,



$$\begin{array}{l}CO{\cdot}NHC_2H_5\\ |\\ CO{\cdot}NHC_2H_5\end{array} + 2KOH = 2NH_2{\cdot}C_2H_5 + C_2O_4K_2$$



$$\begin{array}{l}CO{\cdot}N(C_2H_5)_2\\ |\\ COOC_2H_5\end{array} + 2KOH = NH(C_2H_5)_2 + C_2O_4K_2 + C_2H_5{\cdot}OH.$$

The three ethylamines and the tetrethylammonium compounds may be taken as typical examples of the several classes of alkyl derivatives of ammonia; the corresponding methyl bases, and those of the higher alkyl radicles, are prepared by methods so similar to those described in the case of the ethylamine compounds, and have properties so closely resembling those of the latter, that a detailed description would be of little value.

Methylamine, $NH_2{\cdot}CH_3$, *dimethylamine*, $NH(CH_3)_2$, and *trimethylamine*, $N(CH_3)_3$, are usually produced in small quantities during the decomposition of nitrogenous organic substances, and occur in herring brine, the last named especially in large relative proportions. Dimethylamine and trimethylamine are prepared on the large scale by distilling the waste-products obtained in refining beet-sugar, and are used in considerable quantities for various technical purposes; trimethylamine is employed in the manufacture of potassium carbonate, and its hydrochloride is used in the preparation of methyl chloride (p. 172).

The physical properties of the amines undergo a gradual change with increasing molecular weight, just as is the case in other series; the boiling-points of the four simplest primary amines may be taken as an illustration:

Methylamine, $CH_3{\cdot}NH_2$	Ethylamine, $C_2H_5{\cdot}NH_2$
B.p. – 6°	B.p. 19°
Propylamine, $C_3H_7{\cdot}NH_2$	Butylamine, $C_4H_9{\cdot}NH_2$
B.p. 49°	B.p. 76°.

The higher amines, like the higher ethers, ethereal salts, &c., exist in various metameric forms: there are, for example, three compounds of the molecular formula C_3H_9N (see below). The amines, like the ethers, may be classed into *simple* amines, such as propylamine, $C_3H_7{\cdot}NH_2$, diethylamine, $(C_2H_5)_2NH$, &c., and *mixed* amines, such as methylethylamine, $NH(CH_3){\cdot}C_2H_5$, dimethylethylamine, $N(CH_3)_2{\cdot}C_2H_5$, according as they contain alkyl groups of the same or of different kinds.

Identification of Amines.—The most important methods by which a given amine may be recognised as a primary, secondary, or tertiary compound consist, as already stated, firstly, in applying the carbylamine reaction, and secondly, in treating the compound with nitrous acid. If a primary amine, it is converted by nitrous acid into a primary alcohol with evolution of nitrogen; if a secondary base, it yields a nitroso-compound, the presence of which is readily detected by Liebermann's reaction; if a tertiary amine, it is usually unchanged.

The experiment is made as follows: To a concentrated neutral solution of the hydrochloride of the base a small quantity of a solution of sodium nitrite is added; evolution of nitrogen, the separation of an oily nitrosamine (which is insoluble in water), or no visible change occurs, according to the nature of the base; further tests, which readily suggest themselves, are then made to confirm the results of the experiment.

As methylamine is a gas, and all the lower amines are volatile liquids, which are very difficult to characterise by ordinary tests, the nature of a given amine is usually ascertained by preparing and analysing its platinochloride or aurochloride; the percentage of metal in the salt, together with the behaviour of the base with nitrous acid, afford evidence sufficient, in most cases, to determine the identity of the compound.

Example.—A base produced by the destructive distillation of the molasses obtained in the preparation of beet-sugar gave a platinochloride, which, on analysis, was found to contain 37·2 per cent. of platinum; the probable molecular weight of the base is therefore 59 (see p. 40), so that it may be propylamine or isopropylamine, $C_3H_7{\cdot}NH_2$, methylethylamine, $CH_3(C_2H_5)NH$, or trimethylamine, $(CH_3)_3N$. On treatment with nitrous acid, it is found to be a tertiary amine; it is, therefore, trimethylamine.

Phosphines.

Since phosphorus and nitrogen belong to the same natural group of elements, it might be expected that phosphoretted hydrogen, PH_3, like ammonia, would be capable of yielding substitution products analogous to the amines. As a matter of fact, the **phosphines**, or alkyl substitution products of phosphorus trihydride, are readily obtained by heating the alkyl iodides with phosphonium iodide in presence of zinc oxide. In the case of ethyl iodide, for example, salts of *ethylphosphine* and *diethylphosphine*, corresponding with those of the primary and secondary amines respectively, are formed,

$$2PH_4I + 2C_2H_5I + ZnO = 2[PH_2{\cdot}C_2H_5, HI] + ZnI_2 + H_2O$$
$$PH_4I + 2C_2H_5I + ZnO = PH(C_2H_5)_2, HI + ZnI_2 + H_2O.$$

Tertiary phosphines, such as *triethylphosphine*, are *not* produced under the above conditions, but may be prepared by heating the alkyl iodides with phosphonium iodide alone; as in the case of the corresponding amines, the tertiary phosphines combine with alkyl iodides, forming salts of quaternary bases, such as *tetrethylphosphonium iodide*, so that the product is a mixture of two organic compounds,

$$PH_4I + 3C_2H_5I = P(C_2H_5)_3, HI + 3HI$$
$$P(C_2H_5)_3 + C_2H_5I = P(C_2H_5)_4I.$$

With the exception of *methylphosphine*, $PH_2{\cdot}CH_3$, which is a gas, the primary, secondary, and tertiary phosphines are colourless, volatile, highly refractive, very unpleasant-smelling liquids; they differ from the amines in smell, in being, as a rule, insoluble, or only sparingly soluble, in water (PH_3, unlike NH_3, is only sparingly soluble), and in readily undergoing oxidation on exposure to the air; in many cases, so much heat is developed during this process, that the compound takes fire—that is to say, many of the phosphines are spontaneously inflammable. When tertiary phosphines undergo slow oxidation in presence of air, they are converted into stable oxides, such as *triethylphosphine oxide*, $P(C_2H_5)_3O$.

Although phosphoretted hydrogen is only a feeble base compared with ammonia, and forms salts, such as phosphonium iodide, PH_4I, which are decomposed even by water, each successive substitution of an alkyl group for an atom of hydrogen is accompanied by an increase in basic properties, just as in the case of the amines. Salts of the primary phosphines, such as *ethylphosphine hydriodide*, $PH_2{\cdot}C_2H_5$, HI, are almost, if not quite, as unstable as those of hydrogen phosphide, and are decomposed into acid and base on treatment with water; they may thus be separated from the more stable salts of the secondary and tertiary phosphines, such as *diethylphosphine hydriodide*, $PH(C_2H_5)_2$, HI, and *triethylphosphine hydriodide*, $P(C_2H_5)_3$, HI, which are not acted on by water as a rule, but are readily decomposed by potash and soda. Salts of the tetralkylphosphonium compounds, such as *tetrethylphosphonium iodide*, $P(C_2H_5)_4I$, are not acted on by water or by alkalies, but, on treatment with moist silver oxide, they are converted into *quaternary phosphonium hydroxides*,

$$P(C_2H_5)_4I + Ag{\cdot}OH = P(C_2H_5)_4{\cdot}OH + AgI.$$

These compounds have a *strong* alkaline reaction, readily absorb carbon dioxide, and dissolve freely in water; they are, in fact, similar in properties to the hydroxides of the fixed alkalies, and their salts are much more stable than the phosphine salts, just as those of the corresponding tetralkylammonium bases are more stable than those of ammonia.

Arsines.

Arsenic, antimony, and bismuth, although belonging to the same natural group as nitrogen and phosphorus, differ from these two elements in many important particulars; although the two former give hydrides, the hydrogen atoms in which may be (indirectly) displaced by alkyl groups, substitution products corresponding with the *primary* and *secondary* amines and phosphines have not yet been prepared; in other words, the only known alkyl compounds theoretically derived from the trihydrides of arsenic, antimony, and bismuth correspond with the *tertiary* amines and phosphines, and have the composition AsR_3, SbR_3, and BiR_3 respectively.

The tertiary **arsines** are obtained by treating arsenious chloride with the zinc alkyl compounds (p. 215), or by heating the alkyl iodides with sodium arsenide,

$$2AsCl_3 + 3Zn(C_2H_5)_2 = 2As(C_2H_5)_3 + 3ZnCl_2$$
$$AsNa_3 + 3CH_3I = As(CH_3)_3 + 3NaI.$$

Triethylarsine, $As(C_2H_5)_3$, may be described as a typical arsine. It is a colourless, very unpleasant-smelling, highly poisonous liquid, and is only sparingly soluble in water; it fumes in the air, and takes fire when heated, but does not ignite spontaneously. It differs from the amines and phosphines in being a neutral compound, and, like arseniuretted hydrogen, it does not form salts with acids; it resembles the tertiary amines and phosphines in combining readily with alkyl iodides, forming salts of *quaternary arsonium hydroxides*,

$$As(C_2H_5)_3 + C_2H_5I = As(C_2H_5)_4I.$$

Tetrethylarsonium iodide, $As(C_2H_5)_4I$, for example, is a crystalline substance, and, like other quaternary organic salts, it is *not* decomposed by potash, although it interacts with silver hydroxide, giving **tetrethylarsonium hydroxide,**

$$As(C_2H_5)_4I + Ag{\cdot}OH = As(C_2H_5)_4{\cdot}OH + AgI.$$

This substance has a strong alkaline reaction, and neutralises even the most powerful acids; here, again, as in the case of nitrogen and phosphorus, the basic character increases with the number of alkyl groups in the molecule.

The tertiary arsines resemble the tertiary phosphines in readily undergoing oxidation on exposure to the air, forming oxides such as *triethylarsine oxide*, $As(C_2H_5)_3O$.

The tertiary *stibines*, the organic derivatives of antimony, are on the whole similar to those of arsenic, but have not been so carefully investigated; the tertiary bismuth compounds, such as $Bi(CH_3)_3$, cannot be converted into quaternary hydroxides, corresponding with those of arsenic and antimony, and owing to the more pronounced metallic character of bismuth, its compounds resemble rather those of the metals zinc, mercury, &c. (p. 214).

Derivatives of the Arsines.—Tertiary arsines combine directly with two atoms of a halogen, forming compounds, such as triethylarsine dichloride, $As(C_2H_5)_3Cl_2$, in which the arsenic atom is pentavalent; these substances are decomposed on heating, yielding an alkyl halogen compound and a *halogen derivative* of a secondary arsine,

$$As(C_2H_5)_3Cl_2 = As(C_2H_5)_2Cl + C_2H_5Cl.$$

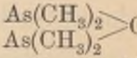
Although, then, the secondary arsines are unknown, their halogen derivatives can be prepared; so, also, can those of primary arsines, since, when the derivatives of the secondary compounds are treated with halogens, direct union takes place,

$$As(C_2H_5)_2Cl + Cl_2 = As(C_2H_5)_2Cl_3,$$

and the products, on heating, are decomposed into *dihalogen derivatives* of primary arsines,

$$As(C_2H_5)_2Cl_3 = As(C_2H_5)Cl_2 + C_2H_5Cl.$$

The derivatives of dimethylarsine are of considerable interest, and have been very carefully investigated by Bunsen.

Dimethylarsine oxide, or **cacodyl oxide,** 
$\begin{matrix} As(CH_3)_2 \\ As(CH_3)_2 \end{matrix}\!\!>O$, is formed when a mixture of equal parts of arsenic trioxide and potassium acetate is submitted to dry distillation; during the operation highly poisonous gases are evolved, and an oily liquid collects in the receiver,

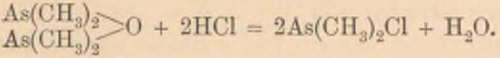
$$As_2O_3 + 4CH_3{\cdot}COOK = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2.$$

This liquid has an intensely obnoxious smell,* and is excessively poisonous, for which reasons its preparation, except in *minute* quantities, should not be attempted; its formation may, however, be used as a test for acetates if due care be taken, as the substance is readily recognisable by its smell.

Cacodyl oxide boils at 150°, and is insoluble in water; the substance prepared in the above-mentioned manner is spontaneously inflammable owing to the presence of cacodyl, but the pure compound is not. In chemical properties cacodyl oxide resembles the feebly basic metallic oxides; it has a neutral reaction, but interacts readily with acids,

* The name cacodyl is derived from the Greek κακώδης, 'stinking.'

forming salts, such as *cacodyl chloride* and *cacodyl cyanide*, $As(CH_3)_2{\cdot}CN$,



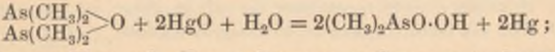
$$\begin{matrix}As(CH_3)_2\\ As(CH_3)_2\end{matrix}{>}O + 2HCl = 2As(CH_3)_2Cl + H_2O.$$

When cacodyl chloride is heated with zinc in an atmosphere of carbon dioxide, it yields **cacodyl** or diarsenic tetramethyl, a change which is analogous to the formation of ethane from methyl iodide,

$$2As(CH_3)_2Cl + Zn = As(CH_3)_2 - As(CH_3)_2 + ZnCl_2$$
$$2CH_3I + 2Na = CH_3 - CH_3 + 2NaI.$$

Cacodyl, like the oxide, is a colourless, excessively poisonous liquid, and has an intensely disagreeable smell; it takes fire on exposure to the air.

Cacodylic acid, $(CH_3)_2AsO{\cdot}OH$, is formed when cacodyl oxide is oxidised with mercuric oxide,



$$\begin{matrix}As(CH_3)_2\\ As(CH_3)_2\end{matrix}{>}O + 2HgO + H_2O = 2(CH_3)_2AsO{\cdot}OH + 2Hg;$$

it is a crystalline, odourless substance, and seems to be non-poisonous.

Organic Silicon Compounds.

The organic compounds of silicon are of exceptional interest, because their study exhibits in a very strong light the close relationship between silicon and carbon. Just as the paraffins may be considered as derived from the hydride, methane, CH_4, by the substitution of alkyl groups for hydrogen, so may the simplest silicon compounds be regarded as derivatives of silicon hydride, SiH_4. Up to the present, however, only those compounds containing four alkyl radicles have been prepared, as, for example, silicon tetramethyl, $Si(CH_3)_4$, corresponding with carbon tetramethyl or tetramethylmethane, $C(CH_3)_4$; substances such as $SiH(CH_3)_3$, $SiH_2(CH_3)_2$, &c., which would be analogous to the hydrocarbons $CH(CH_3)_3$, $CH_2(CH_3)_2$, &c., are not known.

Silicon tetramethyl, $Si(CH_3)_4$, is produced when silicon tetrachloride is heated with zinc methyl,

$$SiCl_4 + 2Zn(CH_3)_2 = Si(CH_3)_4 + 2ZnCl_2.$$

It is a colourless, mobile, volatile liquid, boiling at 30°, and has properties very similar to those of tetramethylmethane.

Silicon tetrethyl, $Si(C_2H_5)_4$, may be obtained from silicon tetrachloride and zinc ethyl in a similar manner, and closely resembles the normal paraffin, nonane, C_9H_{20}, in properties. It may, in fact, be regarded as derived from the as yet unknown isomeride of nonane, tetrethylmethane, $C(C_2H_5)_4$, by the substitution of one atom of silicon for one atom of carbon; for this reason it is sometimes named *siliconbackslash*.

The great similarity between siliconbackslash and nonane is strikingly shown by the following facts: Siliconbackslash, like nonane, is a colourless liquid, insoluble in, and specifically lighter than water; like nonane, it is a very stable substance, and is not acted on by nitric acid or caustic alkalies. On treatment with chlorine it behaves like a paraffin, and yields the substitution product *siliconbackslash chloride*, $Si(C_2H_5)_3 \cdot C_2H_4Cl$, a colourless liquid, boiling at 185°; this chloride closely resembles the alkyl chlorides in properties, and, like the latter, interacts with silver acetate, giving *siliconbackslash acetate*,

$$Si(C_2H_5)_3 \cdot C_2H_4Cl + C_2H_3O_2Ag = Si(C_2H_5)_3 \cdot C_2H_4 \cdot C_2H_3O_2 + AgCl.$$

This ethereal salt is readily hydrolysed by alkalies, yielding *siliconbackslash alcohol*, just as ethyl acetate gives ethyl alcohol,

$$Si(C_2H_5)_3 \cdot C_2H_4 \cdot C_2H_3O_2 + KOH = Si(C_2H_5)_3 \cdot C_2H_4 \cdot OH + C_2H_3O_2K;$$

this alcohol, again, is a colourless, neutral liquid, boiling at 190°, analogous in most respects to the higher alcohols of the general formula $C_nH_{2n+1} \cdot OH$.

Organic silicon compounds, such as $Si_2(C_2H_5)_6$, corresponding with Si_2Cl_6, are known, but are of less importance.

Organo-Metallic Compounds.

Many of the metals, such as mercury, zinc, tin, and lead, form compounds with alkyl groups, although their hydrides are unknown. These alkyl compounds are named 'organo-metallic' compounds, but there is no sharp division between them and the alkyl compounds of other elements, just as there is none between the metals and non-metals. If, in fact, the alkyl compounds of elements belonging to the same natural group be considered, it will be evident that they show a *gradual* change in properties, just as do the elements themselves, and pass into organo-metallic compounds without any abrupt transition. The compounds of the elements of the fourth group, for example, such as

$$C(CH_3)_4 \qquad Si(CH_3)_4 \qquad Sn(CH_3)_4 \qquad Pb(CH_3)_4,$$

may be divided into two fairly distinct classes; but in the case of those of the elements of the fifth group,

$$N(CH_3)_3 \quad P(CH_3)_3 \quad As(CH_3)_3 \quad Sb(CH_3)_3 \quad Bi(CH_3)_3,$$

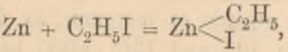
it is practically impossible to say which of them, if any, should be classed as organo-metallic compounds.

The zinc alkyl compounds are perhaps of the greatest importance, on account of their frequent employment in the synthesis of other organic substances, of which many examples have already been given; their properties, moreover, are in many respects typical of those of other organo-metallic compounds.

Zinc ethyl, $Zn(C_2H_5)_2$, is formed when ethyl bromide or iodide is digested with an alloy of sodium and zinc,

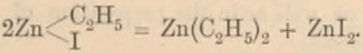
$$ZnNa_2 + 2C_2H_5I = Zn(C_2H_5)_2 + 2NaI.$$

It is usually prepared by heating zinc with ethyl iodide in an atmosphere of carbon dioxide; the first product is a colourless, solid substance (zinc ethiodide), containing iodine,



$$Zn + C_2H_5I = Zn\begin{matrix} \diagup C_2H_5 \\ \diagdown I \end{matrix},$$

but on heating more strongly, a second change occurs, and zinc ethyl is formed,



$$2Zn\begin{matrix} \diagup C_2H_5 \\ \diagdown I \end{matrix} = Zn(C_2H_5)_2 + ZnI_2.$$

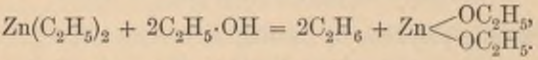
Zinc filings (100 grams) and an equal weight of ethyl iodide are placed in a flask connected with a reflux condenser, and the air is completely expelled from the apparatus by passing a stream of dry carbon dioxide through a narrow tube which runs through the condenser to the bottom of the flask. The condenser is then quickly fitted with a cork through which passes a tube, dipping under mercury, in order to prevent access of air; the materials and the apparatus must be perfectly dry.

The flask is now heated on a water-bath, when a rapid evolution of gas (butane) takes place, and the white intermediate product is gradually formed; after two to three hours' time the interaction is at an end. When cold, the flask is quickly fitted with a cork and glass tubes (just as in an ordinary wash-bottle), and the smaller tube is connected with a condenser; the flask is then heated in an oil-bath, and the zinc ethyl distilled, a stream of dry carbon dioxide being passed through the longer tube into the apparatus during the whole operation; the distillate is collected in a vessel which can be easily sealed.

Zinc ethyl is a colourless liquid, and boils at 118° without decomposition; it must be distilled in an atmosphere free from oxygen, since it inflames spontaneously on exposure to the air, burning with a luminous, greenish flame, and emitting clouds of zinc oxide. It decomposes water with great energy, yielding ethane and zinc hydroxide,

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2,$$

and owing to its dehydrating action, it causes painful sores when brought into contact with the skin; it is also decomposed by alcohol, but not so quickly as by water,



$$Zn(C_2H_5)_2 + 2C_2H_5{\cdot}OH = 2C_2H_6 + Zn{<}\begin{matrix}OC_2H_5,\\OC_2H_5.\end{matrix}$$

Zinc ethyl interacts readily with all substances containing the hydroxyl-group, and also with almost all halogen compounds, whether organic or inorganic, as, for example, with acid chlorides (pp. 107 and 136), alkyl halogen compounds (p. 69), and metallic chlorides; for these reasons it is extensively used in the synthesis of paraffins, ketones, tertiary alcohols, &c., as well as in the preparation of other organo-metallic compounds.

Zinc methyl, $Zn(CH_3)_2$, resembles zinc ethyl in most respects, and is prepared by heating methyl iodide with zinc, or, better, with the zinc-copper couple. It is a colourless liquid, boiling at 46°, and is decomposed by water, yielding methane and zinc hydroxide.

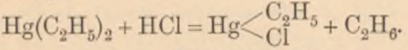
Mercuric ethyl, $Hg(C_2H_5)_2$, is formed when zinc ethyl is treated with mercuric chloride,

$$Zn(C_2H_5)_2 + HgCl_2 = Hg(C_2H_5)_2 + ZnCl_2,$$

but it is usually prepared by shaking ethyl iodide with sodium amalgam,

$$HgNa_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI.$$

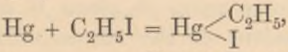
Mercuric ethyl is a colourless, very heavy liquid, of sp. gr. 2·44; it boils at 159° without decomposition, and is not spontaneously inflammable at ordinary temperatures, although it ignites readily when strongly heated. It is much less active than zinc ethyl, does not oxidise on exposure to the air, and is not decomposed by water, in which it is only sparingly soluble; both the liquid and its vapour are highly poisonous. On treatment with halogen acids, mercuric ethyl is converted into salts, analogous in some respects to the halogen salts of the alkali metals,



$$Hg(C_2H_5)_2 + HCl = Hg{<}\begin{matrix}C_2H_5\\ Cl\end{matrix} + C_2H_6.$$

Mercuric Ethochloride.

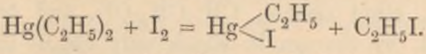
These salts are also formed by the direct union of mercury and alkyl halogen compounds at ordinary temperatures, especially in sunlight,



$$Hg + C_2H_5I = Hg{<}\begin{matrix}C_2H_5\\ I\end{matrix},$$

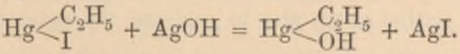
Mercuric Ethiodide.

and by treating di-alkyl mercury compounds with halogens,



$$Hg(C_2H_5)_2 + I_2 = Hg{<}\begin{matrix}C_2H_5\\ I\end{matrix} + C_2H_5I.$$

They interact with moist silver oxide, being converted into *hydroxides*, just as sodium iodide, for example, gives sodium hydroxide,



$$Hg{<}\begin{matrix}C_2H_5\\ I\end{matrix} + AgOH = Hg{<}\begin{matrix}C_2H_5\\ OH\end{matrix} + AgI.$$

The hydroxides thus formed are thick, caustic liquids, readily soluble in water; they have an *alkaline* reaction, neutralise acids, liberate ammonia from its salts, and precipitate metallic hydroxides from their salts. Here, as in the case of nitrogen, phosphorus, arsenic, &c., the influence of alkyl groups in increasing the basic character of an element is very pronounced; mercuric oxide is a comparatively feeble base.

Of the other organo-metallic compounds those of tin, lead, and aluminium may be mentioned. Tin and lead form compounds, such as $Sn(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$, $Pb(C_2H_5)_4$ and $Pb_2(C_2H_5)_6$, in which the metal is tetravalent; stannous ethyl, $Sn(C_2H_5)_2$, corresponding with stannous chloride, is also said to exist. Aluminium appears only to give alkyl compounds, such as $Al(CH_3)_3$ and $Al(C_2H_5)_3$, in which the metal is trivalent.

The organo-metallic compounds are of great service in determining the valency of metals, because, unlike the great majority of metallic compounds, most of them vaporise without decomposition; by ascertaining experimentally the density of the vapour, the molecular weight of the substance and the valency of the metal may be established.

CHAPTER XIII.

THE GLYCOLS AND THEIR OXIDATION PRODUCTS.

It may be assumed as a general rule that the changes which any particular group of atoms is capable of undergoing are independent of the nature of the groups with which it is combined; just as ethane, $CH_3{\cdot}CH_3$, for example, may be successively transformed into ethyl chloride, $CH_3{\cdot}CH_2Cl$, ethyl alcohol, $CH_3{\cdot}CH_2{\cdot}OH$, and acetic acid, $CH_3{\cdot}CO{\cdot}OH$, by changes in which only *one* of the methyl groups takes part, so also may it be converted into ethylene dichloride (dichlorethane), $CH_2Cl{\cdot}CH_2Cl$, dihydroxyethane, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and oxalic acid, $HO{\cdot}CO{\cdot}CO{\cdot}OH$, by causing the *other* methyl group also to undergo the same modifications.

It follows, therefore, that, in many cases, a series of monosubstitution products of the paraffins may be directly or indirectly converted into a corresponding series of di-substitution products, between which there is, on the whole, a close relationship. The **glycols**, or dihydroxy-derivatives of the paraffins, discovered by Würtz in 1856, afford an example of this point; they form a homologous series of the general formula $C_nH_{2n}(OH)_2$, and are closely related to the monohydric alcohols.

Ethylene glycol, ethene glycol, or ethylene alcohol, $C_2H_4(OH)_2$, is the simplest glycol, and corresponds with ethyl alcohol, the compound, methylene glycol, $CH_2(OH)_2$, which would correspond with methyl alcohol, being unknown. Ethylene glycol is formed in small quantities when ethylene is oxidised with a dilute alkaline solution of potassium permanganate,

$$C_2H_4 + H_2O + O = C_2H_4(OH)_2.$$

It is prepared by heating ethylene dibromide, or ethylene dichloride, with dilute aqueous alkalies, or alkali carbonates, the change which occurs being similar to that which takes place in the formation of ethyl alcohol from ethyl chloride,

$$C_2H_4Br_2 + 2KOH = C_2H_4(OH)_2 + 2KBr.$$

For this purpose potassium carbonate (138 grams) is dissolved in water (1 litre), ethylene dibromide (188 grams) added, and the mixture boiled in a flask connected with a reflux condenser. As the insoluble oily dibromide is converted into ethylene glycol, it passes into solution, so that the change is known to be complete when globules of oil are no longer visible. The solution is then slowly evaporated on a water-bath* to expel most of the water, the semi-solid residue mixed with alcohol and ether (which precipitate potassium bromide, but dissolve the glycol), and the glycol isolated from the filtered solution by fractional distillation.

Ethylene glycol is a thick, colourless liquid, and has a rather sweet taste; it boils at 197·5°, and is miscible with water and alcohol in all proportions, but is only sparingly soluble in ether. Although it is a neutral substance, it dissolves sodium at ordinary temperatures with evolution of hydrogen, yielding *sodium glycol*, $C_2H_5O_2Na$, one atom of the metal

---

* If the solution be kept in rapid ebullition, a considerable quantity of the glycol escapes with the steam.

displacing one atom of hydrogen; if this substance be now heated with sodium, hydrogen is again evolved, and *disodium glycol*, $C_2H_4O_2Na_2$, is formed by a repetition of the substitution process. These sodium derivatives, like those of the monohydric alcohols, are colourless, crystalline, and hygroscopic, and are readily decomposed by water, being reconverted into glycol,

$$C_2H_4O_2Na_2 + 2H_2O = C_2H_6O_2 + 2NaOH.$$

From its behaviour with sodium it might be assumed that glycol contained hydroxyl-groups, and that the reason of its giving di-substitution products (whereas the monohydric alcohols yield only mono-substitution products) was due to the presence of *two* hydroxyl-groups. If this were so, it would be expected that glycol, like alcohol, would be readily attacked by the chlorides and bromides of phosphorus; this is indeed the case. When glycol is treated with phosphorus pentabromide, it is converted into ethylene dibromide, whereas with phosphorus pentachloride it yields the dichloride,

$$C_2H_4(OH)_2 + 2PBr_5 = C_2H_4Br_2 + 2POBr_3 + 2HBr.$$

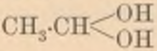
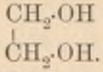
Again, it has been shown that ethyl alcohol and other hydroxy-compounds interact with acetic anhydride and with acetyl chloride, so that if glycol contain two hydroxyl-groups, it should be converted into a diacetyl-derivative; this, also, is the fact, since *glycol diacetate* is readily obtained on heating glycol with acetic anhydride,

$$C_2H_4(OH)_2 + 2(CH_3\cdot CO)_2O = C_2H_4(O\cdot CO\cdot CH_3)_2 + 2C_2H_4O_2.$$

Glycol diacetate is also formed when ethylene dibromide is digested with silver acetate,

$$C_2H_4Br_2 + 2C_2H_3O_2Ag = C_2H_4(C_2H_3O_2)_2 + 2AgBr;$$

this ethereal salt is decomposed by boiling alkalies, yielding ethylene glycol, which was first obtained by Würtz in this way.

Constitution of Glycol.—The facts already stated show clearly that glycol contains two hydroxyl-groups; the only matter requiring further attention is, therefore, whether these two groups are combined with the same, or with different carbon atoms—that is to say, whether glycol has the constitution  $CH_3\cdot CH<\begin{matrix}OH\\OH\end{matrix}$ or $OH\cdot CH_2\cdot CH_2\cdot OH$. This question is easily answered on considering the formation of glycol from ethylene dibromide; since the latter has the constitution $CH_2Br\cdot CH_2Br$, and its conversion into glycol is a simple process of substitution, glycol must be represented by the formula $OH\cdot CH_2\cdot CH_2\cdot OH$ or  $\begin{matrix}CH_2\cdot OH\\ | \\ CH_2\cdot OH\end{matrix}$. This conclusion is confirmed by a study of the behaviour of glycol under other conditions, and of its relation to other compounds.

Homologues of Ethylene Glycol.—The higher glycols, or dihydroxy-derivatives of the paraffins, as, for example, *αβ-propylene glycol*, $CH_3\cdot CH(OH)\cdot CH_2\cdot OH$, and *αγ*-butylene glycol, $CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot OH$, are named after the unsaturated hydrocarbons of the olefine series, from which they may be regarded as derived. As they exist in isomeric forms, these are distinguished by employing α, β, γ, &c. to denote the positions of the hydroxyl-groups, commencing at the terminal carbon atom.

The glycols are neutral, thick liquids, similar to ethylene glycol in properties; they are usually prepared by treating the olefines with bromine, and decomposing the dibromo-additive products obtained in this way by boiling with alkali carbonates.

The great advantage of employing constitutional formulæ is well illustrated by the case of ethylene glycol. From a consideration of its method of formation and of one or two simple reactions, it is concluded that glycol has the constitution $OH\cdot CH_2\cdot CH_2\cdot OH$. Assuming this to be true, its behaviour under given conditions can be foretold with tolerable certainty from the facts established in the case of ethyl alcohol, because the constitutional formula of a compound is a summary of its most important reactions. Ethylene glycol contains two $-CH_2\cdot OH$ groups, each of which is similar to that in ethyl alcohol; it may be supposed, then, that any property of ethyl alcohol which is dependent on the presence of this group will also be exhibited by glycol. Since, for example, alcohol acts like a metallic hydroxide, and forms salts with one molecule of a monobasic acid, ethylene glycol, which contains two hydroxyl-groups, should behave as a diacid hydroxide, and form salts with two molecules of a monobasic acid.

When hydrogen chloride is passed into glycol heated at about 100°, *glycol chlorohydrin* is formed,

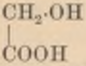
$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2{\cdot}OH + H_2O,$$

and when this product is heated with hydrogen chloride at a higher temperature, glycol dichloride, or ethylene dichloride, is produced,

$$CH_2Cl{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2Cl + H_2O,$$

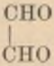
changes which are strictly analogous to the conversion of alcohol into ethyl chloride.

Again, when ethyl alcohol is carefully oxidised, it is first converted into aldehyde (the group $-CH_2{\cdot}OH$ being transformed into $-CHO$), and then into acetic acid (by the oxidation of the $-CHO$ group to $-COOH$). Since, therefore, glycol contains two $-CH_2{\cdot}OH$ groups, each of which may undergo these changes, it might be foretold that, on oxidation, glycol would probably yield several compounds, according as one or both the $-CH_2{\cdot}OH$ groups were attacked. This also is the fact; on oxidation with nitric acid glycol yields the following compounds:



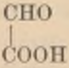
$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ COOH \end{array}$$

Glycollic Acid.



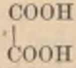
$$\begin{array}{l} CHO \\ | \\ CHO \end{array}$$

Glyoxal.



$$\begin{array}{l} CHO \\ | \\ COOH \end{array}$$

Glyoxylic Acid.



$$\begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Oxalic Acid.

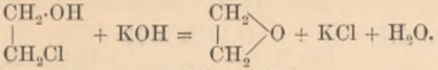
These examples show clearly that the constitution of any substance having been ascertained from a study of some of its reactions, its behaviour under given conditions may be foretold with tolerable certainty; in other words, the general reactions and the constitutional formulæ of organic compounds are the most important points to bear in mind.

When an olefine is treated with hypochlorous acid, direct combination ensues, and a *chlorohydrin* is formed,

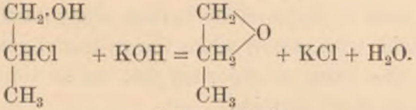
$$\underset{\text{Ethylene.}}{CH_2{:}CH_2} + HOCl = \underset{\text{Ethylene Chlorohydrin.}}{OH{\cdot}CH_2{\cdot}CH_2Cl}$$

$$\underset{\text{Propylene.}}{CH_3{\cdot}CH{:}CH_2} + HOCl = \underset{\text{Propylene Chlorohydrin.}}{CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH.}$$

These chlorohydrins are usually readily acted on by alkalies, being converted into oxides by loss of one molecule of hydrogen chloride, a change which recalls the conversion of ethyl bromide into ethylene,



Ethylene Oxide.



Propylene Oxide.

Ethylene oxide is isomeric with aldehyde, C_2H_4O; it is a liquid, boils at 13·5°, and is slowly decomposed by water, being converted into glycol.

OXIDATION PRODUCTS OF THE GLYCOLS.

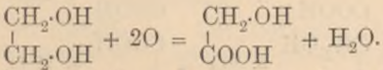
Glyoxal, $CHO{\cdot}CHO$, is produced by the oxidation of glycol, but it is usually prepared by slowly oxidising alcohol or aldehyde with nitric acid,

$$CH_3{\cdot}CHO + 2O = CHO{\cdot}CHO + H_2O.$$

It is an amorphous substance, readily soluble in alcohol and ether; it shows all the properties of an aldehyde, reduces ammoniacal silver nitrate, and combines with sodium bisulphite to form a crystalline compound of the composition $C_2H_2O_2, 2NaHSO_3 + H_2O$. It also combines with hydroxylamine and with phenylhydrazine, giving the compounds $HON{:}CH{\cdot}CH{:}NOH$ and $C_6H_5N_2H{:}CH{\cdot}CH{:}N_2HC_6H_5$.

Hydroxycarboxylic Acids.

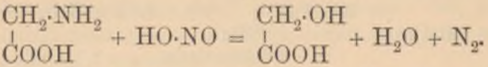
Glycollic acid, $OH{\cdot}CH_2{\cdot}COOH$, may be obtained by the oxidation of glycol, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, with nitric acid, just as acetic acid is produced by the oxidation of alcohol, $CH_3{\cdot}CH_2{\cdot}OH$,



$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array} + 2O = \begin{array}{l} CH_2{\cdot}OH \\ | \\ COOH \end{array} + H_2O.$$

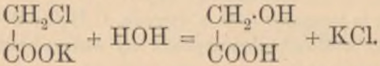
As, however, several other substances are formed, the isolation of the acid from the oxidation product is very troublesome.

It is also formed when amido-acetic acid (glycine, p. 292) is treated with nitrous acid, a reaction exactly analogous to the conversion of ethylamine into alcohol,



$$\begin{array}{l}CH_2\cdot NH_2\\ |\\ COOH\end{array} + HO\cdot NO = \begin{array}{l}CH_2\cdot OH\\ |\\ COOH\end{array} + H_2O + N_2.$$

Glycollic acid is prepared by boiling the potassium salt of chloracetic acid with water, when the hydroxyl-group is substituted for one atom of chlorine, just as in the formation of alcohol from ethyl chloride,



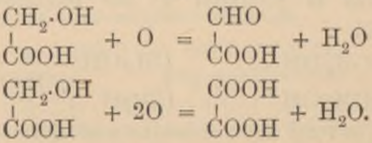
$$\begin{array}{l}CH_2Cl\\ |\\ COOK\end{array} + HOH = \begin{array}{l}CH_2\cdot OH\\ |\\ COOH\end{array} + KCl.$$

The solution is evaporated to dryness, and the residue extracted with acetone, which dissolves the glycollic acid, but not the potassium chloride.

Glycollic acid is a crystalline, hygroscopic substance, and melts at 80°; it is readily soluble in water, alcohol, and ether. Assuming that its constitution is correctly represented by the formula given above, and of this there can be little doubt when its methods of formation are carefully considered, it is almost unnecessary to describe at length the chemical behaviour of glycollic acid, because this is expressed by its constitutional formula.

Glycollic acid contains one carboxyl-group; therefore, like the fatty acids, it is a monobasic acid, neutralises carbonates, and forms salts with metallic hydroxides and with alcohols.

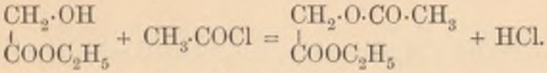
Glycollic acid also contains one $-CH_2\cdot OH$ group; therefore it behaves like a primary alcohol, as well as like an acid. On oxidation, for example, it yields glyoxylic acid and oxalic acid, just as alcohol gives aldehyde and acetic acid,



$$\begin{array}{l}CH_2\cdot OH\\ |\\ COOH\end{array} + O = \begin{array}{l}CHO\\ |\\ COOH\end{array} + H_2O$$

$$\begin{array}{l}CH_2\cdot OH\\ |\\ COOH\end{array} + 2O = \begin{array}{l}COOH\\ |\\ COOH\end{array} + H_2O.$$

Even when the hydrogen atom of the carboxyl-group has been displaced, glycollic acid still contains one atom of hydrogen, which, like that in alcohols, may be displaced by the alkali metals and by the acetyl-group; ethyl glycollate, for example, is readily converted into an acetyl-derivative on treatment with acetyl chloride,



$$\begin{matrix} CH_2{\cdot}OH \\ | \\ COOC_2H_5 \end{matrix} + CH_3{\cdot}COCl = \begin{matrix} CH_2{\cdot}O{\cdot}CO{\cdot}CH_3 \\ | \\ COOC_2H_5 \end{matrix} + HCl.$$

Homologues of Glycollic Acid.—Glycollic acid may be regarded as hydroxyacetic acid, or acetic acid in which a hydroxyl-group has been substituted for one atom of hydrogen; as, moreover, other fatty acids yield similar hydroxyl-derivatives, a homologous series of *hydroxycarboxylic acids* may be obtained.

The more important members of the series are:

Glycollic acid, or hydroxyacetic acid, $OH{\cdot}CH_2{\cdot}COOH$.
Lactic acid, or hydroxypropionic acid, $OH{\cdot}C_2H_4{\cdot}COOH$.

These compounds may also be regarded as oxidation products of the glycols; just as glycollic acid is formed on oxidising ethylene glycol, so the higher members of the series may be obtained from the corresponding glycols by oxidising a $-CH_2{\cdot}OH$ group to $-COOH$.

The lowest member of this series, carbonic acid or hydroxyformic acid, $OH{\cdot}COOH$, is not known in the free state, since, when liberated from its salts, it immediately loses water, and is converted into the anhydride, carbon dioxide.

The third member of the series exists in two isomeric forms—namely, as α- and β-hydroxypropionic acid; these isomerides are related to propionic acid, in the manner shown by the following formulæ:

$$CH_3{\cdot}CH_2{\cdot}COOH$$

Propionic Acid.

$$CH_3{\cdot}CH(OH){\cdot}COOH \qquad CH_2(OH){\cdot}CH_2{\cdot}COOH.$$

α-Hydroxypropionic or Lactic Acid. β-Hydroxypropionic or Hydracrylic Acid.

Lactic acid, or α-hydroxypropionic acid, $C_3H_6O_3$, or

$$CH_3{\cdot}CH(OH){\cdot}COOH,$$

is formed during the lactic fermentation of sugar, starch, and other substances in presence of nitrogenous animal matter, and occurs in sour milk. It can be obtained by methods analogous to those given in the case of glycollic acid—namely, by oxidising $\alpha\beta$-propylene glycol with nitric acid,

$$CH_3\cdot CH(OH)\cdot CH_2\cdot OH + 2O = CH_3\cdot CH(OH)\cdot COOH + H_2O,$$

by heating α-chloro- or α-bromo-propionic acid with water, alkalies, or silver hydroxide,

$$CH_3\cdot CHBr\cdot COOH + H_2O = CH_3\cdot CH(OH)\cdot COOH + HBr,$$

and by treating α-amido-propionic acid with nitrous acid,

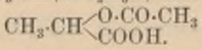
$$CH_3\cdot CH(NH_2)\cdot COOH + HO\cdot NO = CH_3\cdot CH(OH)\cdot COOH + N_2 + H_2O.$$

It is prepared by the lactic fermentation of sugar (see butyric acid, p. 156), or simply by heating sugar with alkalies. Lactic acid is a thick, sour, hygroscopic liquid, miscible with water, alcohol, and ether in all proportions; it cannot be distilled as it undergoes decomposition into aldehyde, water, carbon monoxide, and other products. When heated with dilute sulphuric acid, it is decomposed into aldehyde and formic acid, a fact which shows that, compared with the fatty acids, lactic acid is very unstable,

$$CH_3\cdot CH(OH)\cdot COOH = CH_3\cdot CHO + H\cdot COOH.$$

Lactic acid is a monocarboxylic acid, and forms metallic and ethereal salts.

Calcium lactate, $[CH_3\cdot CH(OH)\cdot COO]_2Ca + 5H_2O$, and *zinc lactate*, $(C_3H_5O_3)_2Zn + 3H_2O$, are crystalline, and readily soluble in hot water. *Ethyl lactate*, $CH_3\cdot CH(OH)\cdot COOC_2H_5$, is a neutral liquid, but, since it contains a $>CH(OH)$ group, it yields metallic derivatives with potassium and sodium, and, like other hydroxyl-compounds, it interacts with acetyl chloride, giving *ethyl acetyl-lactate*, $CH_3\cdot CH(O\cdot C_2H_3O)\cdot COOC_2H_5$, an ethereal salt of acetyl-lactic acid,



$CH_3\cdot CH\begin{matrix}\diagup O\cdot CO\cdot CH_3\\ \diagdown COOH.\end{matrix}$

Lactic acid also contains the group $>CH\cdot OH$, and shows, therefore, most of the reactions of a secondary alcohol. When, for example, it is heated with concentrated hydrobromic acid, it is converted into α-bromo-propionic acid, just as isopropyl alcohol gives isopropyl bromide,

$$CH_3 \cdot CH(OH) \cdot COOH + HBr = CH_3 \cdot CHBr \cdot COOH + H_2O;$$

with concentrated hydriodic acid, however, it yields propionic acid, because the α-iodo-propionic acid which is first produced is reduced by the excess of hydriodic acid,

$$CH_3 \cdot CHI \cdot COOH + HI = CH_3 \cdot CH_2 \cdot COOH + I_2.$$

On oxidation with potassium permanganate, lactic acid again behaves like a secondary alcohol, and is converted into pyruvic acid, just as isopropyl alcohol gives acetone,

$$CH_3 \cdot CH(OH) \cdot COOH + O = CH_3 \cdot CO \cdot COOH + H_2O.$$

Sarcolactic acid, or *paralactic acid*, $C_3H_6O_3$, is the name given to an acid which occurs in animals, more especially in the muscle juices, and which is best prepared from extract of meat. It has the same constitution as lactic acid, because it undergoes the same chemical changes, and differs from it only in being optically active (part ii.).

Hydracrylic acid, or β-hydroxypropionic acid, $C_3H_6O_3$, or

$$CH_2(OH) \cdot CH_2 \cdot COOH,$$

is not formed during lactic fermentation, but may be obtained by reactions exactly similar to those which give the corresponding α-acid—namely, by oxidising $\alpha\gamma$-propylene glycol, and by boiling β-chloro-, bromo-, or iodo-propionic acid, $CH_2X \cdot CH_2 \cdot COOH$, with water or weak alkalies.

It is a thick, sour syrup, and, when heated alone or with moderately dilute sulphuric acid, it is converted into acrylic acid (p. 257), with loss of the elements of water, a change analogous to the conversion of ethyl alcohol into ethylene,

$$CH_2(OH) \cdot CH_2 \cdot COOH = CH_2{:}CH \cdot COOH + H_2O.$$

In most respects hydracrylic behaves like lactic acid; it is a monocarboxylic acid, but also contains a $-CH_2 \cdot OH$ group, so that it shows most of the reactions of a primary alcohol as well as those of a monobasic acid; on oxidation with chromic acid, for example, it yields malonic acid,

$$CH_2(OH)\cdot CH_2\cdot COOH + 2O = COOH\cdot CH_2\cdot COOH + H_2O.$$

Constitutions of the Hydroxypropionic Acids.—Since lactic acid and hydracrylic acid are both hydroxymonocarboxylic acids of the molecular composition $C_3H_6O_3$, and only two formulæ—namely,

$$\underset{\text{I.}}{CH_3\cdot CH(OH)\cdot COOH} \quad \text{and} \quad \underset{\text{II.}}{CH_2(OH)\cdot CH_2\cdot COOH}$$

—can be constructed, making the usual assumptions regarding valency, all that is necessary is to determine which represents the one and which the other acid. This point is, of course, already settled if the constitutions of the chloro-propionic or amido-propionic acids be taken as known; supposing, however, this were not the case, the following syntheses of the hydroxy-acids establish their constitutions.

When aldehyde is treated with hydrocyanic acid, direct combination occurs, and the product is converted into lactic acid on boiling it with hydrochloric acid,

$$CH_3\cdot CH(OH)\cdot CN + 2H_2O = CH_3\cdot CH(OH)\cdot COOH + NH_3.$$

Lactic acid, therefore, is represented by formula I., a conclusion which is fully borne out by all other facts.

When ethylene is treated with an aqueous solution of hypochlorous acid, glycol chlorohydrin is formed (p. 222); this compound interacts with potassium cyanide in dilute alcoholic solution, giving glycol cyanohydrin,

$$CH_2(OH)\cdot CH_2Cl + KCN = CH_2(OH)\cdot CH_2\cdot CN + KCl,$$

which, when boiled with mineral acids, is converted into hydracrylic acid,

$$CH_2(OH)\cdot CH_2\cdot CN + 2H_2O = CH_2(OH)\cdot CH_2\cdot COOH + NH_3.$$

Hydracrylic acid, therefore, is represented by formula II.

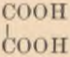
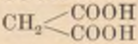
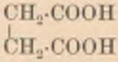
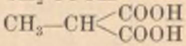
Since, moreover, aldehyde and ethylene may be prepared from their elements, this is also true as regards the two hydroxypropionic acids.

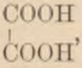
Lactic acid is sometimes called *ethylidenelactic acid*, hydracrylic acid being named *ethylenelactic acid;* these names serve to recall the facts that lactic acid contains the ethylidene group $CH_3{\cdot}CH<$, hydracrylic acid the ethylene group $-CH_2{\cdot}CH_2-$.

Dicarboxylic Acids.

Glycollic acid, $CH_2(OH){\cdot}COOH$, being derived from ethylene glycol, $CH_2(OH){\cdot}CH_2{\cdot}OH$, by the oxidation of *one* of the $-CH_2{\cdot}OH$ groups, it might be concluded that the *other* $-CH_2{\cdot}OH$ group would be capable of undergoing a similar change; this is found to be so, since on further oxidation glycollic acid is converted into oxalic acid, $COOH{\cdot}COOH$. As, moreover, other glycols, such as $\alpha\gamma$-propylene glycol, $CH_2(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$, which contain two $-CH_2{\cdot}OH$ groups, behave in the same way as ethylene glycol, it is possible to prepare a homologous series of *dicarboxylic* acids of the general formula $C_nH_{2n}(COOH)_2$. These compounds may also be considered as derived from the fatty acids by the substitution of the carboxyl-group for one atom of hydrogen, and, since they contain two such groups, they are dibasic acids.

The most important members of this series are:

Oxalic, or carboxyformic acid............	$C_2H_2O_4$	or	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$
Malonic, or carboxyacetic acid.....	$C_3H_4O_4$	or	 $CH_2<\begin{array}{l}COOH\\ COOH\end{array}$
Succinic, or β-carboxypropionic acid ...	$C_4H_6O_4$	or	 $\begin{array}{l}CH_2{\cdot}COOH\\ \vert\\ CH_2{\cdot}COOH\end{array}$
Isosuccinic, or α-carboxypropionic acid	$C_4H_6O_4$	or	 $CH_3-CH<\begin{array}{l}COOH\\ COOH\end{array}$
Glutaric acid..................................	$C_5H_8O_4$		
Adipic acid	$C_6H_{10}O_4$		

Oxalic acid, $C_2H_2O_4$, or  $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$, occurs in rhubarb (*rheum*), the dock (*rumex*), sorrel (*oxalis acetosella*), and other plants, usually in the form of its potassium hydrogen salt, or as calcium oxalate; it is formed when alcohol, glycol, sugar, fats, and a great many other organic substances are oxidised with nitric acid, and may be obtained by numerous reactions, of which the following are the most instructive:

It is formed when sodium is heated at about 350° in a stream of carbon dioxide,

$$2CO_2 + 2Na = \underset{\text{Sodium Oxalate.}}{C_2O_4Na_2},$$

and when sodium or potassium formate is quickly heated to about 440°,

$$2H{\cdot}COONa = C_2O_4Na_2 + H_2;$$

it is also produced, together with many other compounds, when an aqueous solution of cyanogen (p. 277) is kept for some time, a change which is analogous to the conversion of methyl cyanide into acetic acid,

$$(CN)_2 + 4H_2O = \underset{\text{Ammonium Oxalate.}}{C_2O_4(NH_4)_2}.$$

Each of these three reactions affords a means of synthesing oxalic acid from its elements, since carbon dioxide, formic acid, and cyanogen may be obtained from their elements.

Oxalic acid may be prepared by gently warming cane-sugar with about six times its weight of concentrated nitric acid.

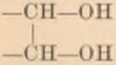
The operation is performed in a good draught cupboard, and as soon as brown fumes appear the heating is discontinued, in spite of which oxidation proceeds very vigorously; after some time, as the solution cools, crystals of oxalic acid are deposited. The solution is decanted or filtered through glass wool, and the oxalic acid purified by crystallisation from boiling water; further quantities may be obtained from the acid mother-liquors.

Oxalic acid is prepared on the large scale from sawdust, which contains organic compounds (cellulose, lignin, &c.) somewhat similar in composition to cane-sugar, and which, when heated with alkalies, undergo profound decomposition.

The sawdust is made into a paste with a concentrated solution of a mixture of equal parts of potash and soda, and then heated in iron pans at about 210°; afterwards the mass is treated with water, the solution of potassium and sodium oxalates boiled with lime, the precipitated calcium oxalate washed with water and decomposed with dilute sulphuric acid,

$$C_2O_4Ca + H_2SO_4 = C_2O_4H_2 + CaSO_4;$$

the solution of oxalic acid is then filtered from the calcium sulphate and evaporated to crystallisation. The acid obtained in this way contains small quantities of potassium and sodium hydrogen oxalates, from which it is separated only with great difficulty, so that on ignition it gives a residue of alkali carbonates; the pure acid is most conveniently prepared from cane-sugar. The formation of oxalic acid from sawdust and from sugar cannot be expressed by a simple equation; in both cases a complex molecule containing



$$\begin{array}{l}-CH-OH\\ \;\;| \\ -CH-OH\end{array}$$

groups undergoes simultaneous decomposition and oxidation.

Oxalic acid crystallises in colourless prisms, which contain two molecules of water; it is readily soluble in alcohol and moderately so in water, but only sparingly in ether. When quickly heated, it melts at about 100° and loses its water; the anhydrous acid sublimes at about 150°, but, if heated too strongly, it decomposes into carbon dioxide and formic acid, or its decomposition products,

$$C_2O_4H_2 = H{\cdot}COOH + CO_2 = H_2O + CO + CO_2;$$

the anhydrous acid is very hygroscopic, and a powerful dehydrating agent.

Oxalic acid is decomposed by concentrated sulphuric acid, but only on heating moderately strongly (distinction from formic acid),

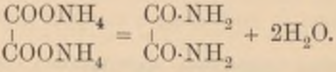
$$C_2O_4H_2 = CO_2 + CO + H_2O;$$

it is a feeble reducing agent, precipitates gold from its solutions, and is readily oxidised by warm potassium permanganate (or chlorine water), being converted into carbon dioxide and water, a reaction which is employed for the volumetric estimation of oxalic acid and also in standardising permanganate solutions,

$$C_2O_4H_2 + O = 2CO_2 + H_2O.$$

Oxalic acid is dibasic, and forms salts with two equivalents of a metallic hydroxide, and with two molecules of a monohydric alcohol; it has an acid reaction, decomposes carbonates, and dissolves certain metallic oxides. The salts of the alkalies are readily soluble in hot water, but most of the other salts are sparingly soluble or insoluble.

Ammonium oxalate, $C_2O_4(NH_4)_2$, is decomposed into oxamide when carefully heated, just as ammonium acetate yields acetamide,



$$\begin{array}{l}COONH_4\\ \vert\\ COONH_4\end{array} = \begin{array}{l}CO{\cdot}NH_2\\ \vert\\ CO{\cdot}NH_2\end{array} + 2H_2O.$$

Potassium oxalate, $C_2O_4K_2 + H_2O$, is readily soluble in water, but *potassium hydrogen oxalate*, C_2O_4KH, a salt which occurs in many plants, is more sparingly soluble; the latter forms with oxalic acid a crystalline compound of the composition $C_2O_4KH + C_2O_4H_2 + 2H_2O$, known as 'salts of sorrel,' or potassium quadroxalate; this salt is used in removing iron-mould and ink-stains, as it converts the iron into soluble iron potassium oxalate.

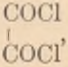
Silver oxalate, $C_2O_4Ag_2$, is obtained in crystals on adding silver nitrate to a neutral solution of an oxalate; it is only sparingly soluble in water, and explodes when quickly heated in the dry state, leaving a residue of silver.

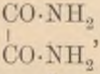
Calcium oxalate, $C_2O_4Ca + H_2O$, occurs in crystals in the cells of various plants, and is obtained as a white precipitate on adding a solution of a calcium salt to a neutral or ammoniacal solution of an oxalate; it is insoluble in water, and also in acetic acid, whereas magnesium oxalate is soluble in the latter, a fact which is made use of in the separation of the two metals. Oxalic acid and its salts are used to a considerable extent in the manufacture of organic dyes, in calico-printing, in photography (as developers), and in analytical chemistry. The metallic salts of oxalic acid are all decomposed by dilute mineral acids, yielding oxalic acid, whereas, when heated with concentrated sulphuric acid, they give carbon dioxide, carbon monoxide, water, and a sulphate. Oxalic acid and its soluble salts are poisonous. The detection of oxalic acid or of an oxalate is chiefly based on (*a*) the behaviour of the neutral solution with calcium chloride, and the insolubility of the precipitate in acetic acid; (*b*) the behaviour of the dry substance with sulphuric acid.

Methyl oxalate, $C_2O_4(CH_3)_2$, is a colourless, crystalline compound, melting at 54°, and is easily prepared by boiling anhydrous oxalic acid with methyl alcohol; it is readily hydrolysed by alkalies and boiling water, and is sometimes employed in the preparation of pure methyl alcohol.

Ethyl oxalate, $C_2O_4(C_2H_5)_2$, can be obtained in a similar manner; it is a pleasant-smelling liquid, boiling at 181°, and sparingly soluble in water. It is a curious fact that the methyl salts of organic acids are frequently crystalline, even when the ethyl, propyl, butyl, &c., salts are liquid at ordinary temperatures.

The *constitution* of oxalic acid is determined by its formation from glycol, glycollic acid, and formates; it may be regarded as composed of two carboxyl-groups, and is for this reason sometimes called dicarboxyl.

Probably owing to the fact that oxalic acid is very rich in oxygen, it is a comparatively unstable compound; its *anhydride* is unknown, and, when treated with phosphorus pentachloride, instead of yielding the chloride,  $\begin{array}{l}COCl\\ \mid\\ COCl\end{array}$, as might have been expected, oxalic acid is decomposed into the oxides of carbon and water.

Oxamide,  $\begin{array}{l}CO\cdot NH_2\\ \mid\\ CO\cdot NH_2\end{array}$, is formed as an intermediate product in the conversion of cyanogen into ammonium oxalate (p. 278), also when ammonium oxalate is heated. It is prepared by shaking methyl or ethyl oxalate with concentrated ammonia, a method very generally employed in the preparation of amides from ethereal salts.

$$C_2O_4(C_2H_5)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2C_2H_5{\cdot}OH.$$

It is a colourless, crystalline powder, insoluble in water; when heated with water, alkalies, or mineral acids, it is converted into oxalic acid or an oxalate, a change exactly analogous to that undergone by acetamide (p. 162),

$$C_2O_2(NH_2)_2 + 2H_2O = C_2O_4H_2 + 2NH_3.$$

If methyl oxalate be treated with an aqueous solution of a primary or secondary amine instead of with ammonia, alkyl substitution products of oxamide or of oxamic acid, $NH_2\cdot CO\cdot COOH$, respectively are formed (compare amines, p. 206).

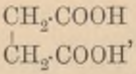
Malonic acid, $CH_2(COOH)_2$, the next homologue of oxalic acid, has already been mentioned, and the preparation of its ethyl salt from chloracetic acid has been described (p. 196).

If instead of the ethyl salt the free acid be required, the product of the action of potassium cyanide on potassium chloracetate is mixed with twice its volume of concentrated hydrochloric acid, and the solution saturated with hydrogen chloride; the clear liquid is then decanted from the precipitated potassium chloride, evaporated to dryness on a water-bath, and the malonic acid extracted from the residue by digesting with ether.

Malonic acid is a colourless, crystalline substance, readily soluble in water; it melts at 132°, and at higher temperatures undergoes decomposition into acetic acid and carbon dioxide,

$$CH_2(COOH)_2 = CH_3\cdot COOH + CO_2.$$

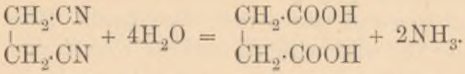
Other dicarboxylic acids, in which *both* the carboxyl-groups are united to one and the same carbon atom, are decomposed in a similar manner under the influence of heat.

Succinic acid, $C_4H_6O_4$, or  $\begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array}$, occurs in amber, and also in smaller quantities in lignite (fossil-wood), in many plants, and in certain animal secretions. It is formed during the alcoholic fermentation of sugar, and in several other fermentation processes; also when fats are oxidised with nitric acid.

It can be obtained from its elements in the following manner: acetylene, which can be prepared from carbon and hydrogen, is reduced to ethylene, the latter passed into bromine, and the ethylene dibromide thus produced boiled with potassium cyanide in aqueous alcoholic solution, when ethylene dicyanide is formed,

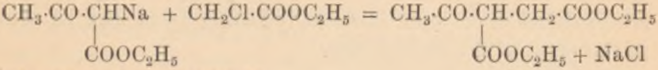
$$\mathrm{C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + 2KBr};$$

this compound is decomposed by boiling it with alkalies or mineral acids, succinic acid and ammonia being obtained,

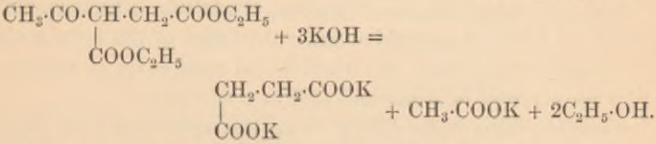


$$\begin{array}{l}\mathrm{CH_2{\cdot}CN}\\ |\\ \mathrm{CH_2{\cdot}CN}\end{array} + \mathrm{4H_2O} = \begin{array}{l}\mathrm{CH_2{\cdot}COOH}\\ |\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \mathrm{2NH_3}.$$

It may also be prepared synthetically from ethyl acetoacetate (or ethyl malonate) and ethyl chloracetate,



$$\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CHNa}\\ \qquad\qquad |\\ \qquad\qquad \mathrm{COOC_2H_5}\end{array} + \mathrm{CH_2Cl{\cdot}COOC_2H_5} = \begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}CH_2{\cdot}COOC_2H_5}\\ \qquad\qquad |\\ \qquad\qquad \mathrm{COOC_2H_5} + \mathrm{NaCl}\end{array}$$



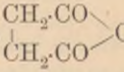
$$\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}CH_2{\cdot}COOC_2H_5}\\ \qquad\qquad |\\ \qquad\qquad \mathrm{COOC_2H_5}\end{array} + \mathrm{3KOH} = \begin{array}{l}\mathrm{CH_2{\cdot}CH_2{\cdot}COOK}\\ |\\ \mathrm{COOK}\end{array} + \mathrm{CH_3{\cdot}COOK} + \mathrm{2C_2H_5{\cdot}OH}.$$

Succinic acid is usually prepared by distilling amber from iron retorts; the dark-brown oily distillate is evaporated, and the dirty-brown crystalline residue of succinic acid purified by recrystallisation from hot dilute nitric acid.

Succinic acid crystallises in colourless prisms, melts at 180°, and sublimes readily; it has an acid, unpleasant taste, and is only sparingly soluble in cold water, alcohol, and ether. It is a dibasic acid, and its salts, the **succinates**, with the exception of those of the alkalies, are sparingly soluble or insoluble in water.

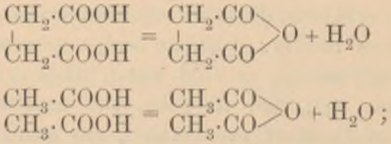
Ammonium succinate, $\mathrm{C_4H_4O_4(NH_4)_2}$, is sometimes employed in the separation of iron from manganese, as, on adding a solution of a ferric salt to ammonium succinate, the whole of the iron is converted into an insoluble basic salt, which is obtained as a buff precipitate.

The *constitution* of succinic acid is determined by its formation from ethylene dibromide, and by the fact that the only alternative formula for a dicarboxylic acid of the molecular composition $C_4H_6O_4$ must be assigned to isosuccinic acid (see below).

Succinic anhydride,  $\left.\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\right>O$, is formed when succinic acid is distilled, $C_4H_6O_4 = C_4H_4O_3 + H_2O$, but a large proportion of the acid passes over unchanged. It is prepared by heating the acid with phosphorus oxychloride for some time and then distilling, the oxychloride combining with the water which is produced, and thus preventing the reconversion of the anhydride into the acid; phosphorus pentoxide, acetyl chloride, or some other dehydrating agent may be used in the place of the oxychloride.

Succinic anhydride is a colourless, crystalline substance, and melts at 120°; it resembles the anhydrides of the fatty acids in chemical properties, and when boiled with water or alkalies, it is reconverted into succinic acid or a succinate.

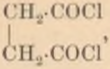
Succinic anhydride differs from the anhydrides of fatty acids in this, that it is formed from *one* molecule of the acid with elimination of one molecule of water, whereas the anhydride of a fatty acid is produced from *two* molecules of the acid in a similar manner,

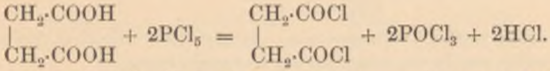


$$\begin{array}{l}CH_2\cdot COOH\\ CH_2\cdot COOH\end{array} = \left.\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\right>O + H_2O$$

$$\begin{array}{l}CH_3\cdot COOH\\ CH_3\cdot COOH\end{array} = \left.\begin{array}{l}CH_3\cdot CO\\ CH_3\cdot CO\end{array}\right>O + H_2O;$$

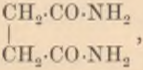
the constitution of succinic anhydride is therefore expressed by the above formula, which recalls the fact that *both* the carboxyl-groups take part in the change, as is shown by the neutral character of the anhydride. Many other dicarboxylic acids are converted into their anhydrides in a similar manner.

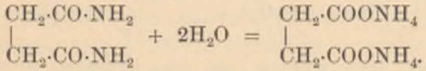
*Succinyl chloride,**  $\begin{array}{l} CH_2\cdot COCl \\ | \\ CH_2\cdot COCl \end{array}$, is formed when succinic acid is treated with two molecules of phosphorus pentachloride, the interaction recalling that which occurs in the formation of acetyl chloride,



$$\begin{array}{l} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + 2PCl_5 = \begin{array}{l} CH_2\cdot COCl \\ | \\ CH_2\cdot COCl \end{array} + 2POCl_3 + 2HCl.$$

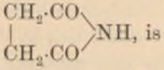
It is a colourless liquid, boils at 190°, and resembles acetyl chloride in chemical properties; like the latter, it is decomposed by water, alkalies, and hydroxy-compounds, yielding succinic acid or a succinate.

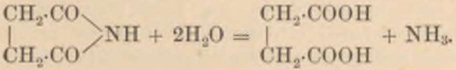
Succinamide,  $\begin{array}{l} CH_2\cdot CO\cdot NH_2 \\ | \\ CH_2\cdot CO\cdot NH_2 \end{array}$, is prepared by shaking ethyl succinate with concentrated ammonia; it is a crystalline substance, melts at 242–243°, and is only very sparingly soluble in cold water. When heated with water, it is slowly converted into ammonium succinate, just as oxamide is converted into ammonium oxalate,



$$\begin{array}{l} CH_2\cdot CO\cdot NH_2 \\ | \\ CH_2\cdot CO\cdot NH_2 \end{array} + 2H_2O = \begin{array}{l} CH_2\cdot COONH_4 \\ | \\ CH_2\cdot COONH_4. \end{array}$$

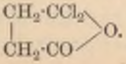
Succinamide cannot be obtained by distilling ammonium succinate, although oxamide and acetamide are produced by the distillation of the corresponding ammonium salts; this fact shows that it is not always safe to judge by analogy, since compounds very closely related in constitution may, in certain respects, behave very differently. When, in fact, ammonium succinate or succinamide is heated, it is converted into succinimide.

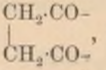
Succinimide,  $\begin{array}{l} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{array}\!\!>\!NH$, is also formed when succinic anhydride is heated in a stream of dry ammonia; it is readily soluble in water, from which it crystallises with one molecule of water, the anhydrous substance melting at 126°. When boiled with water, alkalies, or mineral acids, it is converted into succinic acid,

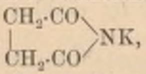


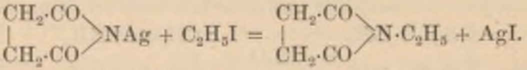
$$\begin{array}{l} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{array}\!\!>\!NH + 2H_2O = \begin{array}{l} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + NH_3.$$

---

* The constitution of succinyl chloride is not definitely established, certain facts pointing to the formula  $\begin{array}{l} CH_2\cdot CCl_2 \\ | \\ CH_2\cdot CO \end{array}\!\!>\!O.$

The constitution of succinimide, as expressed by the above formula, is based principally on its methods of formation; it may be regarded as a di-substitution product of ammonia—that is to say, as ammonia in which two atoms of hydrogen have been displaced by the divalent *succinyl*-group  $\begin{array}{l}CH_2\cdot CO\text{-}\\ |\\ CH_2\cdot CO\text{-}\end{array}$, just as an amide is a mono-substitution product of ammonia. Many other dicarboxylic acids yield *imides* similar in constitution to succinimide.

Although succinimide is not an acid in the ordinary sense of the word, has a neutral reaction, and does not decompose carbonates, it contains one atom of hydrogen displaceable by metals. When, for example, a solution of potash in alcohol is added to an alcoholic solution of succinimide, a crystalline derivative, *potassium succinimide*,  $\left.\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\right\rangle NK$, is produced; this compound interacts with silver nitrate, giving *silver succinimide*, and the latter, on treatment with ethyl iodide, yields *ethyl succinimide*,



$$\left.\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\right\rangle NAg + C_2H_5I = \left.\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\right\rangle N\cdot C_2H_5 + AgI.$$

It has already been pointed out, that hydrogen in combination with *carbon* becomes displaceable by metals when the carbon atom is directly united with two $>CO$ groups, as in ethyl acetoacetate and ethyl malonate. From the behaviour of succinimide, and of other imides, it is found that the hydrogen atom of an imido-group $>NH$ is also displaceable by metals when the imido-group is directly united with two $>CO$ groups.

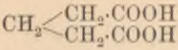
Isosuccinic acid, $CH_3\cdot CH(COOH)_2$, is isomeric with succinic acid; it may be prepared by treating an alcoholic solution of the sodium derivative of ethyl malonate with methyl iodide, and hydrolysing the product, a reaction which shows that isosuccinic acid is methyl-malonic acid,

$$CHNa(COOC_2H_5)_2 + CH_3I = CH_3\cdot CH(COOC_2H_5)_2 + NaI.$$

It is a crystalline substance, sublimes readily, and melts at 130°; it does not form an anhydride, and when heated alone, or with water, it is decomposed into propionic acid and carbon dioxide, just as malonic acid gives acetic acid and carbon dioxide,

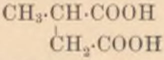
$$CH_3\cdot CH(COOH)_2 = CH_3\cdot CH_2\cdot COOH + CO_2.$$

The higher members of this series of dicarboxylic acids exist in several isomeric forms; four acids of the composition $C_5H_8O_4$, for example, are theoretically possible, and four are actually known—namely,



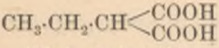
$$CH_2<\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COOH\end{matrix}$$

Normal Glutaric Acid.



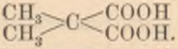
$$\begin{matrix}CH_3\cdot CH\cdot COOH\\ \quad\ \ |\ \ \\ \quad CH_2\cdot COOH\end{matrix}$$

Pyrotartaric Acid or Methylsuccinic Acid.



$$CH_3\cdot CH_2\cdot CH<\begin{matrix}COOH\\ COOH\end{matrix}$$

Ethylmalonic Acid.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}COOH\\ COOH.\end{matrix}$$

Dimethylmalonic Acid.

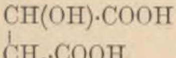
Adipic acid, $C_6H_{10}O_4$, is of some importance, as it is often obtained on oxidising fats with nitric acid ; it may be produced synthetically by heating β-iodo-propionic acid with finely divided silver, the reaction being analogous to the production of ethane by the action of sodium or zinc on methyl iodide,

$$2CH_2I\cdot CH_2\cdot COOH + 2Ag = COOH\cdot[CH_2]_4\cdot COOH + 2AgI\,;$$

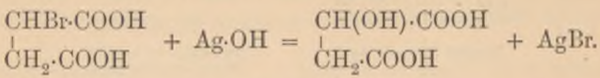
it is a crystalline substance, melting at 148°.

Hydroxydicarboxylic Acids.

With the exception of oxalic acid, the dicarboxylic acids just considered are capable of yielding substitution products in exactly the same way as the fatty acids ; malonic acid, for example, may be converted into chloromalonic acid, $CHCl(COOH)_2$, hydroxymalonic acid, $HO\cdot CH(COOH)_2$, &c.; succinic acid into bromosuccinic acid, $COOH\cdot CHBr\cdot CH_2\cdot COOH$, dibromosuccinic acid, $COOH\cdot CHBr\cdot CHBr\cdot COOH$, hydroxysuccinic acid, $COOH\cdot CH(OH)\cdot CH_2\cdot COOH$, dihydroxysuccinic acid, $COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH$, and so on. Some of these compounds—namely, the hydroxy-derivatives—occur in nature, and for this and other reasons are of considerable importance.



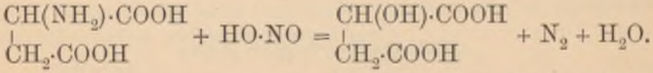
Malic acid, $\begin{matrix}CH(OH)\cdot COOH\\ |\qquad\qquad\\ CH_2\cdot COOH\end{matrix}$ or $C_4H_6O_5$, a monohydroxy-derivative of succinic acid, occurs, not only in the free state, but also in the form of salts, in many plants, more specially in (unripe) apples, from which it derives its name (*acidum malicum*), in grapes, and in the berries of the mountain ash. It may be obtained by boiling bromosuccinic acid with water and silver hydroxide, a reaction analogous to the formation of lactic acid from α-bromo-propionic acid,



$$\begin{array}{l}CHBr\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + Ag\cdot OH = \begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + AgBr.$$

As, therefore, bromosuccinic acid is easily prepared by heating succinic acid with bromine and water, and succinic acid may be synthesised in the manner already described (pp. 234–5), it is possible to obtain malic acid from its elements.

Malic acid is produced on treating amidosuccinic acid, or aspartic acid (a compound which may be obtained indirectly from asparagus*), with nitrous acid, just as lactic acid may be prepared from α-amido-propionic acid,



$$\begin{array}{l}CH(NH_2)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + HO\cdot NO = \begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + N_2 + H_2O.$$

It is usually prepared from the juice of unripe berries of the mountain ash.

The expressed juice is boiled with milk of lime and the crystalline, sparingly soluble calcium salt, $C_4H_4O_5Ca + H_2O$, which is precipitated, dissolved in hot dilute nitric acid; the calcium hydrogen malate, $(C_4H_5O_5)_2Ca + 6H_2O$, which separates in crystals, is then decomposed with the theoretical quantity of oxalic acid, and the filtered solution evaporated.

Malic acid is a crystalline, deliquescent substance, melts at 100°, and is readily soluble in water and alcohol, but only sparingly in ether; its metallic and ethereal salts are of little importance.

Many of the reactions of malic acid may be foretold from a consideration of its constitution, which is established by its methods of formation. Since, for example, it is a hydroxy-derivative of succinic acid, it is to be expected that, on reduction with hydriodic acid at a high temperature, it will be

---

* *Asparagine*, $COOH\cdot CH(NH_2)\cdot CH_2\cdot CO\cdot NH_2$, the amide of aspartic acid occurs, in asparagus; when boiled with acids or alkalies, it is converted into aspartic acid, $COOH\cdot CH(NH)_2\cdot CH_2\cdot COOH$.

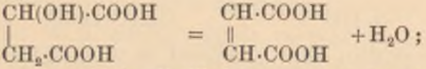
converted into succinic acid, just as lactic acid is converted into propionic acid; also that, when heated with hydrobromic acid, it will yield bromosuccinic acid, a change which would be analogous to the conversion of lactic into bromopropionic acid. Both these changes actually take place,

$$COOH{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH + 2HI = COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + H_2O + I_2$$

$$COOH{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH + HBr = COOH{\cdot}CHBr{\cdot}CH_2{\cdot}COOH + H_2O.$$

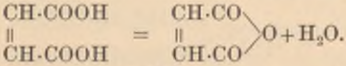
Although the malic acid obtained from plants undergoes exactly the same chemical changes as that prepared from bromosuccinic acid, and that obtained from aspartic acid, the three acids are not identical in all respects; they differ principally in their action on polarised light, a point which is referred to later (part ii.).

When malic acid is heated for a long time at 130°, it does not form malic anhydride, as might have been expected from the behaviour of succinic acid, but is slowly converted into *fumaric acid* and water,



$$\begin{array}{l} CH(OH){\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{array} = \begin{array}{l} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{array} + H_2O;$$

if now the fumaric acid be distilled, part passes over unchanged, the rest being converted into *maleïc anhydride* and water,

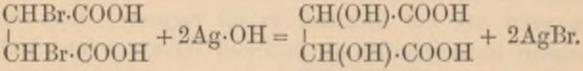


$$\begin{array}{l} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{array} = \begin{array}{l} CH{\cdot}CO \\ \| \\ CH{\cdot}CO \end{array}\!\!\!>O + H_2O.$$

Maleïc anhydride is decomposed by boiling water, giving *maleïc acid*, which has the same constitution as fumaric acid—that is to say, both compounds are unsaturated dicarboxylic acids of the constitution $COOH{\cdot}CH{:}CH{\cdot}COOH$; the existence of these two isomerides, and other cases of isomerism of a similar kind, are accounted for by the theory of stereochemical isomerism proposed by Van't Hoff and Wislicenus, for an account of which other works must be consulted.

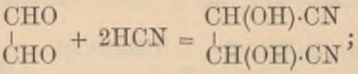
Tartaric acid, or dihydroxysuccinic acid, $C_4H_6O_6$ or $\begin{array}{l} CH(OH){\cdot}COOH \\ | \\ CH(OH){\cdot}COOH \end{array}$ is one of the most commonly occurring vegetable acids, and is contained in grapes, in the berries of the mountain ash, and in other fruits; during the (secondary) fermentation of grape-juice, which takes place in the casks, a considerable quantity of 'argol,' or impure potassium hydrogen tartrate, is deposited, and it is from this salt that the tartaric acid of commerce is obtained.

Tartaric acid can be obtained from succinic acid, and, therefore, from its elements, by reactions similar to those employed in the synthesis of malic acid; dibromosuccinic acid is first prepared by heating succinic acid with bromine (2 mols.) and water, and two hydroxyl-groups are then substituted for the two atoms of bromine in the usual way—namely, by heating the dibromo-derivative with water and silver hydroxide,*



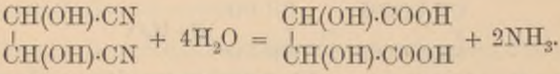
$$\begin{array}{l}\mathrm{CHBr{\cdot}COOH}\\ |\\ \mathrm{CHBr{\cdot}COOH}\end{array} + 2\mathrm{Ag{\cdot}OH} = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH(OH){\cdot}COOH}\end{array} + 2\mathrm{AgBr}.$$

Tartaric acid may also be obtained synthetically from glyoxal (p. 223), which, like other aldehydes, combines directly with hydrocyanic acid,



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array} + 2\mathrm{HCN} = \begin{array}{l}\mathrm{CH(OH){\cdot}CN}\\ |\\ \mathrm{CH(OH){\cdot}CN}\end{array};$$

the dicyanohydrin thus produced is decomposed by mineral acids, giving tartaric acid,† just as cyanoacetic acid yields malonic acid,



$$\begin{array}{l}\mathrm{CH(OH){\cdot}CN}\\ |\\ \mathrm{CH(OH){\cdot}CN}\end{array} + 4H_2O = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH(OH){\cdot}COOH}\end{array} + 2NH_3.$$

Tartaric acid is prepared on the large scale from argol. This crude, dark-red deposit is partially purified by recrystallisation from hot water, and its aqueous solution is then boiled with chalk, when insoluble calcium tartrate is precipitated, neutral potassium tartrate remaining in solution,

$$2C_4H_5O_6K + CaCO_3 = C_4H_4O_6Ca + C_4H_4O_6K_2 + CO_2 + H_2O;$$

the calcium salt is separated, and the solution treated with

---

* The tartaric acid obtained in this way is optically inactive (part ii.), and is a mixture of racemic acid and mesotartaric acid.

† This product is also optically inactive, and consists of racemic acid only.

calcium chloride, when a second precipitate of calcium tartrate is obtained,

$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl.$$

The calcium tartrate from these two operations is washed with water, and decomposed with the theoretical quantity of dilute sulphuric acid; finally, the filtered solution of the tartaric acid is evaporated to crystallisation.

Tartaric acid forms large transparent crystals, and is readily soluble in water and alcohol, but insoluble in ether; it melts at about 167°, but not sharply, owing to decomposition taking place. When heated for a long time at about 150°, it is converted into tartaric anhydride, $C_4H_4O_5$, and several other compounds, and on dry distillation it yields a variety of products, among others, pyruvic acid and pyrotartaric acid.

Tartaric acid, like other dicarboxylic acids, forms both neutral and acid salts, some of which are of considerable importance.

Normal *potassium tartrate*, $C_4H_4O_6K_2 + \frac{1}{2}H_2O$, is readily prepared by neutralising the acid, or the acid potassium salt, with potash; it is readily soluble in cold water, in which respect it differs from *potassium hydrogen tartrate*, $C_4H_5O_6K$, which is only sparingly soluble. The latter is precipitated* on adding excess of tartaric acid to a concentrated neutral solution of a potassium salt (test for potassium), and also on treating an aqueous solution of normal potassium tartrate with one equivalent of a mineral acid,

$$C_4H_4O_6K_2 + HCl = C_4H_5O_6K + KCl;$$

it is known in commerce as 'argol' or 'cream of tartar.'

Potassium sodium tartrate, or 'Rochelle salt,' $C_4H_4O_6KNa + 4H_2O$, is obtained when potassium hydrogen tartrate is neutralised with sodium carbonate and then concentrated; it forms large transparent crystals, and is employed in the preparation of Fehling's solution (p. 263).

---

* The precipitation is much hastened by shaking or stirring with a glass rod.

Calcium tartrate, $C_4H_4O_6Ca + 4H_2O$, being insoluble in water, is precipitated on adding a soluble calcium salt to a neutral solution of a tartrate; it is readily soluble in potash, but is reprecipitated on boiling the solution, a behaviour which is made use of in testing for tartaric acid.

Tartar emetic, or potassium antimonyl tartrate,

$$C_4H_4O_6K(SbO) + \tfrac{1}{2}H_2O,$$

is prepared by boiling potassium hydrogen tartrate with antimonious oxide and water; it is readily soluble in water, and is used in medicine as an emetic, and in calico-printing as a mordant.

The detection of tartaric acid or of a tartrate is based (*a*) on the behaviour of the neutral solution with calcium chloride (in the cold), and on the solubility of the precipitate in potash; (*b*) on the behaviour of the neutral solution with an ammoniacal solution of silver nitrate, from which a mirror of silver is deposited on warming; (*c*) on the fact that the solid compound rapidly chars when heated alone, giving an odour of burnt sugar; it also chars when heated with concentrated sulphuric acid, sulphur dioxide and the two oxides of carbon being evolved.

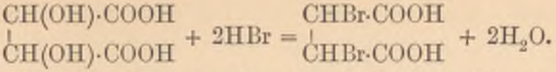
That the *constitution* of tartaric acid is expressed by the formula given above is shown by the methods of formation of the acid; it is a dihydroxy-derivative of succinic acid, just as malic acid is a monohydroxy-derivative of the same compound.

On reduction with hydriodic acid, tartaric acid is converted first into malic, then into succinic acid,

$$\begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH(OH)\cdot COOH\end{array} + 2HI = \begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + H_2O + I_2,$$

$$\begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH(OH)\cdot COOH\end{array} + 4HI = \begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + 2H_2O + 2I_2,$$

whereas, when heated with concentrated hydrobromic acid, it yields dibromosuccinic acid, as was to be expected,



$$\begin{array}{l} CH(OH){\cdot}COOH \\ | \\ CH(OH){\cdot}COOH \end{array} + 2HBr = \begin{array}{l} CHBr{\cdot}COOH \\ | \\ CHBr{\cdot}COOH \end{array} + 2H_2O.$$

It is a remarkable fact that four distinct modifications of tartaric acid are known—namely, dextrotartaric acid (the compound just described), levotartaric acid, racemic acid, and mesotartaric acid. These four compounds have the same constitution—that is to say, they are all dihydroxy-derivatives of succinic acid, as represented by the formula

$$COOH{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH\,;$$

they differ, however, in certain physical properties, as, for example, in crystalline form, solubility, &c., but more especially in their behaviour towards polarised light; the salts of the four acids exhibit similar differences. This point is referred to later (part ii.).

Dextrotartaric acid rotates the plane of polarisation to the right, *levotartaric acid* to an equal extent to the left.

Racemic acid is optically inactive; it is produced when equal quantities of the dextro- and levo-acids are dissolved in water, and the solution of the mixture allowed to crystallise. It may be obtained synthetically by heating an aqueous solution of dibromosuccinic acid with silver hydroxide, as described above; also from glyoxal. Racemic acid may be resolved into dextro- and levotartaric acids.

Mesotartaric acid, like racemic acid, is optically inactive, but it cannot be resolved into the two optically active modifications; it is formed, together with racemic acid, when dextrotartaric acid is heated for a long time with a small quantity of water at about 165°, and when dibromosuccinic acid is heated with silver hydroxide.

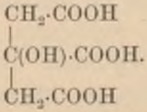
Hydroxytricarboxylic Acids.

Citric acid, $C_6H_8O_7$, like tartaric acid, occurs in the free state in the juice of many fruits; it is found in comparatively large quantities in lemons, in smaller quantities in currants, gooseberries, raspberries, and other sour fruit. It is prepared on the large scale from lemon-juice, which is first boiled, in order to coagulate and precipitate albuminoid matter, and then neutralised with calcium carbonate; the calcium salt, which is precipitated from the hot solution, is washed with water, decomposed with the theoretical quantity of dilute sulphuric acid, and the filtrate from the calcium sulphate evaporated to crystallisation.

Citric acid forms large transparent crystals which contain one molecule of water and melt at 100°, but do not lose their water until about 130°; it is readily soluble in water and fairly so in alcohol, but insoluble in ether. Like tartaric acid, and several other organic acids, it has the property of preventing the precipitation of certain metallic hydroxides from solutions of their salts. Solutions of ferric chloride and of zinc sulphate, for example, give no precipitate with potash or ammonia, if citric acid be present; on account of this property, citric acid and tartaric acid are employed in analytical chemistry and in calico-printing.

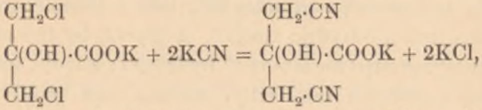
Citric acid is a tricarboxylic acid, and like phosphoric acid forms three classes of salts, as, for example, the three potassium salts, $C_6H_5O_7K_3$, $C_6H_6O_7K_2$, and $C_6H_7O_7K$, all of which are readily soluble in water. *Calcium citrate*, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, is not precipitated on adding a solution of a calcium salt to a neutral solution of a citrate, because it is readily soluble in cold water; on heating, however, a crystalline precipitate is produced, as the salt is less soluble in hot than in cold water. This behaviour, and the fact that the precipitate is insoluble in potash, distinguishes citric from tartaric acid. When heated alone, citric acid chars and gives irritating vapours, but no smell of burnt sugar is noticed; it also differs from tartaric acid, inasmuch as it does not char when gently heated with concentrated sulphuric acid until after some time.

Citric acid may be obtained synthetically by a series of reactions which show it to be a hydroxytricarboxylic acid of the constitution



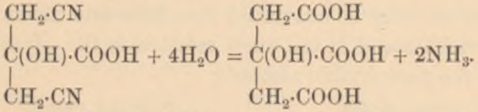
$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH. \\ | \\ CH_2\cdot COOH \end{array}$$

Symmetrical dichloracetone, $CH_2Cl\cdot CO\cdot CH_2Cl$, which may be obtained by oxidising *αα*-dichlorohydrin (p. 252) with chromic acid, like other ketones, combines with hydrogen cyanide, forming the cyanohydrin, $(CH_2Cl)_2C{<}\begin{smallmatrix}OH\\CN\end{smallmatrix}$; this product, like other compounds containing the –CN group, is converted into a carboxylic acid, $(CH_2Cl)_2C{<}\begin{smallmatrix}OH\\COOH\end{smallmatrix}$, by boiling mineral acids. The two atoms of chlorine in this acid may now be displaced by –CN groups by treating the potassium salt of the acid with potassium cyanide,



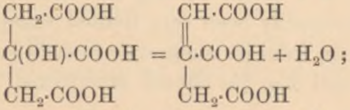
$$\begin{array}{l}CH_2Cl\\ |\\ C(OH)\cdot COOK\\ |\\ CH_2Cl\end{array} + 2KCN = \begin{array}{l}CH_2\cdot CN\\ |\\ C(OH)\cdot COOK\\ |\\ CH_2\cdot CN\end{array} + 2KCl,$$

and this dicyano-derivative may then be converted into citric acid by boiling it with hydrochloric acid,



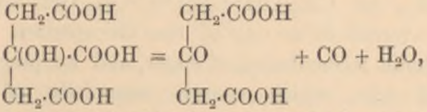
$$\begin{array}{l}CH_2\cdot CN\\ |\\ C(OH)\cdot COOH\\ |\\ CH_2\cdot CN\end{array} + 4H_2O = \begin{array}{l}CH_2\cdot COOH\\ |\\ C(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + 2NH_3.$$

This view of the constitution of citric acid is borne out by all the reactions of the compound; it is shown to contain one hydroxyl-group by the fact that ethyl citrate, $C_3H_4(OH)(COOC_2H_5)_3$, yields a monacetyl-derivative with acetyl chloride. When heated alone at 175°, citric acid is converted into *aconitic acid*, just as malic is converted into fumaric acid,



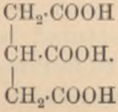
$$\begin{array}{l}CH_2\cdot COOH\\ |\\ C(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH\cdot COOH\\ \|\\ C\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + H_2O;$$

when carefully warmed with sulphuric acid, it yields *acetone-dicarboxylic* acid, with evolution of carbon monoxide,



$$\begin{array}{l}CH_2\cdot COOH\\ |\\ C(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH_2\cdot COOH\\ |\\ CO\\ |\\ CH_2\cdot COOH\end{array} + CO + H_2O,$$

and on reduction with hydriodic acid, it is converted into *tricarballylic acid*,



$$\begin{array}{l}CH_2\cdot COOH\\ |\\ CH\cdot COOH.\\ |\\ CH_2\cdot COOH\end{array}$$

CHAPTER XIV.

TRIHYDRIC AND POLYHYDRIC ALCOHOLS.

In the preceding chapter it has been shown that it is possible to convert a paraffin first into a monohydric alcohol, and then into a dihydric alcohol, or glycol, by the substitution of hydroxyl-groups for atoms of hydrogen; ethane, for example, may be converted into ethyl alcohol and ethylene glycol, propane into propyl alcohol and propylene glycol.

In a similar manner those paraffins containing three or more carbon atoms may be converted into **trihydric alcohols**, compounds which stand in the same relation to the glycols as the latter to the monohydric alcohols,

Propyl Alcohol. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ Propylene Alcohol. $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$

Propenyl Alcohol.

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

As, however, the preparation of such trihydric alcohols from the paraffins is a matter of very considerable difficulty, their study has necessarily been very limited except in the case of glycerol, which, from its occurrence in such large quantities in natural fats and oils, has offered exceptional opportunities for investigation.

Glycerol, glycerin, propenyl alcohol, or trihydroxypropane, $C_3H_5(OH)_3$, or $CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, has been previously referred to as one of the unimportant products of the alcoholic fermentation of sugar, and its preparation from fats and oils, which consist essentially of tripalmitin, tristearin, and trioleïn (ethereal salts of which glycerol is the base) has been described.

The concentrated glycerol obtained on evaporating its aqueous solution (p. 167) may be further purified and freed from water by distillation under reduced pressure, the first fractions, which contain the water, being collected separately.

Glycerol may be obtained from propane, and therefore from its elements, by treating the hydrocarbon with bromine, and then heating the tribromopropane which is thus formed with water at 170°,

$$CH_2Br{\cdot}CHBr{\cdot}CH_2Br + 3H_2O = CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 3HBr.$$

Pure glycerol is a colourless, crystalline substance, melting at 17°; as ordinarily prepared, however, it is a thick syrup of sp. gr. 1·265 at 15°, and does not solidify readily owing to the presence of water and traces of other impurities. It boils at 290° under ordinary atmospheric pressure, without decomposition; if however, it contain even traces of salts, it undergoes slight decomposition, so that in such cases it must first be distilled in a current of steam. Glycerol is very hygroscopic, and rapidly absorbs water from the air, mixing with it and also with alcohol in all proportions; it is insoluble in ether, a property which is common to most substances which contain many hydroxyl-groups. It has a distinctly sweet taste; this property also seems to be connected with the presence of hydroxyl-groups, as is shown by the fact that other trihydric alcohols, and to an even greater extent the tetra-, penta-, and hexa-hydric alcohols, are sweet, sugar-like compounds.

Glycerol readily undergoes decomposition into acroleïn (p. 256) and water,

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O;$$

this change takes place to a slight extent when impure glycerol is distilled, but much more readily and completely when glycerol is heated with potassium hydrogen sulphate, sulphuric acid, phosphorus pentoxide, or other dehydrating agents.

Glycerol, like glycol, yields a variety of oxidation products according to the conditions under which it is treated; when carefully oxidised with dilute nitric acid, it is converted into glyceric acid, a change analogous to the formation of glycollic acid from glycol,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 2O = CH_2(OH)\cdot CH(OH)\cdot COOH + H_2O;$$

under other conditions, however, it is usually oxidised to a mixture of oxalic, glycollic, and carbonic acids,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 4O = CH_2(OH)\cdot COOH + CO_2 + 2H_2O$$

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 6O = COOH\cdot COOH + CO_2 + 3H_2O.$$

Glycerol is extensively used in the preparation of nitroglycerin (p. 252) and toilet-soaps, also for filling gas-meters; it is used in smaller quantities in medicine and as an antiputrescent in preserving food materials.

Derivatives of Glycerol.—Assuming that glycerol is a trihydric alcohol of the constitution given above, its behaviour under various conditions may be foretold with a good prospect of success, if that of ethyl alcohol and of glycol be borne in mind. The fact, for example, that glycerol contains hydrogen displaceable by sodium, was only to be expected, and, just as in the case of glycol, only one atom of hydrogen is displaced at ordinary temperatures; the product, $C_3H_5(OH)_2\cdot ONa$, is hygroscopic, and is immediately decomposed by water.

Again, the behaviour of glycerol with acids is analogous to that of alcohol and of glycol; when treated with acetic acid, for example, it yields the ethereal salt, *triacetin*, or *glyceryl acetate*, and water,

$$C_3H_5(OH)_3 + 3CH_3\cdot COOH = C_3H_5(O\cdot CO\cdot CH_3)_3 + 3H_2O.$$

It is obvious, however, that triacetin is not the only ethereal salt which may be produced by the interaction of glycerol and acetic acid, because, being a *triacid* base, glycerol may yield compounds, such as *monacetin* and *diacetin*, by the displacement of only one or of two atoms of hydrogen,

$$C_3H_5(OH)_3 + CH_3{\cdot}COOH = C_3H_5(OH)_2{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O$$
$$C_3H_5(OH)_3 + 2CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + 2H_2O.$$

These three compounds may all be prepared by heating glycerol with acetic acid, the higher the temperature and the larger the relative quantity of acetic acid employed, the larger the proportion of triacetin produced. Acetic anhydride acts more readily than acetic acid, but gives the same three products.

Chlorohydrins.—The action of concentrated hydrochloric acid on glycerol is similar to that of acetic acid; at moderately high temperatures, and employing only the theoretical quantity of the acid, one atom of chlorine is substituted for one hydroxyl-group, and *glycerol chlorohydrin* is formed, just as ethylene glycol is converted into glycol chlorohydrin,

$$C_3H_5(OH)_3 + HCl = C_3H_5Cl(OH)_2 + H_2O;$$

with excess of hydrochloric acid, however, *glycerol dichlorohydrin* is produced,

$$C_3H_5(OH)_3 + 2HCl = C_3H_5Cl_2{\cdot}OH + 2H_2O.$$

Glyceryl trichloride, or propenyl trichloride,

$$CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl,$$

cannot easily be obtained by heating glycerol with hydrochloric acid, but may be prepared by treating the dichlorohydrin with phosphorus pentachloride,

$$C_3H_5Cl_2{\cdot}OH + PCl_5 = C_3H_5Cl_3 + POCl_3 + HCl;$$

it is a colourless liquid, boiling at 158°, and smells like chloroform. The name '*glyceryl*,' or *propenyl*, is sometimes given to the group of atoms $-CH_2-\overset{|}{C}H-CH_2-$, which may be regarded as a trivalent radicle.

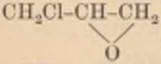
Glycerol chlorohydrin and the dichlorohydrin exist in two isomeric forms,

$CH_2(OH){\cdot}CH(OH){\cdot}CH_2Cl$ α-Chlorohydrin.	$CH_2(OH){\cdot}CHCl{\cdot}CH_2{\cdot}OH$ β-Chlorohydrin.
$CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$ αα-Dichlorohydrin.	$CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OH.$ αβ-Dichlorohydrin.

Glycerol α-chlorohydrin is formed, together with small quantities of the β-compound, when glycerol is heated at 100° with hydrochloric acid; it is an oily liquid, soluble in water. *Glycerol β-chlorohydrin* can be obtained by treating allyl alcohol (p. 254) with hypochlorous acid.

Glycerol αα-dichlorohydrin is produced when glycerol is heated with a solution of hydrogen chloride in glacial acetic acid; it is a mobile liquid, only sparingly soluble in water, and on oxidation with chromic acid it yields symmetrical dichloracetone, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$.

Glycerol αβ-dichlorohydrin is obtained on treating allyl alcohol (p. 254) with chlorine; on oxidation with nitric acid it gives αβ-dichloropropionic acid, $CH_2Cl{\cdot}CHCl{\cdot}COOH$. When treated with potash, both αα- and αβ-chlorohydrin yield *epichlorhydrin*,



$$\underset{\diagdown O \diagup}{CH_2Cl{-}CH{-}CH_2}$$

(compare ethylene oxide, p. 223).

When glycerol is treated with acetyl chloride, it does not yield triacetin, as might have been expected, but *diacetylchlorohydrin*,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5Cl(O{\cdot}CO{\cdot}CH_3)_2 + H_2O + HCl.$$

This behaviour, although apparently abnormal, is not really so; in the first place, the glycerol is converted into a *diacetyl*-derivative in the usual manner,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + 2HCl,$$

and the hydrogen chloride produced during the reaction then acts on the diacetyl-derivative just as it does on other monohydric alcohols,

$$C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + HCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2Cl + H_2O.$$

Ethylene glycol and other di- and poly-hydric alcohols show a similar behaviour.

Nitro-glycerin, glyceryl trinitrate, or propenyl trinitrate, $C_3H_5(O{\cdot}NO_2)_3$, is an ethereal salt of glycerol and nitric acid. It is prepared by slowly adding pure glycerol drop by drop, or in a fine stream, to a *well-cooled* mixture of concentrated sulphuric acid (4 parts) and nitric acid of sp. gr. 1·52 (1 part); the solution is run into cold water, and the nitro-glycerin, which is precipitated as a heavy oil, washed well with water and dried.

It is a colourless oil of sp. gr. 1·6, has a sweetish taste, and is poisonous; although readily soluble in ether, it is only sparingly soluble in alcohol, and insoluble in water, so that, as regards solubility, its behaviour is almost the exact opposite of that of glycerol, a fact which shows the influence of hydroxyl-groups in a very distinct manner. It explodes violently when suddenly heated, or when subjected to percussion, but when ignited with a flame it burns without explosion, and is even rather difficult to ignite.

Nitro-glycerin is readily hydrolysed by boiling alkalies, being converted into glycerol and a nitrate,*

$$C_3H_5(O{\cdot}NO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3\,;$$

on reduction with ammonium sulphide (p. 94) it yields glycerol and ammonia,

$$C_3H_5(O{\cdot}NO_2)_3 + 12H_2S = C_3H_5(OH)_3 + 3NH_3 + 6H_2O + 12S.$$

In these two reactions the behaviour of nitro-glycerin is exactly analogous to that of ethyl nitrate, $CH_3{\cdot}CH_2{\cdot}O{\cdot}NO_2$, but quite different from that of nitro-ethane, $CH_3{\cdot}CH_2{\cdot}NO_2$, which, as previously stated, is not decomposed by alkalies, and on reduction yields amido-ethane or ethylamine; since, moreover, groups of atoms in a similar state of combination show a similar behaviour, it is clear that nitro-glycerol, like ethyl nitrate, is an ethereal salt, and not a nitro-derivative; in other words, the nitro groups $(-NO_2)$ in nitro-glycerin are directly combined with oxygen, and not with carbon. The name nitro-glycerin is, therefore, misleading, but, being so well known, it is usually employed instead of the more correct names, glyceryl trinitrate, or propenyl trinitrate.

Nitro-glycerin is extensively employed as an explosive, sometimes alone, sometimes in the form of *dynamite*, which is simply a mixture of nitro-glycerin and kieselguhr, a porous, earthy powder, consisting of the siliceous remains of small marine animals; the object of absorbing the nitro-glycerin with kieselguhr is to render it less liable to explode, and, consequently, safer to handle and to transport. The presence of acids in nitro-glycerin make it liable to undergo spontaneous decomposition and explosion; great care must, therefore, be taken in washing it thoroughly. Nitro-glycerin

---

* An alkali nitrite is also formed owing to reduction, the glycerol undergoing partial oxidation.

is also employed, mixed with gun-cotton (p. 274), as blasting-gelatine, and in the preparation of smokeless gunpowder; it is used in medicine in cases of heart disease.

Unsaturated Compounds related to Glycerol.

Allyl alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, is formed when anhydrous glycerol is slowly heated with crystallised oxalic acid until the temperature rises to about 260°, and the mixture then distilled; in the first place, the glycerol is converted into monoformin, with evolution of carbon dioxide, water, and a little formic acid (p. 144),

$$C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5(OH)_2{\cdot}O{\cdot}CHO + CO_2 + H_2O$$
$$C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O = C_3H_5(OH)_3 + H{\cdot}COOH,$$

but, on further heating, the rest of the monoformin undergoes decomposition, and allyl alcohol collects in the receiver,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CHO = CH_2(OH){\cdot}CH{:}CH_2 + CO_2 + H_2O.$$

Allyl alcohol is also produced when acroleïn (acraldehyde, p. 256) is treated with nascent hydrogen, a change which is exactly analogous to the formation of alcohol from aldehyde,

$$CH_2{:}CH{\cdot}CHO + 2H = CH_2{:}CH{\cdot}CH_2{\cdot}OH.$$

It is a colourless, neutral liquid, boils at 96–97°, and has a very irritating smell; it is miscible with water, alcohol, and ether in all proportions.

Allyl alcohol is an unsaturated compound, and has, therefore, not only the properties of a primary alcohol, but also those of unsaturated compounds in general. Its alcoholic character is shown by the following facts: it dissolves sodium with evolution of hydrogen,

$$2CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2Na = 2CH_2{:}CH{\cdot}CH_2{\cdot}ONa + H_2,$$

forms ethereal salts with acids,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + HCl = CH_2{:}CH{\cdot}CH_2Cl + H_2O,$$

and on oxidation is converted, first into acroleïn, then into acrylic acid,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + O = CH_2{:}CH{\cdot}CHO + H_2O$$
$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2O = CH_2{:}CH{\cdot}COOH + H_2O.$$

In all these reactions its behaviour is so closely analogous to that of ethyl alcohol and other primary alcohols, that it must be concluded that allyl alcohol contains the group $-CH_2{\cdot}OH$. That it is an unsaturated compound is shown by its behaviour with chlorine and bromine, with which it combines directly, forming a dichloro- or dibromohydrin, isomeric with the corresponding compounds obtained by treating glycerol with halogen acids,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + Br_2 = CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH.$$

Allyl iodide, $CH_2{:}CH{\cdot}CH_2I$, is an unsaturated ethereal salt, related to allyl alcohol in the same way as ethyl iodide to ethyl alcohol. It may be obtained by treating allyl alcohol with iodine and phosphorus, but is more conveniently prepared directly from glycerol.

For this purpose iodine (10 parts) is dissolved in glycerol (15 parts), and small pieces of dry phosphorus (6 parts) added from time to time, the mixture being very gently warmed at first to start the reaction; the operation is conducted in a large retort connected with a condenser, a stream of carbon dioxide being passed through the apparatus during the experiment. It is probable that the glycerol is first converted into the tri-iodide, $CH_2I{\cdot}CHI{\cdot}CH_2I$, which then undergoes decomposition into iodine and allyl iodide; if excess of phosphorus and iodine be employed, isopropyl iodide is formed,

$$CH_2{:}CH{\cdot}CH_2I + HI = CH_2{:}CH{\cdot}CH_3 + I_2.$$
$$CH_2{:}CH{\cdot}CH_3 + HI = CH_3{\cdot}CHI{\cdot}CH_3.$$

Allyl iodide is a colourless liquid, boiling at 101°, and has an odour of garlic; it resembles ethyl iodide in many respects, but has also the properties of an unsaturated compound. When heated with potassium sulphide in alcoholic solution, it is converted into allyl sulphide (see below), just as ethyl iodide gives ethyl sulphide,

$$2CH_2{:}CH{\cdot}CH_2I + K_2S = (CH_2{:}CH{\cdot}CH_2)_2S + 2KI.$$

Allyl bromide, $CH_2{:}CH{\cdot}CH_2Br$, may be obtained by treating allyl alcohol with phosphorus tribromide; it is a heavy liquid, and boils at 70–71°.

Allyl sulphide occurs in nature in many Cruciferæ, but is especially abundant in garlic (*Allium sativum*), from which it is obtained by distilling the macerated plant with water; it is therefore known as *oil of garlic.* It is a colourless, very unpleasant-smelling liquid, boiling at 140°. Another allyl derivative—namely, allyl isothiocyanate, occurs in nature in considerable quantities in black mustard seeds, and is known as *oil of mustard* (p. 289).

Acroleïn, or **acraldehyde,** $CH_2{:}CH{\cdot}CHO$, is formed during the partial combustion of fats, and when impure glycerol is distilled under ordinary pressure; also when allyl alcohol undergoes oxidation. It is prepared by distilling glycerol with some dehydrating agent, potassium hydrogen sulphate being usually employed,

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O.$$

Acroleïn is an aldehyde, and is related to allyl alcohol in the same way as aldehyde to ethyl alcohol; it is a colourless liquid, boils at 52°, and has an exceedingly irritating and disagreeable odour, like that of partially burnt fat; it produces sores when brought on to the skin, and its vapours cause a copious flow of tears. Like other aldehydes, it reduces ammoniacal solutions of silver oxide with formation of a mirror, and readily undergoes polymerisation into an amorphous, brittle substance named *disacryl;* it also gives the aldehyde reaction with rosaniline, but, on the other hand, it does not combine with sodium hydrogen sulphite. On reduction it yields allyl alcohol; on exposure to the air, or on treatment with silver oxide, it readily undergoes oxidation, yielding acrylic acid. That it is an unsaturated compound is shown by the fact that it combines directly with bromine, forming an additive-product of the composition

$$CH_2Br{\cdot}CHBr{\cdot}CHO.$$

Crotonaldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$ is a homologue of acraldehyde; it is obtained on heating acetaldehyde with dilute hydrochloric acid, or with a solution of zinc chloride, aldol being formed as an intermediate product (p. 124),

$$2CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$
$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O.$$

It boils at 104–105°, and closely resembles acraldehyde in properties; on reduction it yields, first, crotonalcohol, $CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$, and then butyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; on oxidation it gives crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$.

Acrylic acid, $CH_2{:}CH{\cdot}COOH$, the oxidation product of allyl alcohol and of acroleïn, may also be obtained from hydracrylic acid (p. 227), which on distillation loses the elements of water,

$$CH_2(OH){\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + H_2O,$$

a change analogous to the formation of ethylene from alcohol; acrylic acid is also produced when β-bromopropionic acid is treated with alcoholic potash, just as ethylene is formed from ethyl bromide,

$$CH_2Br{\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + HBr.$$

Acrylic acid is a liquid at ordinary temperatures, and boils at 139–140°; it smells like acetic acid, is miscible with water in all proportions, and its solutions have an acid reaction. It is a monocarboxylic acid, and forms metallic and ethereal salts just as do the fatty acids; it differs from the latter, however, in being an unsaturated compound, as is shown by its forming additive-products. It combines directly with bromine, giving dibromopropionic acid,

$$CH_2{:}CH{\cdot}COOH + Br_2 = CH_2Br{\cdot}CHBr{\cdot}COOH;$$

with halogen acids, yielding β-halogen derivatives* of propionic acid,

$$CH_2{:}CH{\cdot}COOH + HCl = CH_2Cl{\cdot}CH_2{\cdot}COOH,$$

and with nascent hydrogen, giving propionic acid,

$$CH_2{:}CH{\cdot}COOH + 2H = CH_3{\cdot}CH_2{\cdot}COOH.$$

---

* This behaviour is abnormal, as usually the halogen combines with that carbon atom which is combined with the *least* number of hydrogen atoms (p. 80).

Crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$, the next homologue of acrylic acid, may be obtained by methods similar to those mentioned in the case of acrylic acid—namely, by the oxidation of crotonalcohol or of crotonaldehyde, by the distillation of β-hydroxybutyric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, and by treating α-bromobutyric acid with alcoholic potash. It melts at 72°, and resembles acrylic acid in general behaviour.

Oleïc acid, $C_{18}H_{34}O_2$, one of the higher members of the acrylic series, has been previously mentioned (p. 168).

Polyhydric Alcohols.

The existence of tetra-, penta-, and hexa-hydric alcohols, which theoretically should be obtained from the higher paraffins by the substitution of four, five, or six hydroxyl-groups for an equivalent quantity of hydrogen, just as glycerol is derived from propane, was of course to be expected; nevertheless, owing to the difficulties which would be met with in the actual synthesis of such complex compounds from the paraffins, or by other methods, it is highly probable that they might still have been unknown, were it not that many of them occur in nature, and may also be prepared from products of the vegetable kingdom by simple processes.

Erythritol, $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, for example, is a tetrahydric alcohol which occurs in many lichens, and in certain seaweeds. *Arabitol* and *xylitol* are pentahydric alcohols of the constitution

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH;$$

they may be respectively prepared by reducing *arabinose* and *xylose*, two sugar-like compounds which occur in various vegetable products, with sodium amalgam. Hexahydric alcohols, such as *mannitol* and *dulcitol*, also occur in nature.

Mannitol,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

is found in manna, the dried sap of a species of ash, from which it may be extracted with boiling alcohol; it may also be obtained by reducing levulose, mannose, or dextrose (p. 264) with sodium amalgam. It is a colourless, crystalline substance, has a very sweet taste, and is readily soluble in water and hot alcohol, but insoluble in ether. When carefully oxidised with nitric acid it yields the aldehyde, mannose, and the ketone, levulose (p. 265); on reduction with hydriodic acid it is converted into (secondary) hexyl iodide, a derivative of normal hexane,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 11HI =$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHI{\cdot}CH_3 + 6H_2O + 5I_2.$$

This conversion of mannitol into a derivative of *normal* hexane is a fact of great importance, as it throws much light on the constitution, not only of mannitol, but also of mannose, levulose, and dextrose; since these compounds yield mannitol on reduction, it is proved that they also are derivatives of *normal* hexane, and not of some secondary or tertiary paraffin, isomeric with hexane.

The constitution of mannitol is further established by the usual methods; that it contains six hydroxyl-groups is shown by the fact that it yields a hexacetyl-derivative, $C_6H_8(O{\cdot}CO{\cdot}CH_3)_6$, and a hexanitrate, $C_6H_8(O{\cdot}NO_2)_6$. As, moreover, it is known from experience that in all stable hydroxy-compounds one carbon atom does not unite with more than one hydroxyl-group, each of the six hydroxyl-groups in mannitol must be combined with a different carbon atom.

Mannitol, like tartaric acid, exists in several modifications, which differ principally in their optical properties.

CHAPTER XV.

THE CARBOHYDRATES.

The compounds usually known as the carbohydrates do not form a well-defined group, inasmuch as the term is applied to substances widely different both in properties and in constitution; they may, however, be roughly described as naturally occurring substances, composed of carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen is the same as in water. The word carbohydrate was originally given to such compounds because they might be represented as composed of carbon and water in different proportions: grape-sugar, $C_6H_{12}O_6$, for example, might be represented as $6C + 6H_2O$; cane-sugar, $C_{12}H_{22}O_{11}$, as $12C + 11H_2O$; and starch, $C_6H_{10}O_5$, as $6C + 5H_2O$.

The carbohydrate group is one of the most important in organic chemistry, as it includes all the principal constituents of plants, except water. To this group belong (*a*) the *sugars*, substances which are of great value as food-stuffs and as sources of alcohol, and to which the sweetness of fruits is due; (*b*) the *starches*, the most abundant of all foods; and (*c*) the *celluloses*, substances of which the cell membranes and tissues of plants are principally composed.

The Sugars.

Cane-sugar, or saccharose, $C_{12}H_{22}O_{11}$, is very widely distributed in nature; it occurs in large quantities in the sugar-cane (15–20 per cent.) and in beetroot (some kinds of which contain as much as 16 per cent.), in smaller quantities in strawberries, pine-apples, and other fruits.

The sugar-cane and beetroot are the raw materials from which practically the whole of the sugar of commerce is manufactured, the processes of extraction being much the same in both cases, and requiring expensive apparatus in order to obtain the largest possible yield of crystallised sugar.

The material is crushed in hydraulic presses, and the expressed juice boiled with about 1 per cent. of milk of lime, in order to neutralise acids present, and to coagulate the vegetable albumin which is always contained in the extract. The solution is treated with carbon dioxide, in order to precipitate any excess of lime, decolourised as far as possible by boiling with animal charcoal, and filtered; it is then evaporated under reduced pressure in an apparatus heated with steam, until the syrup is of such a consistency that it deposits crystals on cooling. These crystals are separated from the brown mother-liquor (*molasses*, or treacle) in a centrifugal machine, and purified by recrystallisation from water.

The molasses still contains about 50 per cent. of sugar which does not crystallise from the syrup even on further evaporation, owing to the presence of impurities; nearly the whole of this sugar, however, can be profitably extracted, by adding strontium hydroxide, and separating the insoluble strontium saccharosate (see below) from the dark mother-liquor by filtration. This precipitate is suspended in water, decomposed by passing carbon dioxide, and the filtrate from the strontium carbonate evaporated to a syrup; the impurities having now been removed, the cane-sugar separates in the crystalline form. The annual production of cane-sugar is about 5–6 million tons.

Cane-sugar crystallises from water in hard four-sided prisms, and is soluble in one-third of its weight of water at ordinary temperatures, but only sparingly soluble in alcohol. It melts at about 160–161°, and on cooling does not immediately crystallise, but solidifies to a pale-yellow, glassy mass, called *barley-sugar*, which, however, on long standing, gradually becomes opaque and crystalline. At about 200–210° cane-sugar loses water, and is gradually converted into a brown mass called *caramel*, which is largely used for colouring liqueurs, soups, gravies, &c.

Warm concentrated sulphuric acid chars cane-sugar; if a strong aqueous solution of sugar be mixed with an equal volume of concentrated sulphuric acid, the sugar blackens and the carbonaceous product swells up enormously, owing to the evolution of steam, carbon dioxide, sulphur dioxide, and other gases.

Cane-sugar is *dextrorotatory*—that is, its solutions have the property of rotating the plane of polarisation of light to the *right*,* and the strength of a solution of sugar may be estimated by determining the amount of rotation which it causes. The apparatus used for this purpose is called a *saccharimeter*, and the operation itself, *saccharimetry*.

If a trace of a mineral acid be added to a solution of cane-sugar, and the liquid warmed or simply allowed to stand, the

---

* $[\alpha]_D = +66{\cdot}5^\circ$. For a description of the action of sugar solutions on polarised light, works on physics must be consulted.

cane-sugar is hydrolysed, with formation of equal quantities of dextrose (see below) and levulose (p. 265),

$$\underset{\text{}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

This process is usually called *inversion*, and the mixture of dextrose and levulose is called *invert sugar*. Invert sugar comes into the market as a somewhat brownish-coloured mass, and is extensively used in the manufacture of preserves, confectionery, &c., as well as for the preparation of alcohol. Prolonged boiling with hydrochloric acid (sp. gr. 1·1) converts cane-sugar into levulinic acid (p. 196).

Cane-sugar does not reduce Fehling's solution (p. 263), and it does not directly undergo alcoholic fermentation with yeast; when, however, it is left for some time in contact with yeast, a ferment, *invertase*, which is present in the yeast converts it into dextrose and levulose, and then alcoholic fermentation sets in. When boiled with acetic anhydride and sodium acetate, cane-sugar is converted into *octacetylsaccharose*, $C_{12}H_{14}O_3(C_2H_3O_2)_8$, and therefore contains eight hydroxyl-groups; its constitution, however, has not yet been clearly established.

Cane-sugar combines readily with certain hydroxides, such as those of calcium, barium, and strontium, with formation of metallic compounds called *saccharosates*, in which one or more of the hydroxyl-groups in the sugar is displaced by the metal or hydroxide. These saccharosates are produced by simply mixing the sugar solution with the metallic hydroxide. They are readily decomposed by much water and by carbon dioxide into sugar and the hydroxide or carbonate of the metal.

Strontium saccharosate, $C_{12}H_{20}(SrOH)_2O_{11}$, is a granular substance of great commercial importance, owing to its use in separating sugar from molasses (p. 261).

Dextrose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_4^*\cdot CHO$, also known as **glucose**, or **grape-sugar**, is found in large quantities in grapes—hence its name, grape-sugar; when the grapes are dried in the sun, in the preparation of raisins, the dextrose

---

[*] Compare foot-note, p. 134.

in the juice is deposited in hard, brownish-coloured nodules. Dextrose is more frequently met with associated with levulose as invert sugar, mixtures of these sugars occurring in the juice of a great many sweet fruits, and also in the roots and leaves of plants, and in honey. Pure dextrose may be prepared from cane-sugar by inversion with acids, and recrystallisation of the product (invert sugar) from alcohol, when the more readily soluble levulose remains in solution.

Alcohol (1 litre, 90 per cent.) is mixed with concentrated hydrochloric acid (40 c.c.), heated at about 50°, and powdered cane-sugar (350 grams) added in small portions, the whole being well stirred during the operation. The mixture is now kept for two hours at this temperature, then allowed to cool, and crystallisation promoted by stirring, or, better, by the addition of a crystal of dextrose. After some days the crystals are collected and purified by recrystallisation from 80 per cent. alcohol.

Dextrose crystallises with 1 mol., H_2O, in warty masses which melt at 86°, the anhydrous substance melting at 146°; it is almost insoluble in absolute alcohol, but soluble in about its own weight of water at ordinary temperatures, the solution being less sweet than that of cane-sugar. It is not carbonised when gently warmed with sulphuric acid (distinction from cane-sugar); its solutions are dextrorotatory,* hence the name dextrose.

Dextrose is a strong reducing agent, and quickly precipitates gold, silver, and platinum from solutions of their salts on warming. If a solution of dextrose be mixed with potash, and then copper sulphate added, a deep blue solution is obtained, and on gently warming, a bright red precipitate of cuprous oxide, Cu_2O, is deposited, the solution becoming colourless if sufficient dextrose be added; as, moreover, a given quantity (1 molecule) of dextrose always reduces exactly the same quantity (approximately 5 molecules) of cupric to cuprous oxide, this behaviour affords a method of estimating sugar by simple titration.

The solution used for this purpose is known as *Fehling's solution*, and as it decomposes on keeping, it is best prepared as required by

---

* $[\alpha]_D = +52.5°$.

mixing equal quantities of the following solutions: (1) 34·6 grams of crystallised copper sulphate, made up to 500 c.c. with water; (2) 173 grams of Rochelle salt, and 60 grams of sodium hydrate, made up to 500 c.c. with water. 10 c.c. of the deep blue solution thus obtained are completely reduced—that is, the colour discharged —by 0·05 gram of dextrose, or by 0·0475 gram of cane-sugar (after inversion).

Dextrose ferments readily with yeast in dilute aqueous solution at a temperature of about 20–30°, yielding principally alcohol and carbon dioxide,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2,$$

but at the same time fusel-oil and small quantities of glycerol, succinic acid, and other substances are formed.

Like cane-sugar, dextrose readily combines with certain metallic hydroxides, forming *glucosates*, such as calcium glucosate, $C_6H_{11}(CaOH)O_6$, and barium glucosate, $C_6H_{11}(BaOH)O_6$; these compounds are readily soluble in water, and are decomposed by carbonic acid, with regeneration of the sugar.

Dextrose has the properties of an *aldehyde*, and at the same time those of a *polyhydric alcohol;* its constitution may be expressed by the formula

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO,$$

which is based on a number of facts, only a few of which can be given here.

On reduction with sodium amalgam in aqueous solution, it is converted into the primary alcohol, mannitol,

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CHO + 2H = CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH;$$

whereas, when oxidised with bromine water, it yields *gluconic acid*, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot COOH$. These changes are clearly analogous to those undergone by acetaldehyde, and the fact that gluconic acid contains the same number of carbon atoms as dextrose, shows that the latter is an aldehyde and not a ketone (p. 139). Powerful oxidising agents, such as nitric acid, convert dextrose into *saccharic acid,*

$COOH\cdot[CH\cdot OH]_4\cdot COOH$, the $-CH_2\cdot OH$ group, as well as the $-CHO$ group, undergoing oxidation; ultimately it is resolved into oxalic acid. Dextrose, like other aldehydes, interacts readily with hydroxylamine and with phenylhydrazine, with formation of the oxime, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}NOH$, and the hydrazone (p. 133),

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}N_2H\cdot C_6H_5.$$

Dextrose gives a pentacetyl derivative, $C_5H_6(C_2H_3O_2)_5\cdot CHO$, when warmed with acetic anhydride and a little zinc chloride, showing that it contains five hydroxyl-groups.

Levulose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH$, also called **fructose,** or fruit-sugar, occurs, together with dextrose, in most sweet fruits and in honey; it may be prepared from invert sugar by taking advantage of the fact that its lime compound is sparingly soluble in water, whereas that of dextrose is readily soluble.

Invert sugar (10 grams) is dissolved in water (50 c.c.), the solution well cooled with ice, and slaked lime (6 grams) added in small quantities at a time, with constant stirring. The sparingly soluble lime compound of levulose is collected on a filter, washed with a little water, well pressed, and then decomposed by suspending it in water, and passing carbon dioxide; the filtrate yields, on evaporation, nearly pure fructose as a transparent, uncrystallisable syrup.

Pure crystallised levulose is prepared from *inulin*, $(C_6H_{10}O_5)_n$, a starch which occurs in many plants, and especially in dahlia tubers; for this purpose the inulin is simply boiled with dilute sulphuric acid,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

An aqueous solution of inulin is heated on a water-bath for one hour, with a few drops of sulphuric acid; the sulphuric acid is then removed by precipitation with barium hydroxide, and the solution evaporated at 80°. On the addition of a crystal of levulose the syrup slowly solidifies, and the crystals may then be purified by recrystallisation from alcohol.

Levulose separates from alcohol in small hard crystals, and melts at 95°; it is more soluble in water and alcohol than dextrose, and its taste is just about as sweet as that of the latter. Levulose is *levorotatory**—hence its name ; it rotates the plane of polarisation to the left to a somewhat greater extent than dextrose to the right—hence invert sugar, which consists of equal parts of dextrose and levulose, is slightly levorotatory. When, therefore, a solution of cane-sugar, which is dextrorotatory, is boiled with acids, the resulting solution of invert sugar is levorotatory—that is to say, the direction of the rotation has been reversed or 'inverted.'

Levulose ferments with yeast, but less rapidly than dextrose, consequently, in fermenting a solution of invert sugar, the dextrose is decomposed first, and the operation can be stopped at a point when the solution contains only levulose ; by the further action of yeast, however, the levulose also undergoes fermentation, yielding the same products as dextrose (p. 264).

Levulose has even stronger reducing powers than dextrose, and reduces Fehling's solution more rapidly, although to exactly the same extent as dextrose ; this behaviour is due to the presence of the group $-CO{\cdot}CH_2{\cdot}OH$, as all substances (ketonic alcohols) which contain this group are strong reducing agents.

Levulose has the properties of a *ketone*, as well as those of a *polyhydric alcohol*, and its constitution may be expressed by the formula

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CO{\cdot}CH_2{\cdot}OH.$$

It is reduced by sodium amalgam in aqueous solution more readily than dextrose, mannitol being formed,

$$CH_2(OH){\cdot}[CH{\cdot}OH]_3{\cdot}CO{\cdot}CH_2{\cdot}OH + 2H = CH_2(OH){\cdot}[CH{\cdot}OH]_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

just as acetone, under similar treatment, yields isopropyl alcohol. When oxidised with nitric acid or bromine water, it yields tartaric acid and glycollic acid,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}\,\vdots\,CO{\cdot}CH_2{\cdot}OH + 4O =$$
$$COOH{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH + COOH{\cdot}CH_2{\cdot}OH + H_2O;$$

---

* $[a]_D = -93^\circ$.

whereas, when boiled with mercuric oxide in aqueous solution, it is oxidised to trihydroxybutyric acid and glycollic acid,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot \vdots CO\cdot CH_2\cdot OH + 2O =$$
$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH + COOH\cdot CH_2\cdot OH.$$

This behaviour shows that levulose is a ketone, and not an aldehyde; it does not, like dextrose, yield, on oxidation, an acid containing the same number of carbon atoms, but is decomposed in a variety of ways which throw considerable light on its constitution.

Levulose, like other ketones, interacts with hydroxylamine (yielding the oxime, $CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(NOH)\cdot CH_2\cdot OH$), and with phenylhydrazine; it also combines directly with hydrocyanic acid. When digested with acetic anhydride and zinc chloride, levulose yields a pentacetyl derivative, $C_6H_7O(C_2H_3O_2)_5$, a fact which shows that it contains five hydroxyl-groups.

Dextrose and levulose have recently been prepared synthetically from formaldehyde and also from glycerol. When an aqueous solution of formaldehyde is treated with milk of lime at ordinary temperatures, a sugar-like substance called *formose* (or methylenitan) is produced. Formose consists of a mixture of various sugars of the composition $C_6H_{12}O_6$, produced by the polymerisation of formaldehyde,

$$6CH_2O = C_6H_{12}O_6.$$

From this mixture E. Fischer isolated a sugar which he called α-acrose, and from which, by a series of operations, too numerous to discuss here, he succeeded in preparing both dextrose and levulose.

Action of Phenylhydrazine on Dextrose (Glucose) and Levulose (Fructose).

When the sugars glucose and fructose are treated with phenylhydrazine (1 mol.), they yield hydrazones, just as do other aldehydes and ketones,

$$*\underset{\text{Glucose.}}{M{\cdot}CH(OH){\cdot}CHO} + C_6H_5{\cdot}NH{\cdot}NH_2 = \underset{\text{Glucosephenylhydrazone.}}{M{\cdot}CH(OH){\cdot}CH{:}N_2HC_6H_5} + H_2O.$$

$$\underset{\text{Fructose.}}{M{\cdot}CO{\cdot}CH_2{\cdot}OH} + C_6H_5{\cdot}NH{\cdot}NH_2 = \underset{\text{Fructosephenylhydrazone.}}{M{\cdot}C(N_2HC_6H_5){\cdot}CH_2{\cdot}OH} + H_2O.$$

These hydrazones, when heated with excess of phenylhydrazine, undergo oxidation, the $—CH{\cdot}OH$ group of the one and the $—CH_2{\cdot}OH$ group of the other being transformed into $—CO$ and $—CHO$ respectively by loss of hydrogen, some of the phenylhydrazine being reduced to aniline (part ii.) and ammonia,

$$C_6H_5{\cdot}NH{\cdot}NH_2 + 2H = C_6H_5{\cdot}NH_2 + NH_3.$$

These oxidation products of the hydrazones then combine with a second molecule of phenylhydrazine, with formation of *osazones*,

$$\begin{array}{cc} M{\cdot}CH(OH){\cdot}CH{:}N_2HC_6H_5 & M{\cdot}CO{\cdot}CH{:}N_2HC_6H_5 \\ M{\cdot}C(N_2HC_6H_5){\cdot}CH_2{\cdot}OH & M{\cdot}C(N_2HC_6H_5){\cdot}CHO \\ \textit{Hydrazones.} & \textit{Intermediate Oxidation Products.} \end{array}$$

$$\underset{\textit{Osazone.}}{M{\cdot}C(N_2HC_6H_5){\cdot}CH{:}N_2HC_6H_5.}$$

Although the hydrazones of glucose and fructose are quite distinct substances, they yield one and the same osazone; this fact proves that the two sugars differ in constitution only as regards the two terminal groups.

Many other sugars show a similar behaviour, and yield hydrazones and osazones according as 1 mol. or excess of phenylhydrazine is employed. The hydrazones are usually readily soluble in water, but the osazones are only sparingly soluble; the latter are therefore of the greatest service, not only in the detection and identification of a sugar, but also as offering a means of isolating it from a mixture.

When treated with strong hydrochloric acid, the osazones are decomposed with separation of phenylhydrazine hydrochloride, and formation of *osones*, substances which contain the group $—CO{\cdot}CHO$, and which are therefore both ketones and aldehydes,

$$\underset{\text{Glucosazone.}}{M{\cdot}C(N_2HC_6H_5){\cdot}CH{:}N_2HC_6H_5} + 2HCl + 2H_2O =$$

$$\underset{\text{Glucosone.}}{M{\cdot}CO{\cdot}CHO} + 2C_6H_5NH{\cdot}NH_2,\ HCl.$$

As, moreover, osones may be reduced to sugars with the aid of zinc dust and acetic acid, the sugars may be prepared indirectly

---

* The group $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH)–$, which takes no part in the reaction, is represented by M, for the sake of clearness.

from the osazones. A given osazone does not, however, necessarily yield the sugar from which it was derived; glucosazone, for example, yields first glucosone and then fructose (the group $-CO\cdot CHO$ in the osone being converted into $-CO\cdot CH_2\cdot OH$),

$$\underset{\text{Glucosone.}}{M\cdot CO\cdot CHO} + 2H = \underset{\text{Fructose.}}{M\cdot CO\cdot CH_2\cdot OH}.$$

This series of reactions affords, therefore, a means of converting glucose into fructose.

Maltose, $C_{12}H_{22}O_{11}$, is produced, together with dextrin (p. 272), by the action of malt on starch; this change may be roughly represented by the equation

$$3(C_6H_{10}O_5)_n + nH_2O = nC_{12}H_{22}O_{11} + nC_6H_{10}O_5,$$

and, as already stated in describing the manufacture of alcohol and spirituous liquors, it is brought about by an unorganised ferment, *diastase*, which is contained in the malt.

Preparation of Maltose.—Potato starch (1 kilo) is heated with water (4 litres) on a water-bath until it forms a paste, and after cooling to 60°, malt (60 grams) is added, the mixture being kept at this temperature for an hour. The solution is then heated to boiling, filtered, and evaporated to a syrup, which crystallises on the addition of a crystal of maltose; the crude substance is purified by washing with alcohol, and then recrystallising from this solvent.

Maltose crystallises with one molecule of water in needles, and is very soluble in water, the solution being strongly dextrorotatory;* it reduces Fehling's solution, but only about two-thirds as much as the same weight of dextrose, and ferments readily with yeast. When boiled with dilute sulphuric acid, it is *completely* converted into glucose,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6,$$

a change which indicates that maltose is an anhydride of the latter.

Maltose combines with phenylhydrazine, yielding *phenylmaltosazone*, $C_{12}H_{20}O_9(N_2HC_6H_5)_2$, and gives with acetic anhydride *octacetylmaltose*, $C_{12}H_{14}(C_2H_3O_2)_8O_3$.

Milk-sugar, or lactose, $C_{12}H_{22}O_{11}$, has so far only been

---

* $[\alpha]_D = +140{\cdot}6°$.

found in the animal kingdom. It occurs in the milk of all mammals to the extent of about 4 per cent., and is obtained as a bye-product in the manufacture of cheese.

When milk is treated with rennet, the *caseïn* separates, and milk-sugar remains in solution; on evaporation, the crude sugar is deposited in crystals, which are readily purified by recrystallisation from water.

Milk-sugar forms large, hard, colourless crystals, which contain one molecule of water of crystallisation. It dissolves in six parts of water at ordinary temperatures, and is very much less sweet than cane-sugar; it is dextrorotatory.* It reduces Fehling's solution on boiling, but much more slowly than dextrose. Like cane-sugar, it does not ferment with pure yeast, but ordinary yeast decomposes it into alcohol and lactic acid. When oxidised with nitric acid, it yields a mixture of saccharic and mucic acids, both of which have the constitution $COOH \cdot [CH \cdot OH]_4 \cdot COOH$, and which differ from one another, like the tartaric acids, in their action on polarised light (part ii.). Milk-sugar is decomposed, by boiling with dilute sulphuric acid, into *dextrose* and *galactose*,

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}.$$

Galactose, $C_6H_{12}O_6$, or $CH_2(OH) \cdot [CH \cdot OH]_4 \cdot CHO$, is formed by the hydrolysis of milk-sugar (see above), together with dextrose, from which it may be separated by crystallisation from water. It is also formed by boiling gum-arabic and other gums with dilute sulphuric acid.

It is less soluble than dextrose, and crystallises from water in prisms, which melt at 168°. Its solutions are strongly dextrorotatory,† and ferment readily with yeast. When oxidised with nitric acid, it yields *mucic acid*, $COOH \cdot [CH \cdot OH]_4 \cdot COOH$. It combines with phenylhydrazine, yielding galactosazone,

$$CH_2(OH) \cdot [CH \cdot OH]_3 \cdot C(N_2HC_6H_5) \cdot CH : N_2HC_6H_5;$$

and on reduction with sodium amalgam it is converted into the corresponding alcohol, *dulcitol*, $CH_2(OH) \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot OH$, which is isomeric with mannitol, as explained later (part ii.).

---

* $[\alpha]_D = + 52 \cdot 53°$.

† $[\alpha]_D = + 80 \cdot 3°$.

Starch, or amylum, $(C_6H_{10}O_5)_n$, is widely disseminated throughout the vegetable world, and is found in almost all the organs of plants in the form of nodules.

It occurs in large quantities in all kinds of grain, as, for example, rice, barley, and wheat, and also in tubers, such as potatoes and arrowroot. In Europe, starch is manufactured principally from potatoes, but sometimes also from wheat, maize, and rice.

The potatoes are well washed, crushed, and macerated with water in fine sieves, when the starch passes through with the water, leaving a pulp, consisting of gluten, cellulose, and other substances. The milky liquid, on standing, deposits the starch as a paste, which is repeatedly washed by decantation, and then slowly dried.

The grain is first softened by soaking in warm water, then ground in a mill, and the product run into a large vat, where it is allowed to undergo lactic fermentation. During this process the sugar in the grain is converted into lactic, butyric, and acetic acids, and the gluten (see below) is brought into a less tenacious condition, which favours the subsequent washing of the starch, an operation which is carried out in the manner described above, the crude starch being washed by decantation, and dried.

Starch is a white powder, which, when examined under the microscope, is seen to be made up of peculiarly striated granules, having a definite shape and structure. These granules vary very much in appearance and in size, those composing potato starch being comparatively large, those of wheaten starch considerably smaller.

Starch is insoluble in cold water, but when heated with water, the granules swell up and then burst. The contents of the cells, or the *granulose*, dissolve, but the cell-wall, or *starch cellulose*, is insoluble, and remains in suspension.

The homogeneous, gelatinous mass obtained in this way is called *starch paste*, and is largely used for stiffening linen and calico goods, and also as a substitute for gum. It is best prepared by rubbing starch into a thin paste with cold water, and then adding a considerable quantity of boiling water.

Characteristic of starch is the brilliant blue colour which is produced when a solution of iodine is added to starch paste, or to its solution in water; this colour disappears on heating, but reappears on cooling.

When boiled with dilute acids, starch is first converted into *dextrin* $(C_6H_{10}O_5)_n$, and then into *dextrose*,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

Malt extract, containing the ferment, *diastase*, decomposes starch at 60–70°, with formation of *dextrin* and *maltose*,

$$3C_6H_{10}O_5 + H_2O = C_6H_{10}O_5 + C_{12}H_{22}O_{11},$$

a process which, as already mentioned (p. 98), is of the utmost importance in the manufacture of alcohol and spirituous liquors from grain.

The empirical formula of starch is $C_6H_{10}O_5$; the actual molecular formula has not as yet been determined, but it is undoubtedly many times that represented by the empirical formula, and, therefore, the composition of starch is usually expressed as $(C_6H_{10}O_5)_n$.

Gluten.—Wheaten flour contains about 70 per cent. of starch and 10 per cent. of a sticky, nitrogenous substance called *gluten*. An approximate separation of these two constituents may be brought about by kneading flour in a thin calico bag under water, when the starch passes through with the water, forming a milky liquid, from which it is deposited on standing. The gluten remains in the bag as a tenacious, sticky, gray mass, which soon decomposes and smells disagreeably.

Both starch and gluten are very valuable food-stuffs.

Dextrin, $(C_6H_{10}O_5)_n$, is the name given to the substance, or mixture of substances, obtained as an intermediate product in the conversion of starch into dextrose (see above). It is produced on heating starch to about 210°, or on treating it with dilute acids or infusion of malt.

Dextrin is a colourless, amorphous substance, soluble in water, and is largely used as a cheap substitute for gum; when boiled with dilute acids, it is converted into *dextrose*. It is probably a mixture of various isomeric substances of the empirical formula $C_6H_{10}O_5$.

Cellulose, $(C_6H_{10}O_5)_n$, like starch, occurs very widely distributed throughout the vegetable kingdom. It is the principal constituent of cell membrane and of wood, and constitutes indeed the framework of all vegetable tissues.

Linen, cotton-wool, hemp, and flax, which have been freed from inorganic matter by repeated extraction with acids, consist of almost pure cellulose; an even purer form may be obtained by extracting Swedish filter-paper with hydrofluoric acid, in order to remove traces of silica, washing well with water, and drying at 100°.

Cellulose is insoluble in all the ordinary solvents, but it dissolves in an ammoniacal solution of cupric oxide (Schweitzer's reagent). It is reprecipitated from this solution on the addition of acids, in the form of a jelly, which, when washed with water and dried, is obtained in the form of a grayish powder.

Concentrated sulphuric acid gradually dissolves cellulose, and if the solution be diluted with water and boiled, dextrin and ultimately dextrose are produced. It is thus possible to convert wood into sugar, and indirectly into alcohol.

If unsized paper be subjected to the action of sulphuric acid for a few seconds, then washed with water and dilute ammonia, and again with water, it is converted into a tough substance called *parchment paper* on account of its resemblance to parchment. Such paper serves as a convenient substitute for animal membrane, and is used for a variety of purposes.

Cellulose gives on analysis results agreeing with the formula $C_6H_{10}O_5$, but its molecular weight is certainly very much greater than that expressed by this formula, and probably very much higher than that of starch. Its formula is, therefore, generally written $(C_6H_{10}O_5)_n$, or, more frequently, $(C_{12}H_{20}O_{10})_n$.

It contains ten hydroxyl-groups, because when heated with acetic anhydride and a trace of zinc chloride, it yields cellulose decacetate, $C_{12}H_{10}(C_2H_3O_2)_{10}$, a white flocculent mass, which is reconverted into cellulose by alkalies.

Gun-cotton and Collodion.—When cotton-wool is treated with nitric acid, or, better, with a mixture of nitric and sulphuric acids, nitrates of cellulose of variable composition are produced, according to the amount and concentration of the acids employed, and the length of time during which they are allowed to act.

If cotton-wool be soaked in ten parts of a mixture of one part of nitric acid (sp. gr. 1·5) and three parts of concentrated sulphuric acid for twenty-four hours, the resulting mass, after thoroughly washing and drying, constitutes *gun-cotton.* This substance has, approximately, the composition $C_{12}H_{14}(NO_3)_6O_4$, and is, therefore, cellulose hexa-nitrate. It is insoluble in a mixture of alcohol and ether.

When treated with nitric and sulphuric acids for a short time only, cellulose is converted principally into *tetra-nitrate,* $C_{12}H_{16}(NO_3)_4O_6$, and *penta-nitrate,* $C_{12}H_{15}(NO_3)_5O_5$, both of which dissolve in a mixture of alcohol and ether; a solution of 14 grams of the mixed nitrates in 450 c.c. of alcohol and 550 c.c. of ether constitutes *collodion,* which is largely used for photographic and other purposes.

The nitrates of cellulose are decomposed by alkalies, yielding nitrates of the alkalies and cellulose; they are, therefore, true ethereal salts.

SUMMARY AND EXTENSION.

The carbohydrates are usually subdivided into the following groups:

The saccharoses or monoses.
The disaccharoses or bioses.
The polysaccharoses or polyoses.

The saccharoses, as, for example, dextrose, levulose, and galactose, have the composition $C_6H_{12}O_6$. They all resemble dextrose more or less closely in ordinary physical properties, reduce Fehling's solution, and usually undergo alcoholic fermentation with yeast; they are not resolved into simpler substances on treatment with dilute acids.

The disaccharoses, such as cane-sugar, milk-sugar, and maltose, have the composition $C_{12}H_{22}O_{11}$. From their behaviour under various conditions, more especially with dilute mineral acids, they must be regarded as composed of 2 mols. of identical or of different saccharoses, less 1 mol. of water—that is to say, they are anhydride or ether-like derivatives of the saccharoses. Cane-sugar, for example, is an anhydride or ether-like substance formed from 1 mol. of dextrose and 1 mol. of levulose, whereas milk-sugar is derived from dextrose and galactose in a similar manner. With the exception of maltose, the disaccharoses are not, as a rule, directly fermentable with yeast (compare cane-sugar), nor do they immediately reduce Fehling's solution, as in both cases they must first be converted into saccharoses by hydrolysis.

The polysaccharoses, such as starch and cellulose, have the composition $(C_6H_{10}O_5)_x$, and are much more complex than the disaccharoses, as is shown by their behaviour on hydrolysis; starch, for example, yields, under certain conditions, not only maltose, $C_{12}H_{22}O_{11}$, but also dextrin, a compound which has itself a very high molecular weight, so that the molecule of starch must be highly complex. The high molecular weight of the polysaccharoses, compared with the saccharoses and disaccharoses, is also indicated by their general physical properties, as, for example, their insolubility and their non-crystalline character. The polysaccharoses do not ferment with yeast, and do not reduce Fehling's solution.

The constitutions of the members of the carbohydrate group have been ascertained only in the case of some of the saccharoses, and even here the facts are sometimes not quite conclusive. That the saccharoses are either aldehydes (aldoses) or ketones (ketoses), is shown by their behaviour on oxidation and reduction, and also by the fact that they interact with phenylhydrazine, hydroxylamine, &c.; that they contain hydroxyl-groups is proved by their conversion into acetyl-derivatives (and in the case of the polysaccharose, cellulose, by its conversion into various nitrates).

The constitutions of the saccharoses are further determined by a method which was worked out by Kiliani, and which is based on the following reactions: The saccharoses, like the simpler aldehydes and ketones, combine directly with hydrocyanic acid, forming cyanohydrins (p. 139),

$$M{\cdot}CHO + HCN = M{\cdot}CH(OH){\cdot}CN$$
$$M{\cdot}CO{\cdot}CH_2{\cdot}OH + HCN = M{\cdot}C(OH)(CN){\cdot}CH_2{\cdot}OH,$$

and these products are converted into polyhydric acids on hydrolysis with a mineral acid,

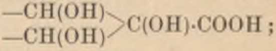
$$M{\cdot}CH(OH){\cdot}CN + 2H_2O = M{\cdot}CH(OH){\cdot}COOH + NH_3$$
$$M{\cdot}C(OH)(CN){\cdot}CH_2{\cdot}OH + 2H_2O = M{\cdot}C(OH)(COOH){\cdot}CH_2{\cdot}OH + NH_3.$$

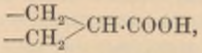
When these polyhydric acids are heated at a high temperature with a large excess of hydriodic acid and a little amorphous phosphorus, all the hydroxyl-groups in the molecule are displaced by hydrogen atoms—that is to say, complete reduction of all the $>CH\cdot OH$ and $-CH_2\cdot OH$ groups is effected, and a fatty acid is obtained. In the case of the polyhydric acid prepared from glucose cyanohydrin, this change is represented by the equation

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH(OH)\cdot COOH + 12HI = CH_3\cdot[CH_2]_4\cdot CH_2\cdot COOH + 6H_2O + 6I_2,$$

and *normal* heptylic acid is obtained; whereas on reducing the corresponding polyhydric acid prepared from levulose cyanohydrin, methylbutylacetic acid, an isomeride of normal heptylic acid, is formed,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(OH)(COOH)\cdot CH_2\cdot OH + 12HI = CH_3\cdot[CH_2]_3\cdot CH(COOH)\cdot CH_3 + 6H_2O + 6I_2.$$

These facts show that dextrose is an aldehyde and a derivative of *normal* hexane. Had it been a ketone, the polyhydric acid produced from it could not have contained the group $-CH(OH)\cdot COOH$, but must have contained the group  $\begin{matrix}-CH(OH)\\-CH(OH)\end{matrix}>C(OH)\cdot COOH$; this, on reduction, would have been transformed into



$$\begin{matrix}-CH_2\\-CH_2\end{matrix}>CH\cdot COOH,$$

and consequently the fatty acid finally produced would not have been normal heptylic acid, but one of its isomerides. In a similar manner, the conversion of levulose into methylbutylacetic acid, taken in conjunction with other facts, shows that this sugar is a ketone and not an aldehyde, and that its constitution is expressed by the formula already given (p. 265). In addition to this evidence, the fact that dextrose and levulose may be converted into mannitol, shows them to be derivatives of normal hexane.

CHAPTER XVI.

CYANOGEN COMPOUNDS.

The cyanogen compounds, like the carbohydrates, do not form a natural group or series, such as that of the paraffins, alcohols, fatty acids, &c.; nevertheless (with the exception of urea and uric acid) they may all be considered as derived from cyanogen, $(CN)_2$, just as the chlorides, hypochlorites, &c., may be regarded as derivatives of chlorine, Cl_2. In many cases the cyanogen compounds are closely related to the compounds of chlorine in properties, although they differ from the latter in composition, and contain the monovalent *group of atoms* –CN in the place of a *single atom* of chlorine, –Cl, as shown by the following examples:

$$Cl_2,\ HCl,\ KCl,\ AgCl,\ HgCl_2,\ HOCl,\ C_2H_5Cl$$
$$(CN)_2,\ HCN,\ KCN,\ AgCN,\ Hg(CN)_2,\ HO{\cdot}CN,\ C_2H_5{\cdot}CN.$$

This fact brings out very clearly the meaning of the term 'radicle,' the monovalent group –CN* playing much the same part as the atom of chlorine, just as the radicle ammonium may play the part of a single atom of an alkali metal.

Cyanogen, dicyanogen, C_2N_2, or Cy_2, or $N{\equiv}C{-}C{\equiv}N$, is produced in small quantities when the electric arc passes between carbon poles in an atmosphere of nitrogen,

$$2C + N_2 = C_2N_2;$$

also when ammonium oxalate is strongly heated,

$$NH_4OOC{\cdot}COONH_4 = N{\equiv}C{-}C{\equiv}N + 4H_2O,$$

a reaction of considerable interest, as it shows that cyanogen is the nitrile (p. 280) of oxalic acid.

Cyanogen is prepared by heating silver cyanide or mercuric cyanide (p. 282) in a hard glass tube, the gas being collected over mercury,

$$Hg(CN)_2 = Hg + C_2N_2.$$

During the operation a considerable quantity of a brown amorphous substance called *paracyanogen*, $(CN)_n$, is produced; this compound is a polymeride of cyanogen, and when heated at a high temperature it is completely resolved into cyanogen gas, just as paraformaldehyde is converted into formaldehyde under like conditions.

Cyanogen is a colourless gas, which condenses to a liquid

---

* The cyanogen radicle -CN is often written Cy.

at ordinary temperatures under a pressure of four atmospheres; it has a peculiar smell, is excessively poisonous, and burns with a characteristic purple or peach-coloured flame, yielding carbon dioxide and nitrogen.

It is moderately soluble in water, readily in alcohol, but its aqueous solution soon decomposes, a brown amorphous precipitate ('azulmic acid') being deposited; the solution then contains ammonium oxalate and other substances.

When an aqueous solution of cyanogen is treated with acids or with alkalies, oxalic acid or an oxalate is produced,

$$N{\equiv}C{-}C{\equiv}N + 4H_2O = NH_4OOC{\cdot}COONH_4,$$

this change being the reverse of that which occurs when ammonium oxalate is heated alone.

All substances which contain the cyanogen group $-C{\equiv}N$ behave in a similar manner, and are converted on hydrolysis into carboxylic acids or their salts, amides being formed as intermediate products.

Cyanogen is readily absorbed by potash, potassium cyanide and cyanate being produced,

$$C_2N_2 + 2KOH = KCN + KOCN + H_2O,$$

just as potassium chloride and hypochlorite are formed when chlorine is led into potash,

$$Cl_2 + 2KOH = KCl + KOCl + H_2O.$$

Derivatives of Cyanogen.—Cyanogen chloride, $CNCl$, is formed by the action of chlorine on a solution of hydrocyanic acid,

$$HCN + Cl_2 = CNCl + HCl.$$

It is a colourless, very poisonous liquid, boils at 15·5°, and readily undergoes spontaneous polymerisation, yielding *cyanuric chloride*, $C_3N_3Cl_3$, a solid substance which melts at 146°, and is decomposed by alkalies, yielding cyanuric acid,

$$C_3N_3Cl_3 + 3H_2O = C_3N_3(OH)_3 + 3HCl.$$

The corresponding bromo- and iodo- derivatives of cyanogen, $CNBr$ and CNI, are also known.

Hydrocyanic acid (prussic acid), $H{-}C{\equiv}N$, is found in the free state in plants, sometimes in considerable quantities;

more frequently it occurs in combination with glucose and benzaldehyde in the form of the glucoside *amygdalin* (part ii.). Bitter almonds and cherry kernels contain this glucoside; when macerated and kept in contact with water, fermentation soon sets in, due to the presence of a ferment, *emulsin*, and the amygdalin is decomposed into hydrocyanic acid, benzaldehyde (part ii.), and glucose,

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + HCN + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

Hydrocyanic acid is formed when the silent electric discharge passes through a mixture of hydrogen and cyanogen,

$$H_2 + C_2N_2 = 2HCN;$$

and also when ammonium formate is heated, a change which is analogous to the formation of cyanogen from ammonium oxalate,

$$H{\cdot}COONH_4 = HCN + 2H_2O.$$

Hydrocyanic acid is prepared by distilling potassium cyanide, or, more usually, potassium ferrocyanide, with dilute sulphuric acid,

$$KCN + H_2SO_4 = KHSO_4 + HCN$$

$$\underset{\text{Potassium Ferrocyanide.}}{2K_4Fe(CN)_6} + 3H_2SO_4 = 6HCN + \underset{\text{Ferrous Potassioferrocyanide.}}{FeK_2Fe(CN)_6} + 3K_2SO_4;$$

in the latter reaction, only half of the potassium ferrocyanide yields hydrocyanic acid.

Powdered potassium ferrocyanide (10 parts) is mixed with concentrated sulphuric acid (7 parts) previously diluted with water (10–40 parts, according to the desired strength of the hydrocyanic acid), and the mixture distilled from a retort connected with a condenser. The anhydrous acid may be prepared from the aqueous solution thus obtained by fractional distillation and dehydration over calcium chloride.

Anhydrous hydrocyanic acid is a colourless liquid; it boils at 26°, and solidifies in a freezing mixture to colourless crystals, which melt at -14°; it has an odour similar to that of oil of bitter almonds, and burns with a pale blue flame, with formation of carbon dioxide, water, and nitrogen. It is a terrible poison, very small quantities being sufficient to cause death.

Hydrocyanic acid dissolves readily in water, but the solution rapidly decomposes, with separation of a brown substance, and the liquid then contains ammonium formate and other compounds,

$$HCN + 2H_2O = H{\cdot}COONH_4.$$

This hydrolysis takes place only slowly if a trace of some mineral acid be present, more quickly if the solution be heated with mineral acids or alkalies.

The facts that hydrocyanic acid is formed on heating ammonium formate, and is reconverted into this substance on hydrolysis, show that it is the nitrile of formic acid. On reduction with nascent hydrogen, hydrocyanic acid is converted into methylamine,

$$HCN + 4H = CH_3{\cdot}NH_2.$$

The constitution of hydrocyanic acid is expressed by the formula $H{\cdot}C{\vdots}N$ for the following reasons: The acid is produced from ammonium formate, by a change similar to that by which acetonitrile is formed from ammonium acetate,

$$H{\cdot}COONH_4 = H{\cdot}CN + 2H_2O$$
$$CH_3{\cdot}COONH_4 = CH_3{\cdot}CN + 2H_2O;$$

when heated with mineral acids, it is converted into formic acid, just as methyl cyanide is converted into acetic acid,

$$H{\cdot}CN + 2H_2O = H{\cdot}COOH + NH_3$$
$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3.$$

As, moreover, many facts show that the methyl group in methyl cyanide and in acetic acid is directly united with carbon, it is very probable that the hydrogen atom in hydrocyanic acid is in a similar state of combination (p. 286).

Hydrocyanic acid is the nitrile of formic acid, or rather of ammonium formate, the name nitrile being given to those compounds which are derived from ammonium salts by the elimination of 2 mols. of water. The fact that the hydrogen atom in hydrocyanic acid, like that in hydrochloric acid, is displaceable by metals, although it is directly united with carbon (and not with oxygen, as in the case of the carboxylic acids), is accounted for by the close similarity between —CN and —Cl, both of which have acid-forming or electro-negative properties.

Hydrocyanic acid is a feeble acid, and scarcely reddens blue litmus. It forms salts with the hydroxides (but not with the carbonates) of potassium, sodium, and many other metals; the alkali salts are decomposed by carbon dioxide with liberation of the acid, and this is the reason why potassium cyanide, for example, in contact with moist air, always smells of hydrocyanic acid.

Potassium cyanide, KCN, may be obtained synthetically by passing nitrogen into a mixture of carbon and fused potash, and by burning potassium in cyanogen. It is prepared on a large scale by strongly heating potassium ferrocyanide,

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2;$$

the fused product is filtered through hot, porous crucibles, to free it from finely-divided iron carbide, and then cast into sticks. The pure salt may be prepared by neutralising hydrocyanic acid with pure potash, and evaporating the solution out of contact with air.

Potassium cyanide crystallises in colourless plates, and is very readily soluble in water, but nearly insoluble in absolute alcohol; it is excessively poisonous.

Fused potassium cyanide is a powerful reducing agent; it liberates the metals from many metallic oxides, being itself converted into potassium cyanate,

$$KCN + PbO = KCNO + Pb,$$

hence its use in analytical chemistry and in some metallurgical operations.

The aqueous solution of potassium cyanide gives, with silver nitrate, a curdy white precipitate of *silver cyanide*, AgCN, which is insoluble in dilute acids, but soluble in ammonia and potassium cyanide; in the latter case, with formation of the soluble double salt, $KAg(CN)_2$, which is used in electroplating. Silver cyanide is thus very similar in its properties to silver chloride, from which, however, it differs in this, that when heated, it is decomposed completely into silver and cyanogen,

$$2AgCN = 2Ag + C_2N_2.$$

Mercuric cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid,

$$HgO + 2HCN = Hg(CN)_2 + H_2O.$$

The solution, on evaporation, deposits the salt in colourless crystals, which are moderately soluble in water; when strongly heated, the salt is decomposed into mercury and cyanogen.

The detection of hydrocyanic acid or of a cyanide is usually based on the following tests: (*a*) The aqueous solution is made strongly alkaline with potash, a few drops of ferrous sulphate added, and the liquid warmed; potassium ferrocyanide is thus formed, and on acidifying and adding ferric chloride, a blue colouration or precipitate of Prussian blue is produced. (*b*) The solution is mixed with a few drops of ammonium sulphide, and evaporated to dryness on a water-bath; the residue contains ammonium thiocyanate, and on the addition of ferric chloride, an intense blood-red colouration is produced.

The cyanides of many of the metals, like many of the metallic chlorides, are capable of forming 'double salts' with the compounds of other metals. Silver cyanide, for instance, is soluble in potassium cyanide, with which it forms a double salt of the composition $AgK(CN)_2$; the compound $KAu(CN)_4$ may be obtained in a similar manner by dissolving auric cyanide, $Au(CN)_3$, in potassium cyanide. These 'double salts' crystallise unchanged from water, but are decomposed by mineral acids in the cold, with evolution of hydrocyanic acid. Like the soluble simple cyanides, they are excessively poisonous.

In addition to these double salts, complex metallic cyanides of a different class are known, the most important of which are potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. These salts are not poisonous, and are more stable than the double salts just referred to. On treatment with mineral acids, in the cold, they do not yield hydrocyanic acid, but hydrogen is substituted for one of the metals only, and an acid, such as hydroferrocyanic acid, is liberated,

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

Potassium ferrocyanide, or yellow prussiate of potash, $K_4Fe(CN)_6$, is formed when ferrous hydrate is dissolved in potassium cyanide,

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

It is manufactured by fusing together in an iron pot nitrogenous animal refuse (horn-shavings, hair, blood, &c.), crude potashes (containing potassium carbonate), and scrap-iron. The product is extracted with hot water, the solution filtered, and evaporated to crystallisation.

Potassium ferrocyanide cannot be present in the melted mass, because it is decomposed at a high temperature ; it must, therefore, be formed when the product is extracted with water.

Probably the melt contains iron, potassium cyanide, and ferrous sulphide (the latter having been produced by the action of the sulphur in the animal refuse on the scrap-iron); these substances would interact in the presence of water, yielding potassium ferrocyanide,

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$
$$2KCN + Fe + 2H_2O = Fe(CN)_2 + 2KOH + H_2$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Potassium ferrocyanide crystallises in lemon-yellow prisms, which contain 3 mols. of water of crystallisation ; it is soluble in about 4 parts of water. When ignited it decomposes, yielding potassium cyanide, nitrogen, and a compound of iron and carbon (iron carbide),

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2,$$

a reaction which is made use of in the preparation of potassium cyanide. When warmed with strong (90 per cent.) sulphuric acid, it gives carbon monoxide,

$$K_4Fe(CN)_6 + 6H_2O^* + 6H_2SO_4 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4,$$

but when boiled with dilute sulphuric acid, hydrocyanic acid is produced.

Solutions of ferric salts in excess give with potassium ferrocyanide a precipitate of 'Prussian blue,' or ferric ferrocyanide,

$$Fe_4[Fe(CN)_6]_3.$$

Potassium ferricyanide, or red prussiate of potash, $K_3Fe(CN)_6$, is prepared by passing chlorine into a solution of potassium ferrocyanide until the liquid ceases to give a blue precipitate with ferric salts; on evaporation, potassium ferricyanide separates out in dark-red crystals.

The transformation of potassium ferrocyanide into ferricyanide is simply a process of oxidation, as other oxidising agents, such as nitric acid, produce the same result; this change is easily understood if it be assumed that potassium ferrocyanide is a compound of potassium cyanide and *ferrous* cyanide, $(4KCN + Fe(CN)_2)$. On oxidation, the ferrous is converted into ferric cyanide, and potassium ferricyanide, which may be regarded as a compound of potassium cyanide and *ferric* cyanide, $(3KCN + Fe(CN)_3)$, is formed.

Potassium ferricyanide gives, with ferrous salts, a precipitate of Turnbull's blue, or ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$; it is employed as a mild oxidising agent, as in alkaline solution, in presence of an oxidisable substance, it is converted into potassium ferrocyanide,

$$2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O.$$

The **nitriles,** or alkyl cyanides, as the *ethereal salts* of *hydrocyanic acid* are termed, may be prepared by heating the alkyl halogen compounds with *potassium* cyanide,

$$KCN + C_2H_5I = C_2H_5{\cdot}CN + KI,$$

or by distilling the ammonium salts, or the amides, of the fatty acids either alone or with some dehydrating agent, such as phosphorus pentoxide,

---

* The water necessary for this decomposition is partly derived from the crystals of the salt, partly from the acid, which is not anhydrous.

$$CH_3\cdot COONH_4 = CH_3\cdot CN + 2H_2O$$
$$C_2H_5\cdot CO\cdot NH_2 = C_2H_5\cdot CN + H_2O.$$

The lower members of the series, such as methyl cyanide (b.p. 81°) and ethyl cyanide (b.p. 97°), are colourless liquids, possessing a strong, but not disagreeable smell, and are readily soluble in water; the higher members, as, for example, octyl cyanide, $C_8H_{17}\cdot CN$, are almost insoluble in water.

When boiled with acids or alkalies, they are decomposed, with formation of fatty acids, the $-CN$ group being converted into the $-COOH$ group,

$$CH_3\cdot CN + KOH + H_2O = CH_3\cdot COOK + NH_3$$
$$C_2H_5\cdot CN + HCl + 2H_2O = C_2H_5\cdot COOH + NH_4Cl.$$

For this reason, and also because they may be obtained from the ammonium salts of the fatty acids, the nitriles are named after the acids which they yield on hydrolysis: methyl cyanide, $CH_3\cdot CN$, for example, is called *acetonitrile*; ethyl cyanide, $C_2H_5\cdot CN$, *propionitrile*, and so on.

On reduction with zinc and sulphuric acid, or, better, with sodium and alcohol, the alkyl cyanides are converted into primary amines, a fact which shows that the alkyl group is directly united with carbon,

$$CH_3\cdot CN + 4H = CH_3\cdot CH_2\cdot NH_2.$$

The *isonitriles*, carbylamines or isocyanides, are isomeric with the nitriles: they may be prepared by heating the alkyl halogen compounds with *silver* cyanide,

$$C_2H_5I + Ag\cdot N{\equiv}C = C_2H_5\cdot N{\equiv}C + AgI,$$

and by treating primary amines with chloroform and potash,

$$CH_3\cdot NH_2 + 3KOH + CHCl_3 = CH_3\cdot N{\equiv}C + 3KCl + 3H_2O.$$

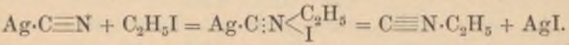
The isonitriles or carbylamines are colourless liquids, sparingly soluble in water; they have an almost unbearable odour and poisonous properties.

They boil at lower temperatures than the isomeric cyanides; methyl isonitrile, $CH_3\cdot NC$, for example, boils at 58°; ethyl isonitrile, $C_2H_5\cdot NC$, at 82°. They differ from the nitriles, inasmuch as they are not decomposed by boiling alkalies; they are, however, readily decomposed by dilute mineral acids, yielding formic acid and an amine,

$$C_2H_5\cdot NC + 2H_2O = H\cdot COOH + C_2H_5\cdot NH_2.$$

This behaviour is also totally different from that of the nitriles, and shows that the alkyl group in the isonitriles is united with nitrogen and not with carbon—that is to say, the nitriles are ethereal salts of hydrocyanic acid, $H\cdot C\vdots N$, whereas the isonitriles may be regarded as derivatives of an isomeric modification of hydrocyanic acid, $H\cdot N\equiv C$.

In order to explain the difference in the constitution of the products produced by the action of alkyl halogen compounds on potassium and silver cyanide respectively, it is necessary to assume either that in the formation of silver cyanide from potassium cyanide by precipitation, *intramolecular change* (p. 290) has taken place, $K\cdot C\equiv N$ yielding $Ag\cdot N\equiv C$, or that silver cyanide, $Ag\cdot C\equiv N$, first yields, with the alkyl halogen compound, an additive product, which is then decomposed, yielding the isonitrile,



$$Ag\cdot C\equiv N + C_2H_5I = Ag\cdot C\vdots N{<}^{C_2H_5}_{I} = C\equiv N\cdot C_2H_5 + AgI.$$

Cyanic acid, $HO\cdot CN$, is produced when cyanuric acid (see below) is heated, and the vapours condensed in a receiver cooled in a freezing mixture,

$$C_3N_3(OH)_3 = 3HO\cdot CN.$$

It is a strongly acid, unstable liquid, and at temperatures above 0° rapidly undergoes polymerisation into an opaque, porcelain-like mass called cyamelide. Its aqueous solution decomposes very rapidly into carbon dioxide and ammonia,

$$HO\cdot CN + H_2O = CO_2 + NH_3,$$

and therefore the acid cannot be prepared by the decomposition of its salts with mineral acids.

Potassium cyanate, $KO\cdot CN$, is produced when potassium cyanide slowly oxidises in the air; it is usually prepared by heating potassium cyanide (or ferrocyanide) with some readily reducible metallic oxide, such as litharge or red-lead, and then extracting the product with dilute alcohol,

$$KCN + PbO = KO\cdot CN + Pb.$$

It is a colourless, crystalline powder, readily soluble in water and dilute alcohol, but insoluble in absolute alcohol; its aqueous solution rapidly decomposes with formation of ammonia and potassium bicarbonate,

$$KO{\cdot}CN + 2H_2O = NH_3 + KHCO_3.$$

When a solution of this salt is mixed with ammonium sulphate and evaporated, *urea* is formed, ammonium cyanate, $NH_4O{\cdot}CN$, being the intermediate product (p. 289).

Ethereal Salts of Cyanic Acid.—Cyanic acid, like hydrocyanic acid, yields two series of ethereal salts—namely, the normal cyanates, such as $C_2H_5O{\cdot}CN$, derived from $HO{\cdot}CN$; and the isocyanates, such as $C_2H_5{\cdot}N{:}CO$, derived from $H{\cdot}N{:}CO$.

The *alkyl (normal) cyanates* are produced by the action of cyanogen chloride on the sodium compounds of the alcohols,

$$NaO{\cdot}C_2H_5 + Cl{\cdot}CN = C_2H_5O{\cdot}CN + NaCl;$$

they are colourless, ethereal-smelling liquids, and are decomposed by alkalies into alkali carbonates, ammonia, and alcohols; this fact shows that the alkyl group is united with oxygen and not with nitrogen.

The *alkyl isocyanates* are obtained by the action of the alkyl halogen compounds on silver isocyanate (obtained as a white precipitate on adding silver nitrate to an aqueous solution of potassium cyanate),

$$AgN{:}CO + CH_3I = CH_3N{:}CO + AgI.$$

They are very unpleasant-smelling, volatile liquids; when heated with alkalies, they are decomposed into alkali carbonates and *primary amines* (Würtz), a reaction which shows that the alkyl group is united with nitrogen,

$$CH_3N{:}CO + 2KOH = CH_3{\cdot}NH_2 + K_2CO_3.$$

Cyanuric acid, $N_3C_3O_3H_3$, is produced by the action of water on cyanuric chloride (p. 278),

$$N_3C_3Cl_3 + 3H_2O = N_3C_3(OH)_3 + 3HCl.$$

It is a crystalline, tribasic acid, forming well-defined salts, of which the crystalline trisodium salt, $N_3C_3(ONa)_3$, is the most characteristic. On distillation, the acid is converted into cyanic acid.

Thiocyanic acid, or sulphocyanic acid, $HS{\cdot}CN$, is obtained in the form of its salts when the alkali cyanides are heated with sulphur,

$$KCN + S = KS{\cdot}CN,$$

the change being analogous to the formation of cyanates by the oxidation of cyanides.

Thiocyanic acid may be obtained by distilling potassium thiocyanate with dilute sulphuric acid; it is a liquid, solidifies at 12·5°, and has a very penetrating odour. It is decomposed by moderately concentrated sulphuric acid, with evolution of carbon oxysulphide,

$$HS{\cdot}CN + H_2O = COS + NH_3.$$

Potassium thiocyanate, $KS{\cdot}CN$, is prepared by fusing potassium cyanide (or ferrocyanide) with sulphur, and extracting the mass with alcohol. On concentrating the alcoholic solution, the salt is deposited in colourless, very deliquescent needles. The *ammonium salt*, $NH_4S{\cdot}CN$, is most conveniently prepared by agitating strong ammonia with carbon bisulphide,

$$4NH_3 + CS_2 = NH_4S{\cdot}CN + (NH_4)_2S.$$

The thiocyanates are used in inorganic analysis, as reagents for ferric salts, with which they give an intense blood-red colouration, caused by the formation of a double salt. Thiocyanates are also employed in dyeing and calico-printing as mordants, and are known commercially as 'rhodanates.'

Thiocyanic acid, like cyanic acid, forms two series of ethereal salts—namely, the normal thiocyanates, such as $C_2H_5S{\cdot}CN$, derived from $HS{\cdot}C{\vdots}N$, and the isothiocyanates, such as $C_2H_5N{:}CS$, derived from $HN{:}C{:}S$. The *alkyl* (*normal*) *thiocyanates* are produced by the action of the alkyl iodides on potassium thiocyanate, or from the mercaptides (especially lead mercaptide), by the action of cyanogen chloride,

$$(C_2H_5S)_2Pb + 2ClCN = 2C_2H_5S{\cdot}CN + PbCl_2,$$

a reaction which is exactly similar to the formation of ethyl cyanate by the action of cyanogen chloride on sodium ethoxide (see above).

The normal thiocyanates are volatile liquids possessing a slight though not penetrating smell of garlic; when oxidised with nitric acid they are converted into alkyl sulphonic acids, $C_2H_5S{\cdot}CN$, for example, yielding $C_2H_5{\cdot}SO_3H$, a reaction which shows that the alkyl group is united with sulphur.

The *alkyl isothiocyanates*, or *mustard-oils*, are produced by heating the normal thiocyanates at 180°, or by simply repeatedly distilling them, intramolecular change (p. 290) taking place; the alkyl group in these compounds is combined with nitrogen, because when heated with hydrochloric acid they are decomposed into primary amines, carbon dioxide, and sulphuretted hydrogen,

$$C_2H_5N{:}CS + 2H_2O = C_2H_5{\cdot}NH_2 + CO_2 + SH_2.$$

Allyl isothiocyanate, or '**mustard-oil**,' $CH_2{:}CH{\cdot}CH_2{\cdot}N{:}CS$, is prepared by distilling macerated black mustard seeds with steam. Mustard seeds contain a glucoside, 'potassium myronate,' $C_{10}H_{18}NS_2O_{10}K$, which is soluble in water; its solution gradually undergoes fermentation, owing to the presence of a ferment, 'myrosin,' mustard-oil, glucose, and potassium hydrogen sulphate being produced,

$$C_{10}H_{18}NS_2O_{10}K = C_3H_5{\cdot}N{:}CS + C_6H_{12}O_6 + KHSO_4.$$

Allyl isothiocyanate is a colourless, pungent-smelling liquid, which boils at 151°; when dropped on the skin, it produces blisters.

Urea,* or carbamide, CH_4N_2O or $CO(NH_2)_2$, is a compound of great physiological importance. It occurs in the urine of mammals and of carnivorous birds and reptiles, and is one of the principal nitrogenous constituents of human urine, of which it forms about 3 per cent.

It was discovered in urine in 1773, and was first artificially produced in 1828 by Wöhler, who found that on warming an aqueous solution of ammonium cyanate the salt was converted into urea,

$$NH_4{\cdot}O{\cdot}CN = CO(NH_2)_2,$$

a discovery which, being the first synthetical production of an animal product, was of fundamental importance (compare p. 10).

---

* Although urea, uric acid, and glycine are not derivatives of cyanogen, they are in many ways related to the cyanogen compounds, and for this reason may be conveniently considered in this chapter.

When one substance is converted into another which has the same molecular formula, the change is spoken of as 'intramolecular.' Ammonium cyanate, NH_4OCN, has the same molecular formula as urea, $CO(NH_2)_2$; but the atoms in the molecules of the two compounds are arranged differently—that is to say, their constitutions are different. Many cases of intramolecular change are met with in organic chemistry.

Urea may be prepared from urine by evaporating to a small bulk and adding strong nitric acid. The precipitate of crude urea nitrate (see below) is recrystallised from nitric acid, dissolved in boiling water, and decomposed with barium carbonate; the solution is then evaporated to dryness, and the urea extracted with alcohol, in which barium nitrate is insoluble.

It is more commonly prepared by mixing a solution of potassium cyanate (2 mols.) with an equivalent quantity of ammonium sulphate (1 mol.), evaporating to dryness, and extracting with alcohol. In both cases the crude urea is purified by recrystallisation from water or alcohol.

Urea may be also synthetically obtained by treating ethyl carbonate, or phosgene gas* (carbonyl chloride), with ammonia,

$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2C_2H_5{\cdot}OH$$
$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

It crystallises in colourless needles, melts at 132°, and is readily soluble in water and alcohol, but almost insoluble in ether; when heated with water at 120°, or boiled with dilute acids, it is decomposed into carbon dioxide and ammonia (or one of its salts),

$$CO(NH_2)_2 + H_2O + 2HCl = CO_2 + 2NH_4Cl,$$

but when heated alone it yields ammonia, cyanuric acid, and complex cyanogen compounds,

$$3CO(NH_2)_2 = H_3C_3N_3O_3 + 3NH_3.$$

Urea is decomposed by nitrous acid into nitrogen and carbon dioxide,

---

* *Ethyl carbonate* is formed when silver carbonate is treated with ethyl iodide: it is an agreeably-smelling, neutral liquid, which boils at 126°. *Carbonyl chloride* is obtained by the direct combination of carbon monoxide and chlorine in sunlight; it is a gas which decomposes rapidly in contact with water, into carbon dioxide and hydrochloric acid.

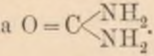
$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O,$$

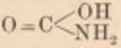
a similar change taking place when it is mixed with solutions of hypochlorites or hypobromites,

$$CO(NH_2)_2 + 3NaOCl = CO_2 + N_2 + 2H_2O + 3NaCl;$$

by measuring the volume of nitrogen given off, on treating a solution of urea with nitrous acid, the quantity in solution can be readily estimated.

Urea possesses basic properties, and combines with *one* equivalent of acids to form salts, most of which are soluble in water. The most characteristic salt is *urea nitrate*, $CO(NH_2)_2,HNO_3$, which crystallises in glistening plates, and is sparingly soluble in nitric acid.

Constitution.—The formation of urea from the ethyl salt and from the chloride of carbonic acid is exactly analogous to the formation of acetamide from ethyl acetate and from acetyl chloride; urea is therefore the diamide of carbonic acid—hence the name carbamide—and its constitution is represented by the formula  $O=C<^{NH_2}_{NH_2}$.

The monamide of carbonic acid,  $O=C<^{OH}_{NH_2}$ (carbamic acid), is not known in a free state. Ammonium carbamate is formed by the action of carbon dioxide on ammonia,

$$CO_2 + 2NH_3 = CO(NH_2)\cdot ONH_4,$$

and is one of the constituents of commercial ammonium carbonate, which is frequently prepared by this method.

Uric acid, $C_5H_4N_4O_3$, occurs in small quantities in human urine, from which it separates on exposure to the air in the form of a light yellow powder; it also occurs in the excrements of birds and reptiles, and is present in large quantities in *guano*. The excrements of serpents consist almost entirely of ammonium urate: from this source uric acid is conveniently prepared by boiling the excrement with caustic soda until all the ammonia has been expelled, and pouring the hot filtered liquid into hydrochloric acid; on cooling, uric acid separates as a fine crystalline powder.

Uric acid is insoluble in alcohol and ether, and very sparingly soluble in water (1 part dissolves in 1800 parts of water at 100°). If uric acid be moistened with nitric acid in a porcelain basin, and the mixture then evaporated to dryness on a water-bath, a yellow stain is left, which, on the addition of ammonia, becomes intensely violet (murexide reaction).

Uric acid is a weak dibasic acid; when dissolved in sodium carbonate, it yields an acid sodium salt, $C_5H_3N_4O_3Na + \frac{1}{2}H_2O$; the neutral sodium salt, $C_5H_2N_4O_3Na_2 + H_2O$, is formed when uric acid is dissolved in caustic soda. The salts, like the acid itself, are all sparingly soluble in water.

Uric acid has been prepared synthetically by heating glycine with urea at 200–230°.

Glycine, glycocoll, or amido-acetic acid, $CH_2(NH_2)\cdot COOH$, like urea and uric acid, is found in animal secretions, but usually in combination. As *hippuric acid*, or benzoylglycine, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$ (part ii.), it occurs in considerable quantities in the urine of horses, and it is best prepared from this substance by treatment with hydrochloric or sulphuric acid,

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH + H_2O + HCl = \underset{\text{Benzoic Acid.}}{C_6H_5\cdot COOH} + \underset{\text{Glycine Hydrochloride.}}{NH_2\cdot CH_2\cdot COOH, HCl}.$$

It may also be conveniently prepared by treating monochloracetic acid with ammonia,

$$CH_2Cl\cdot COOH + 3NH_3 = CH_2(NH_2)\cdot COONH_4 + NH_4Cl.$$

Glycine crystallises from water in colourless prisms, and melts at 235°. It is readily soluble in water; the aqueous solution gives with ferric chloride a red colouration, and with phenol and sodium hypochlorite an intense blue colouration.

Glycine contains an amido-group and a carboxyl-group, and is therefore capable of forming salts both with acids and bases.

The most characteristic metallic salt is the *copper salt*,

$(C_2H_4NO_2)_2Cu$, which is readily formed by dissolving cupric hydrate in a hot, strong, aqueous solution of glycine; on cooling, the salt crystallises in deep blue needles.

Glycine hydrochloride, $C_2H_5NO_2$, HCl, is produced by dissolving glycine in hydrochloric acid, or by decomposing hippuric acid with hydrochloric acid; it crystallises in colourless needles, is readily soluble in water, and is decomposed by alkalies or alkali carbonates, with liberation of glycine.

When treated with nitrous acid, glycine is converted into glycollic acid (p. 223),

$$CH_2(NH_2)\cdot COOH + NO_2H = CH_2(OH)\cdot COOH + N_2 + H_2O.$$

Other *amido-acids* such as *alanine* or α-amidopropionic acid,

$$CH_3\cdot CH(NH_2)\cdot COOH,$$

may be prepared from the corresponding halogen acids by the action of ammonia; in their properties they are very similar to glycine.

ORGANIC CHEMISTRY.

PART II.

CHAPTER XVII.

MANUFACTURE, PURIFICATION, PROPERTIES, AND CONSTITUTION OF BENZENE.

Distillation of Coal-tar.—When coal is strongly heated out of contact with air, it undergoes very complex changes, and yields a great variety of gaseous and liquid products, together with a solid, non-volatile residue of coke. This process of dry or destructive distillation is carried out on the large scale in the manufacture of **coal-gas**, for which purpose the coal is heated in clay or iron retorts, provided with air-tight doors; the gas and other volatile products escape from the retort through a pipe, and when distillation is at an end, the **coke**, a porous mass of carbon, containing the ash or mineral matter of the coal, is withdrawn.

The hot coal-gas passes first through a series of pipes or *condensers*, kept cool by immersion in water or simply by exposure to the air, and, as its temperature falls, it deposits a considerable quantity of **tar** and **gas-liquor**, which are run together into a large tank; it is then forced through, or washed with, water, in *washers* and *scrubbers*, and, after having been further freed from tar, ammonia, carbon dioxide, and sulphuretted hydrogen by suitable processes of purification, it is led into the gas-holder and used for illuminating and heating purposes. The average volume percentage composition of purified coal-gas is $H_2 = 47$,$CH_4 = 36$,$CO = 8$,$CO_2 = 1$,$N_2 = 4$, and hydrocarbons, other than marsh-gas (acetylene, ethylene, benzene, &c.) = 4.

The coal-tar and the gas-liquor in the tank separate into two layers; the upper one consists of gas-liquor or ammoniacal-liquor (a yellow, unpleasant-smelling, aqueous solution of ammonium carbonate, ammonium sulphide, and numerous other compounds), from which practically the whole of the ammonia and ammonium salts of commerce are obtained. The lower layer in the tank is a dark, thick, oily liquid of sp. gr. 1·1 to 1·2, known as coal-tar. It is a mixture of a great number of organic compounds, and, although not long ago it was considered to be an obnoxious bye-product, it is now the sole source of very many substances of great industrial importance.

In order to partially separate the several constituents, the tar is submitted to fractional distillation; it is heated in large wrought-iron stills or retorts, and the vapours which pass off are condensed in long iron or lead worms immersed in water, the liquid distillate being collected in fractions. The point at which the receiver is changed is ascertained by means of a thermometer, which dips into the tar, as well as by the character of the distillate.

In this way tar may be roughly separated into the following fractions:

I. Light oil or crude naphtha	Collected up to 170°.
II. Middle oil or carbolic oil	„ between 170 and 230°.
III. Heavy oil or creosote oil	„ „ 230 „ 270°.
IV. Anthracene oil	„ above 270°.
V. Pitch	Residue in the still.

I. The first crude fraction separates into two layers—namely, gas-liquor (which the tar always retains mechanically to some extent) and an oil which is lighter than water, its sp. gr. being about 0·975, hence the name, *light oil*. This oil is first redistilled from a smaller iron retort and the distillate collected in three principal portions, passing over between 82–110°, 110–140°, and 140–170° respectively. All these fractions consist principally of **hydrocarbons**, but contain basic substances, such as **pyridine**, acid substances, such as **phenol** or **carbolic acid**, and various other impurities; they are, therefore, separately agitated, first with concentrated sulphuric acid, which dissolves out the basic substances, and then with caustic soda, which removes the phenols (p. 385), being washed with water after each treatment; afterwards they are again distilled. The oil obtained in this way from the fraction collected between 82 and 110° consists principally of the hydrocarbons **benzene** and **toluene**, and is sold as '90 per cent. benzol;' that obtained from the fraction 110–140° consists essentially of the same two hydrocarbons (but in different proportions) together with **xylene**, and is sold as '50 per cent. benzol.'* These two products are not usually further treated by the tar-distiller, but are worked up in the manner described later. The oil from the fraction collected between 140–170° consists of xylene, pseudocumene, mesitylene, &c., and is principally employed as '**solvent naphtha**,' also as 'burning naphtha.'

II. The second crude fraction, or middle oil, collected between 170 and 230°, has a sp. gr. of about 1·002, and consists principally of **naphthalene** and **carbolic acid**. On cooling, the naphthalene separates in crystals, which are drained and pressed to squeeze out adhering carbolic acid and other substances; the crude crystalline product is further purified by treatment with caustic soda and sulphuric acid successively, and finally sublimed or distilled. The oil from which the crystals have been separated is agitated with warm caustic soda to dissolve the carbolic acid; the alkaline solution is then drawn off from the insoluble portions of the oil and

---

* Commercial '90 per cent. benzol' contains about 70 per cent., and '50 per cent. benzol' about 46 per cent. of pure benzene; the terms refer to the proportion of the mixture which passes over below 100° when the commercial product is distilled. Benzene, toluene, and xylene are known commercially as benzol, toluol, and xylol respectively.

treated with sulphuric acid, whereupon crude carbolic acid separates as an oil, which is washed with water and again distilled; it is thus separated into crystalline (pure) carbolic acid and liquid (impure) carbolic acid.

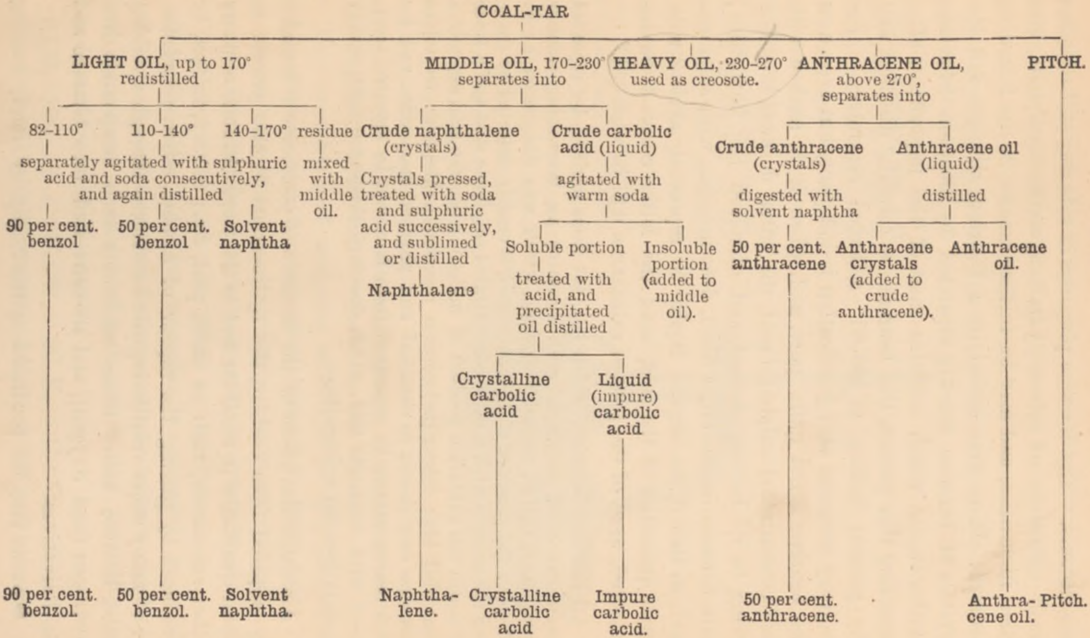
III. The third crude fraction, collected between 230 and 270° is a greenish-yellow, fluorescent oil, specifically heavier than water; it contains **carbolic acid, cresol, naphthalene, anthracene,** and other substances, and is chiefly employed under the name of '**creosote oil**' for the preservation of timber.

IV. The fourth crude fraction, collected at 270° and upwards, consists of **anthracene, phenanthrene,** and other hydrocarbons which are solid at ordinary temperatures; the crystals which are deposited on cooling, after having been freed from oil by pressure, contain about 30 per cent. of anthracene, and are further purified by digestion with solvent naphtha, which dissolves the other hydrocarbons more readily than the anthracene; the product is then sold as '50 per cent. anthracene,' and is employed in the manufacture of alizarin dyes. The oil drained from the anthracene is redistilled, to obtain a further quantity of the crystalline product, the non-crystallisable portions being known as '**anthracene oil.**'

V. The **pitch** in the still is run out while still hot, and is employed in the preparation of varnishes, for protecting wood and metal work, and in making asphalt.

The following table, taken partly from Ost's *Lehrbuch der technischen Chemie*, shows in a condensed form the process of tar distillation and the more important commercial products obtained.

Benzene, C_6H_6.—The crude '90 per cent. benzol' of the tar-distiller consists essentially of a mixture of benzene and toluene, but contains small quantities of xylene and other substances; on further fractional distillation in specially constructed apparatus (similar to that employed in the rectification of spirit), it is separated more or less completely into its


COAL-TAR
LIGHT OIL, up to 170° redistilled
MIDDLE OIL, 170–230° separates into
HEAVY OIL, 230–270° used as creosote.
ANTHRACENE OIL, above 270°, separates into
PITCH.
82–110°
110–140°
140–170°
residue
separately agitated with sulphuric acid and soda consecutively, and again distilled
mixed with middle oil.
90 per cent. benzol
50 per cent. benzol
Solvent naphtha
Crude naphthalene (crystals)
Crystals pressed, treated with soda and sulphuric acid successively, and sublimed or distilled
Naphthalene
Crude carbolic acid (liquid)
agitated with warm soda
Soluble portion
treated with acid, and precipitated oil distilled
Insoluble portion (added to middle oil).
Crystalline carbolic acid
Liquid (impure) carbolic acid
Crude anthracene (crystals)
digested with solvent naphtha
50 per cent. anthracene
Anthracene oil (liquid)
distilled
Anthracene crystals (added to crude anthracene).
Anthracene oil.
90 per cent. benzol.
50 per cent. benzol.
Solvent naphtha.
Naphthalene.
Crystalline carbolic acid
Impure carbolic acid.
50 per cent. anthracene.
Anthracene oil.
Pitch.

constituents. The benzene prepared in this way still contains small quantities of toluene, paraffins, carbon bisulphide, and other impurities, and may be further treated in the following manner: It is first cooled in a freezing mixture and the crystals of benzene quickly separated by filtration from the mother-liquor, which contains most of the impurities; after repeating this process, the benzene is carefully distilled, and the portion boiling at 80–81° collected separately. For ordinary purposes this purification is sufficient, but even now the benzene is not quite pure, and, when it is shaken with cold concentrated sulphuric acid, the latter darkens in colour owing to its having charred and dissolved the impurities; pure benzene, on the other hand, does not char with sulphuric acid, so that if the impure liquid be repeatedly shaken with small quantities of the acid, until the latter ceases to be discoloured, most of the foreign substances will be removed.

All coal-tar benzene, which has not been purified by repeated treatment with sulphuric acid, contains an interesting sulphur compound, C_4H_4S, named *thiophene*, which was discovered by V. Meyer; the presence of this substance is readily detected by shaking the sample with a little concentrated sulphuric acid and a trace of isatin (an oxidation product of indigo), when the acid assumes a beautiful blue colour (indophenin reaction); thiophene resembles benzene very closely in chemical and physical properties, and for this reason cannot be separated from it except by repeated treatment with sulphuric acid, which dissolves thiophene more readily than it does the hydrocarbon.

Although the whole of the benzene of commerce ('benzol') is prepared from coal-tar, the hydrocarbon is also present in small quantities in wood-tar and in the tarry distillate of many other substances, such as shale, peat, &c.; it may, in fact, be produced by passing the vapour of alcohol, ether, petroleum, or of many other volatile organic substances through a red-hot tube, because under these conditions such compounds lose hydrogen (and oxygen), and are converted into benzene and its derivatives.

Benzene may be produced synthetically by simply heating acetylene at a dull-red heat, when 3 mols. (or 6 vols.) of the latter are converted into 1 mol. (or 2 vols.) of benzene,

$$3C_2H_2 = C_6H_6.$$

Acetylene, generated from its copper derivative (part i. p. 83), is collected over mercury in a piece of hard glass-tubing, closed at one end and bent at an angle of about 120°; when the tube is about half full of gas, the lower end is closed with a cork, and a piece of copper gauze wrapped round a portion of the horizontal limb, as shown (fig. 19). This portion of the tube is then carefully and strongly heated with a bunsen burner, the other end remaining immersed in the mercury; after a short time vapours appear in the tube, and minute drops of benzene condense on the sides, and if, after heating for about fifteen minutes, the tube be allowed to cool and the cork then removed, the mercury will rise, showing that a diminution in volume has taken place.

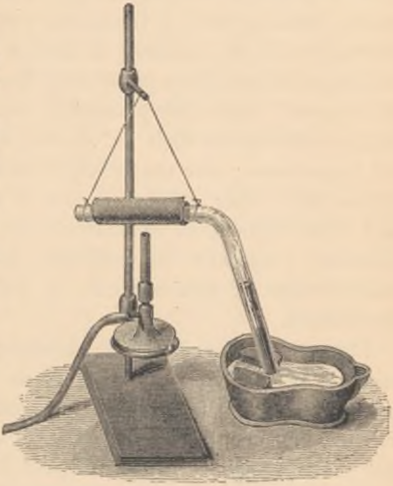


Fig. 19.

This conversion of acetylene into benzene is a process of polymerisation, and was first accomplished by Berthelot. It is, at the same time, an exceedingly important synthesis of benzene from its elements, because acetylene may be obtained by the direct combination of carbon and hydrogen.

Pure benzene may be conveniently prepared in small quantities by heating pure benzoic acid or calcium benzoate with soda-lime, a reaction which recalls the formation of marsh-gas from calcium acetate,

$$(C_6H_5{\cdot}COO)_2Ca + 2NaOH = 2C_6H_6 + CaCO_3 + Na_2CO_3,$$
$$\text{or } C_6H_5{\cdot}COOH = C_6H_6 + CO_2.$$

At ordinary temperatures benzene is a colourless, highly-refractive, mobile liquid of sp. gr. 0·8799 at 20°, but when cooled in a freezing mixture it solidifies to a crystalline mass, melting again at 6°, and boiling at 80·5°. It has a burning taste, a peculiar, not unpleasant smell, and is highly inflammable, burning with a luminous, very smoky flame, which is indicative of its richness in carbon; the luminosity of an ordinary coal-gas flame is, in fact, largely due to the presence of benzene. Although practically insoluble in water, benzene mixes with liquids such as alcohol, ether, and petroleum in all proportions; like the latter, it readily dissolves fats, resins, iodine, and other substances which are insoluble in water, and is for this reason extensively used as a solvent and for cleaning purposes; its principal use, however, is for the manufacture of nitrobenzene (p. 352) and other benzene derivatives.

Benzene is a very stable substance, and is resolved into simpler substances only with great difficulty; when boiled with concentrated alkalies, for example, it undergoes no change, and even when heated with solutions of such powerful oxidising agents as chromic acid or potassium permanganate, it is only very slowly attacked and decomposed, carbon dioxide and traces of other substances being formed. Under certain conditions, however, benzene readily yields *substitution* products; concentrated nitric acid, even at ordinary temperatures, converts the hydrocarbon into nitrobenzene by the substitution of the monovalent nitro-group $-NO_2$, for an atom of hydrogen,

$$C_6H_6 + HNO_3 = C_6H_5{\cdot}NO_2 + H_2O,$$

and concentrated sulphuric acid, slowly at ordinary temperatures, but more rapidly on heating, transforms it into benzenesulphonic acid,

$$C_6H_6 + H_2SO_4 = C_6H_5{\cdot}SO_3H + H_2O.$$

The action of chlorine and bromine on benzene is very remarkable: at moderately high temperatures, or in presence of direct sunlight, it is rapidly converted into *additive* products, such as benzene hexachloride, $C_6H_6Cl_6$, and benzene hexabromide, $C_6H_6Br_6$, by direct combination with six (but never more than six) atoms of the halogen; in absence of sunlight and at ordinary temperatures, however, the hydrocarbon is slowly attacked, yielding *substitution* products, such as chlorobenzene, C_6H_5Cl, bromobenzene, C_6H_5Br, dichlorobenzene, $C_6H_4Cl_2$, &c.; when, again, some halogen carrier (p. 342), such as ferric chloride, iodine, &c., is present, action takes place readily at ordinary temperatures even in the dark, and substitution products are formed.

Constitution of Benzene.—It will be seen from these facts that although benzene, like the paraffins, is an extremely stable substance, it differs from them very considerably in chemical behaviour, more especially in being comparatively readily acted on by nitric acid, sulphuric acid, and halogens, and in forming additive products with the last named under certain conditions; if, again, its properties be compared with those of the unsaturated hydrocarbons of the ethylene or acetylene series, the contrast is even more striking, particularly when it is borne in mind that the molecular formula of benzene, C_6H_6, indicates a relation to these unsaturated hydrocarbons rather than to the saturated compounds of the methane series.

In order, then, to obtain some clue to the constitution of benzene, it is clearly of importance to carefully consider the properties of other unsaturated hydrocarbons of known constitution, and to ascertain in what respects they differ from benzene; for this purpose the compound *dipropargyl* may be chosen, as it has the same molecular formula as benzene.

Dipropargyl, C_6H_6, is obtained as follows: *diallyl* is first prepared by treating allyl iodide with sodium,

$$2CH_2{:}CH{\cdot}CH_2I + 2Na = CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + 2NaI;$$

diallyl combines directly with bromine, yielding *diallyl tetra-*

bromide, and this, on treatment with alcoholic potash, loses 4 molecules of hydrogen bromide, and is converted into dipropargyl,

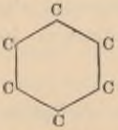
$$CH_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_2Br = CH\vdots C\cdot CH_2\cdot CH_2\cdot C\vdots CH + 4HBr.$$

Now although dipropargyl and benzene are isomeric and similar in ordinary physical properties, they are absolutely different in chemical behaviour; the former is very unstable, readily undergoes polymerisation, combines energetically with bromine, giving *additive* compounds, and is immediately oxidised even by weak agents; it shows, in fact, all the properties of an unsaturated hydrocarbon of the acetylene series. Benzene, on the other hand, is extremely stable, is comparatively slowly acted on by bromine, giving (usually) *substitution* products, and is oxidised only very slowly even by the most powerful agents. Since, therefore, dipropargyl must be represented by the above formula in order to account for its method of formation and chemical properties, the constitution of benzene could not possibly be expressed by any similar formula, such as

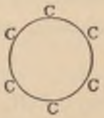
$$CH_3\cdot C\vdots C\cdot C\vdots C\cdot CH_3 \text{ or } CH_2{:}C{:}CH\cdot CH{:}C{:}CH_2,$$

because compounds similar in constitution are always more or less similar in properties, and such a formula, therefore, would not afford the slightest indication of the enormous differences between benzene and dipropargyl.

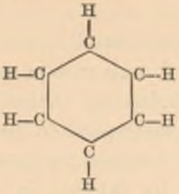
This, and many other reasons which will be stated later, led to the conclusion that *the six carbon atoms in benzene form a closed-chain or nucleus* as represented by the symbol



or



and this view, first suggested by Kekulé in 1865, is now universally accepted as the best explanation of the behaviour of benzene. Kekulé also pointed out that numerous facts established during the study of the derivatives of benzene, admit of only one conclusion—namely, that *the molecule of benzene is symmetrical*, and that *each carbon atom is directly united with one* (and only one) *atom of hydrogen*, as represented by the formula

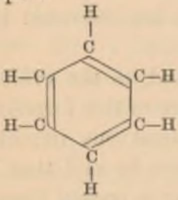


or

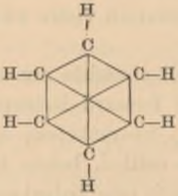
Of these, however, the former is always used in preference to the latter, partly because straight lines are invariably employed to represent direct union between two atoms, and partly on account of certain views which are discussed in a later chapter (p. 528).

Up to this point all chemists are agreed, as the evidence which can be brought forward in support of this formula is simply overwhelming; nevertheless, at least one important matter has still to be settled, before it can be said that the constitution of benzene is established as far as present theories permit. The point referred to is, the manner in which the carbon atoms are united with one another. The whole theory of the constitution of organic compounds is based on the assumption that carbon is always tetravalent, and this assumption, as already explained (part i. p. 53), is expressed in graphic formulæ by drawing four lines from each carbon atom, in such a way as to show in what manner, and to which other atoms, the particular carbon atom in question is directly united. Now, if this be done in the case of benzene, it is clear that two of the four lines or bonds, which represent the valency of each carbon atom, must be drawn to meet two other carbon atoms, because unless each carbon atom is directly united with two others, the six could not together form a closed-chain; a third line or bond is easily accounted for, because each carbon atom is directly united with hydrogen. In this way, however, only three of the four affinities of each carbon atom are disposed of, whereas it is assumed that carbon is always tetravalent, and it is known that each of the carbon atoms in benzene is still capable of combining with one monovalent group or atom.

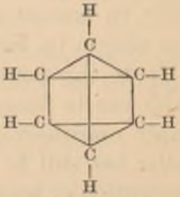
The next question, then, to be considered is, how may the fourth affinity or combining power of each carbon atom be represented so as to give the clearest indication of the behaviour of benzene? Many chemists have attempted to answer this question, and several constitutional formulæ for benzene have been put forward; that suggested by Kekulé in 1865 was for a long time considered to be the most satisfactory, but others, such as those of Claus and Ladenburg, also received support.



Kekulé.



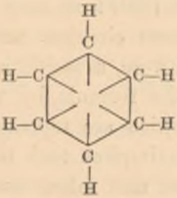
Claus.
(Diagonal formula.)



Ladenburg.
(Prism formula.)

It will be seen that these three formulæ all represent the molecule of benzene as a symmetrical closed-chain of six carbon atoms, and that they differ, in fact, only as regards the way in which the carbon atoms are represented as being united with one another; a little consideration will make it clear, moreover, that the only difference between them lies in the manner of indicating the state or condition of the fourth affinity of each carbon atom. In Kekulé's formula, for example, two lines (or a double bond) are drawn between alternate carbon atoms, a method of representation which is analogous to that adopted in the case of ethylene and other olefines; in the formulæ of Claus and Ladenburg, on the other hand, each carbon atom is represented as directly united with three others (but with a different three in the two cases).

As it would be impossible to enter here into a discussion of the relative merits of the above three formulæ, it may at once be stated that they are all to some extent unsatisfactory, as they do not account for certain facts which have been established by Baeyer during an extended study of benzene derivatives. In order to meet these objections, it has recently been suggested by Armstrong, and shortly afterwards by Baeyer, that the constitution of benzene may be best represented by the formula



Armstrong (Centric formula).

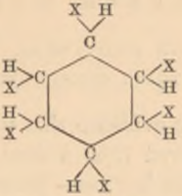
which, although in the main similar to those given above, especially to that of Claus, differs from them all in this: The fourth affinity of each of the six carbon atoms is represented as directed towards a centre (as shown by the short lines) in order to indicate that, by the mutual action of the six affinities, the power of each is exhausted or rendered latent, without bringing about actual union with another carbon atom. This formula, named by Baeyer the *centric formula*, accounts for all facts relating to benzene and its derivatives, at least as well as, and in some respects better than any which has yet been advanced, and its very indefiniteness must be regarded as a point in its favour; it is, therefore, generally adopted at the present time.

It now becomes necessary to give at greater length a few of the more important arguments which, in addition to those already considered, have led to the conclusion that the molecule of benzene consists of a symmetrical closed-chain of six carbon atoms, each of which is united with one atom of hydrogen; also to point out how simply and accurately this view of its constitution accounts for a number of facts, relating to benzene and its derivatives, which would otherwise be incapable of explanation.

In the first place, then, it may be repeated that benzene is a very stable substance; although it is readily acted on by powerful chemical agents, such as nitric acid, sulphuric acid, and bromine, and thereby converted into new compounds, all these products or derivatives of benzene contain six carbon atoms; the hydrogen atoms may be displaced by certain atoms or groups, and these, in their turn, may be displaced by others, but in spite of all these changes, the six atoms of carbon remain, forming, as it were, a stable and permanent *nucleus*. This is expressed in the formula by the closed-chain of six carbon atoms, all of which are represented in the same state of combination, which implies that there is no reason why one should be attacked and taken away more readily than another.

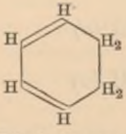
Again, a great many compounds, which may be prepared from, and converted into, benzene, contain more than six atoms of carbon; when, however, such compounds are treated in a suitable manner, they are easily converted into substances containing six, but not less than six atoms of carbon. This fact shows that in these benzene derivatives there are six atoms of carbon which are in some way different from the others, and this is also accounted for by assuming the existence of the stable nucleus; the additional carbon atoms, not forming part of, but being simply united with, this nucleus, are more easily attacked and removed.

Further, it will be remembered that although benzene usually gives substitution products, it is capable, under certain conditions, of forming additive products of the type $C_6H_6X_6$; this behaviour is also accounted for, since, in the formula, only three of the four affinities of each carbon atom are represented as actively engaged, and each carbon atom is therefore capable of combining directly with one monovalent atom or group, so as to form finally a fully saturated compound of the type,

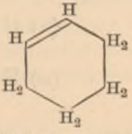


When benzene is *partially* reduced and converted into a di- or tetra-additive derivative, the compounds obtained differ very much from the original hydrocarbon, the difference being, in fact, much the same as that which exists between saturated and unsaturated compounds; in other words, when benzene or a derivative of benzene combines with two or four monad atoms, the product is no longer characterised by great stability, but shows the ordinary behaviour of unsaturated compounds, inasmuch as it is readily oxidised and readily combines with bromine.

Dihydrobenzene, C_6H_8, and tetrahydrobenzene, C_6H_{10}, combine directly with bromine at ordinary temperatures to form the compounds $C_6H_8Br_4$ and $C_6H_{10}Br_2$ respectively, just as ethylene under similar conditions yields ethylene dibromide. These facts are accounted for by assuming that, whenever benzene and its derivatives are converted into di- and tetra-additive compounds, the symmetry of the molecule is disturbed; two or four of the six carbon affinities (represented in the centric formula by the short lines directed towards the centre) being now occupied in combining with the additive atoms, the remainder are released from their original state of combination, and become united in the same way as in ethylene; di- and tetra-hydrobenzene, for example, may be represented by the formulæ



Dihydrobenzene, or benzene dihydride.



Tetrahydrobenzene, or benzene tetrahydride.

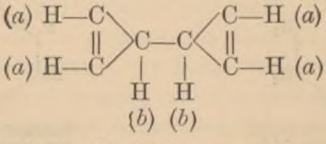
CHAPTER XVIII.

ISOMERISM OF BENZENE DERIVATIVES, AND DETERMINATION OF THEIR CONSTITUTION.

The most convincing evidence that the molecule of benzene is symmetrical is derived from a study of the isomerism of benzene derivatives. It has been proved, in the first place, that it is possible to substitute 1, 2, 3, 4, 5, or 6 monovalent atoms or groups for a corresponding number of the hydrogen atoms in benzene, compounds such as bromobenzene, C_6H_5Br, dinitrobenzene, $C_6H_4(NO_2)_2$, trimethylbenzene, $C_6H_3(CH_3)_3$, tetrachlorobenzene, $C_6H_2Cl_4$, pentamethylbenzene, $C_6H(CH_3)_5$, and hexacarboxybenzene, $C_6(COOH)_6$, being produced; the substituting atoms or groups may, moreover, be identical or dissimilar.

An examination of such substitution products of benzene has shown that when only *one* atom of hydrogen is displaced by any given atom or group, the same compound is always produced—that is to say, *the mono-substitution products of benzene exist only in one form;* when, for example, one atom of hydrogen is displaced by a nitro-group, no matter in what way this change may be brought about, the same substance, nitrobenzene, $C_6H_5{\cdot}NO_2$, is always produced.

The only conclusion to be drawn from this fact is that the molecule of benzene is symmetrical; if it were not, but were represented by any formula, such as



it would be possible, by displacing one atom of hydrogen, to obtain (at least) two isomeric products; one by displacing one of the (*a*), another by displacing one of the (*b*), hydrogen atoms.

The existence of the mono-substitution products of benzene in one form only, might, of course, be explained by assuming that one particular hydrogen atom was always displaced first; when, for example, acetic acid is treated with soda, only one of the four hydrogen atoms is displaceable, and consequently the same salt is invariably produced. In the case of benzene, however, it has been shown that the same substance is formed no matter which of the six hydrogen atoms is displaced; therefore they are all in the same state of combination.

The manner in which this has been done may be indicated by the following example: Phenol, $C_6H_5{\cdot}OH$, or hydroxybenzene, obtained indirectly by displacing one atom of hydrogen (A) by the hydroxyl-group, may, with the aid of phosphorus pentabromide, be directly converted into bromobenzene, C_6H_5Br, and the latter may be transformed into benzoic acid (or carboxybenzene), $C_6H_5{\cdot}COOH$, by submitting it to the action of sodium and carbon dioxide; as these three substances are produced from one another by simple interactions, there is every reason to suppose that the carboxyl-group in benzoic acid is united with the same carbon atom as the bromine atom in bromobenzene and the hydroxyl-group in phenol; that is to say, that the same hydrogen atom (A) has been displaced in all three cases. Now the benzoic acid obtained in this way may be converted into three different hydroxybenzoic acids of the composition $C_6H_4(OH){\cdot}COOH$, the difference between them being due to the fact that the hydroxyl-group has displaced a different hydrogen atom (B.C.D.) in each case; each of these hydroxybenzoic acids forms a calcium salt which yields phenol on distillation (the carboxyl-group being displaced by hydrogen), and the three specimens of phenol thus produced are identical with the original phenol; it is evident, therefore, that at least four (A.B.C.D.) hydrogen atoms in benzene are in the same state of combination, and occupy the same relative position in the molecule; in a similar manner it can be shown that this is true of all six.

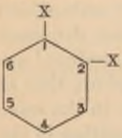
By substituting *two* monovalent atoms or groups for two of the atoms of hydrogen in benzene, three, but not more than three substances having different properties are obtained;

there are, for example, three dinitrobenzenes, $C_6H_4(NO_2)_2$, three dibromobenzenes, $C_6H_4Br_2$, three dihydroxybenzenes, $C_6H_4(OH)_2$, three nitrohydroxybenzenes, $C_6H_4(NO_2)\cdot OH$, and so on.

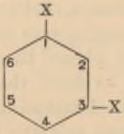
Three isomerides are not always produced in any particular reaction, and all di-substitution products of benzene are not *known* to exist in three forms; but from the study of a great many compounds of this kind, it is practically certain that they all could be obtained in three isomeric modifications.

Now the existence of these three isomerides can be accounted for in a very simple manner with the aid of the formula already given, which, for this purpose, may conveniently be represented by a simple hexagon, numbered as shown, the symbols C and H being omitted for the sake of simplicity.

Suppose that any mono-substitution product, C_6H_5X, which, as already stated, exists only in one form, be converted into a di-substitution product, $C_6H_4X_2$; then if it be assumed that the atom or group (X) first introduced occupied any given position, say that numbered 1, the second atom or group may have substituted any one of the hydrogen atoms at 2, 3, 4, 5, or 6, giving a substance, the constitution of which might be represented by one of the following five formulæ:

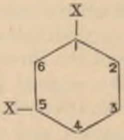


I.

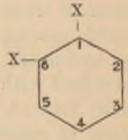


II.

III.



IV.



V.

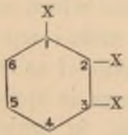
These five formulæ, however, represent three isomeric substances, and three only. The formula (IV.) represents a compound in which the several atoms occupy the same relative positions as in the substance represented by the formula (II.), and for the same reason the formula (V.) is identical with (I.). Although there is at first sight an apparent difference, a little consideration will show that this is simply due to the fact that the formulæ are viewed from one point only; if the formulæ IV. and V. be held before a mirror, or viewed through the paper, it will be seen at once that they are identical with II. and I. respectively. Each of the formulæ I., II., and III., on the other hand, represents a different substance, because in no two cases are all the atoms in the same relative positions; in other words, the di-substitution products of benzene exist theoretically in three isomeric forms.

In the foregoing examples the two substituting atoms or groups have been considered to be identical, but even when they are different, experience has shown that only three di-substitution products can be obtained, and this fact, again, is in accordance with the theory. If in the above five formulæ either of the X's be written Y to express a difference in the substituting groups, it will be seen that, as before, the formula I. is identical with V., and II. with IV., but that I., II., and III. all represent different arrangements of the atoms—that is to say, three different substances.

Since *the di-substitution products of benzene exist in three isomeric forms*, it is convenient to have some way of distinguishing them by name; for this reason all di-substitution products which are found to have the constitution represented by formula I. are called **ortho**-compounds, and the substituting atoms or groups are said to be in the ortho- or 1:2-position to one another; those substances which may be represented by the formula II. are termed **meta**-compounds, and the substituting atoms or groups are spoken of as occupying the meta- or 1:3-position; the term **para** is applied to compounds represented by the formula III., in which the atoms or groups are situated in the para- or 1:4-position.

Ortho-compounds, then, are those in which it is assumed, for reasons given below, that the two substituting atoms or groups are combined with carbon atoms which are themselves *directly united;* instead of expressing the constitution of any ortho-compound by the formula I., and representing the substituting atoms or groups as combined with the carbon atoms 1 and 2, it would therefore be just the same if they were represented as united with the carbon atoms 2 and 3, 3 and 4, 4 and 5, 5 and 6, or 6 and 1; the arrangement of all the atoms would be the same, because the benzene molecule is symmetrical, and the numbering of the carbon atoms simply a matter of convenience. In a similar manner the substituting atoms or groups in meta-compounds may be represented as combined with any two carbon atoms which are themselves not directly united, but linked together by one carbon atom; it is quite immaterial which two carbon atoms are chosen, since atoms or groups occupying the 1:3, 2:4, 3:5, 4:6, or 5:1-position are identically situated with regard to all the other atoms of the molecule. For the same reason para-compounds may be represented by placing the substituting atoms or groups in the 1:4, 2:5, or 3:6-position.

When more than two atoms of hydrogen in benzene are substituted, it has been found that the number of isomerides differs according as the substituting atoms or groups are identical or not. By displacing *three* atoms of hydrogen by three identical atoms or groups, three isomerides can be obtained, three trimethylbenzenes, $C_6H_3(CH_3)_3$, for example, being known. Again, the existence of these isomerides can be easily accounted for, since their constitutions may be represented as follows:



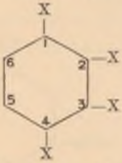
Adjacent.

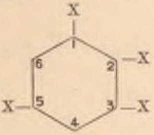
Asymmetrical.

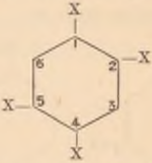
Symmetrical.

No matter in what other positions the substituting atoms or groups be placed, it will be found that the arrangement is the same as that represented by one of the above formulæ; the position 1:2:3, for example, is identical with 2:3:4, 3:4:5, &c.; 1:3:4 with 2:4:5, 3:5:6, &c., and 1:3:5 with 2:4:6. For the purpose of referring to such tri-substitution products, the terms given above are often employed.

The tetra-substitution products of benzene, in which all the substituting atoms or groups are identical, also exist in three isomeric forms represented by the following formulæ:





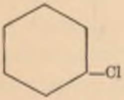


When, however, five or six atoms of hydrogen are displaced by identical atoms or groups, only one substance is produced.

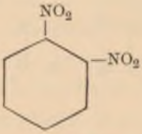
When more than two atoms of hydrogen are displaced by atoms or groups which are not all identical, the number of isomerides which can be obtained is very considerable; in the case of any tri-substitution product, $C_6H_3X_2Y$, for example, six isomerides might be formed, as may be easily seen by assigning a definite position, say 1, to Y; the isomerides would then be represented by formulæ in which the groups occupied the position 1:2:3, 1:2:4, 1:2:5, 1:2:6, 1:3:4, or 1:3:5, all of which would be different.

All the cases of isomerism considered up to the present have been those due to the substituting atoms or groups occupying different relative positions in the benzene nucleus; as, however, many benzene derivatives contain groups of atoms which themselves exist in isomeric forms, such compounds also exhibit isomerism exactly similar to that already met with in the case of the paraffins, alcohols, &c. There are, for example, two isomeric hydrocarbons of the composition $C_6H_5{\cdot}C_3H_7$, namely, *propylbenzene*, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, and *isopropylbenzene*, $C_6H_5{\cdot}CH(CH_3)_2$, just as there are two isomeric ethereal salts of the composition C_3H_7I. As, moreover, the two propylbenzenes, $C_6H_5{\cdot}C_3H_7$, are isomeric with the three (ortho-, meta-, and para-) ethylmethylbenzenes, $C_6H_4(C_2H_5)\cdot CH_3$, and also with the three (adjacent, symmetrical, and asymmetrical) trimethylbenzenes, $C_6H_3(CH_3)_3$, there are in all eight hydrocarbons of the molecular formula C_9H_{12}, derived from benzene.

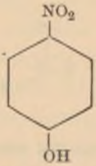
In studying the isomerism of benzene derivatives, the clearest impressions will be gained by invariably making use of a simple, unnumbered hexagon to represent C_6H_6, and by expressing the constitutions of simple substitution products by formulæ such as ·



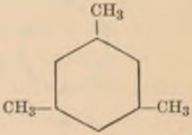
Chlorobenzene.



Dinitrobenzene.



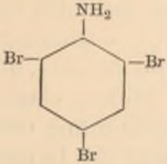
Nitrophenol.



Trimethylbenzene.

The omission of the symbols C and H is attended by no disadvantage whatsoever, because, in order to convert the above into the ordinary molecular formulæ, it is only necessary to write C_6 instead of the hexagon, and then to count the unoccupied corners of the hexagon to find the number of hydrogen atoms in the nucleus, the substituting atoms or groups being added afterwards. In the case of chlorobenzene, for example, there are five unoccupied corners, so that the molecular formula is C_6H_5Cl; whereas in the case of trimethylbenzene there are three, and the formula, therefore, is $C_6H_3(CH_3)_3$.

As, however, such graphic formulæ occupy a great deal of space, their constant use in a text-book is out of the question, and other methods have to be adopted. The most usual course in the case of the di-derivatives is to employ the terms ortho-, meta-, and para-, or simply the letters *o*, *m*, and *p*, as, for example, ortho-dinitrobenzene or *o*-dinitrobenzene, meta-nitraniline or *m*-nitraniline, para-nitrophenol or *p*-nitrophenol; the relative positions of the atoms or groups may also be expressed by numbers; ortho-chloronitrobenzene, for example, may be described as 1:2-chloronitrobenzene, as $C_6H_4{<}\begin{matrix}Cl\ (1)\\ NO_2(2)\end{matrix}$, or as $C_6H_4\overset{1}{Cl}\cdot\overset{2}{NO_2}$, the corresponding para-compound as 1:4-chloronitrobenzene, as $C_6H_4{<}\begin{matrix}Cl\ (1)\\ NO_2(4)\end{matrix}$, or as $C_6H_4\overset{1}{Cl}\cdot\overset{4}{NO_2}$. In the case of the tri-derivatives the terms symmetrical, asymmetrical, and adjacent (compare p. 314) may be employed when all the atoms or groups are the same, but when they are different the constitution of the compound is usually expressed with the aid of numbers; the tribromaniline of the constitution



for example, is described as $C_6H_2Br_3\cdot NH_2[\overset{1}{Br}:\overset{3}{Br}:\overset{5}{Br}:\overset{6}{NH_2}]$, or as $C_6H_2Br_3\cdot NH_2[3Br:NH_2 = 2:4:6:1]$, and it is of course quite immaterial from which corner of the imaginary hexagon the numbering is commenced.

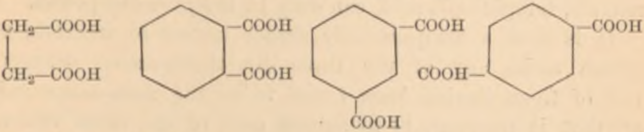
Determination of the Constitution of Benzene Derivatives.

It has been pointed out that the di-substitution products of benzene, such as dibromobenzene, $C_6H_4Br_2$, dihydroxybenzene, $C_6H_4(OH)_2$, and nitraniline, $C_6H_4(NO_2)\cdot NH_2$, exist in three isomeric forms, and that their isomerism is due to the different relative positions of the substituting atoms or groups in the benzene nucleus; it is evident, however, that in order to arrive at the constitution of any one of these substances, and to be able to say whether it is an ortho-, meta-, or para-compound, a great deal of additional information is required.

Now the methods which are adopted in deciding questions of this kind at the present time are comparatively simple, but they are based on the results of work which has extended over many years. It has been found, in the first place, that a given di-substitution product of benzene may be converted by more or less indirect methods into many of the other di-substitution products of the *same series; ortho*-dinitrobenzene, $C_6H_4(NO_2)_2$, for example, may be transformed into *o*-diamidobenzene, $C_6H_4(NH_2)_2$, *o*-dihydroxybenzene, $C_6H_4(OH)_2$, *o*-dibromobenzene, $C_6H_4Br_2$, *o*-dimethylbenzene, $C_6H_4(CH_3)_2$, and so on, similar changes being also possible in the case of meta- and para-compounds. If, therefore, it can be ascertained to which series a given di-substitution product belongs, the constitution of other di-substitution products of this series may be easily determined; suppose, for example, that it could be proved that of the three dinitrobenzenes, the compound melting at 90° is a meta-compound, then it would necessarily follow that the diamido-, dihydroxy-, dibromo-, and other di-derivatives of benzene obtained from this particular dinitro-compound by substituting other atoms or groups for the two nitro-groups, must also be meta-compounds; it would also be known that the di-derivatives of benzene obtained from the other two dinitrobenzenes, melting at 118° and 173° respectively, in a similar manner must be either ortho- or para-compounds.

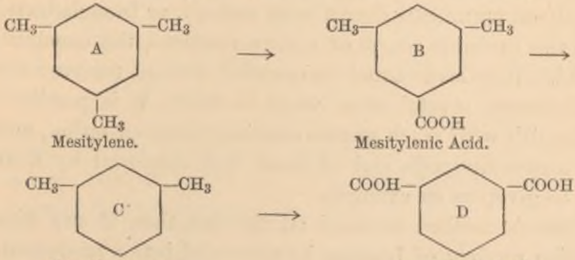
It was necessary, therefore, in the first place, to determine the constitution of one or two di-derivatives of each series; these substances then served as standards, and the constitution of any other di-derivative was established by converting it by suitable reactions into one of these standards.

As an illustration of the methods and arguments originally employed in the solution of problems of this nature, the case of the dicarboxy- and dimethyl-derivatives of benzene may be quoted. Of the three dicarboxybenzenes, $C_6H_4(COOH)_2$, one—namely, phthalic acid (p. 425), is very readily converted into its anhydride, but all attempts to prepare the anhydrides of the other two acids (isophthalic acid and terephthalic acid, pp. 426, 427) result in failure; it is assumed, therefore, that the acid which gives the anhydride is the *o*-compound, because, from a study of the behaviour of many other dicarboxylic acids, it has been found that anhydride formation takes place most readily when the two carboxyl-groups are severally combined with two carbon atoms which are themselves directly united, as, for example, in the case of succinic acid. In other words, if the graphic formulæ of succinic acid and of the three dicarboxy-derivatives of benzene be compared, it will be evident that in the *o*-compound the relative position or state of combination of the two carboxyl-groups is practically the same as in succinic acid, but quite otherwise in the case of the *m*- and *p*-compounds.



For this, and other reasons not stated here, phthalic acid may be provisionally regarded as an *ortho*-dicarboxybenzene.

Again, the hydrocarbon mesitylene or trimethylbenzene, $C_6H_3(CH_3)_3$, may be produced synthetically from acetone (p. 337), and its formation in this way can be explained in a simple manner, only by assuming that mesitylene is a symmetrical trimethylbenzene of the constitution (A).



Mesitylene. Mesitylenic Acid.

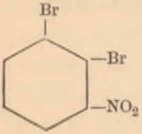
Dimethylbenzene. (Isoxylene.) Isophthalic Acid.

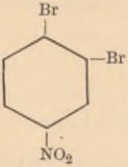
When this hydrocarbon is carefully oxidised, it yields an acid (B) of the composition $C_6H_3(CH_3)_2 \cdot COOH$ (by the conversion of one of the methyl-groups into carboxyl), from which a dimethylbenzene, $C_6H_4(CH_3)_2$ (C), is easily obtained by the substitution of hydrogen for the carboxyl-group. This dimethylbenzene, therefore, is a *meta*-compound, because no matter which of the original three methyl-groups in mesitylene has been finally displaced by hydrogen, the remaining two must occupy the *m*-position. Now when this dimethylbenzene is oxidised with chromic acid, it is converted into a dicarboxylic acid (D)—namely, isophthalic acid, $C_6H_4(COOH)_2$, which, therefore, must also be regarded as a meta-compound; the constitution of two of the three isomeric dicarboxy-derivatives of benzene having been thus determined, the third—namely, terephthalic acid, can only be the *para*-compound.

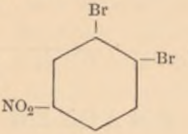
It is now a comparatively simple matter to ascertain to which series any of the three dimethylbenzenes belongs; one of them having been found to be the meta-compound, all that is necessary is to submit each of the other two to oxidation, and that which gives phthalic acid will be the ortho-compound, whilst that which yields terephthalic acid will be the para-derivative. Moreover, the constitution of any other di-substitution product of benzene may now be determined without difficulty, provided that it is possible to convert it into one of these standards by simple reactions.

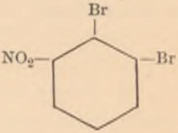
As the methods which have just been indicated are based entirely on arguments drawn from analogy, or from deductions as to the probable course of certain reactions, the conclusions to which they lead cannot be accepted without reserve; there are, however, several other ways in which it is possible to distinguish with much greater certainty between ortho-, meta-, and para-compounds, and of these that employed by Körner may be given as an example.

Körner's method is based on the fact that, if any di-substitution product of benzene be converted into a tri-derivative by further displacement of hydrogen of the nucleus, the number of isomerides which may be obtained from an ortho-, meta-, and para-compound is different in the three cases, so that by ascertaining the number of these products the constitution of the original di-derivative may be established. Suppose, for example, that one of the three isomeric dibromobenzenes be converted into nitrodibromobenzene by treatment with nitric acid; then, if it be the *ortho*-dibromo-compound, it is possible to obtain from it *two*, but only two, nitrodibromobenzenes, because, although there are four hydrogen atoms, any one of which may be displaced by a nitro-group, as represented by the following formulæ,


I.

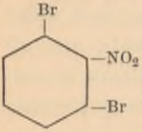

II.

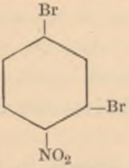

III.

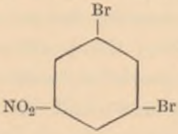

IV.

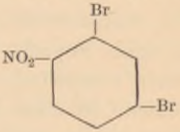
the compound of the constitution (III.) is identical with (II.), and (IV.) with (I.), the relative positions of all the atoms being the same in the two cases respectively.

If, on the other hand, the dibromobenzene be the *meta*-compound, it might yield *three*, and only three, isomeric nitro-derivatives, which would be represented by the first three of the following formulæ, the fourth being identical with the second:

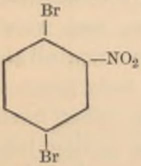


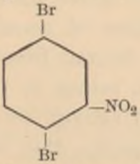


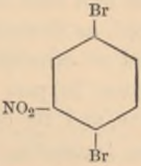


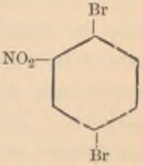


Finally, if the substance in question be *para*-dibromobenzene, it could give only *one* nitro-derivative, the following four formulæ being identical :









It is obvious, then, that this method may be applied in ascertaining to which series any di-substitution product belongs; it may also be employed in determining the constitution of the tri-derivatives in a similar manner.

At the present time, therefore, the constitution of any new benzene derivative is, as a rule, very easily ascertained; it is simply converted into some compound of known constitution, or the number of isomerides obtained from it by substitution is determined.

CHAPTER XIX.

GENERAL PROPERTIES OF AROMATIC COMPOUNDS.

Classification of Organic Compounds.—The examples given in the foregoing pages will have afforded some indication of the large number of compounds which it is possible to prepare from benzene, by the substitution of various elements or groups for atoms of hydrogen; as the substances formed in this way, and many other benzene derivatives which occur in nature, or may be prepared synthetically, still retain much of the characteristic chemical behaviour of benzene, and differ in many respects from the paraffins, alcohols, acids, and all other compounds previously considered (part i.), it is convenient to class benzene and its derivatives in a separate group.

Organic compounds are therefore classed in two principal divisions, the **fatty** and the **aromatic.** The word 'fatty,' originally applied to some of the acids of the $C_nH_{2n}O_2$ series (part i. p. 142), is now used to denote all compounds which may be considered as derivatives of marsh-gas, and which cannot be regarded as directly derived from benzene; all the compounds described in part i. belong to the fatty group or division. Benzene and its derivatives, on the other hand, are classed in the 'aromatic' group, this term having been first applied to certain naturally occurring compounds (which have since been proved to be benzene derivatives) on account of their peculiar aromatic odour.

The fundamental distinction between fatty and aromatic compounds is one of constitution. The reasons which have led to the conclusion that benzene contains a closed chain of six carbon atoms being equally valid in the case of its derivatives, it is assumed that this (or a similar) nucleus is present in all aromatic compounds. The constitution of a fatty compound, however, is almost invariably expressed by a formula such as $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2(OH)$, and $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, in which the carbon atoms do not form a closed-, but an open-chain;[*] such compounds, moreover, may be regarded as derived from marsh-gas by a series of simple steps. For these reasons, compounds belonging to the fatty series are often spoken of as *open-chain* compounds, in contradistinction to the *closed-chain* compounds of the aromatic group.

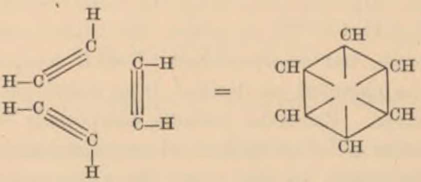
It must not, however, be supposed that all aromatic are sharply distinguished in any way from all fatty compounds, or that either class can be defined in any exact terms. Many compounds, the constitutions of which must be represented by closed-chain formulæ, are nevertheless placed in the fatty group, simply because to class them in the aromatic division would remove them from those substances to which they are most closely related; succinimide (part i. p. 237), for example, is a closed-chain compound in the strict sense of the word, but is clearly more conveniently considered in the fatty series, because of its relationship to succinic acid. Although, again, the members of the aromatic group may all be regarded as derivatives of benzene, they may also be considered as derived from marsh-gas, since not only benzene itself, but many other aromatic compounds, may be directly obtained from members

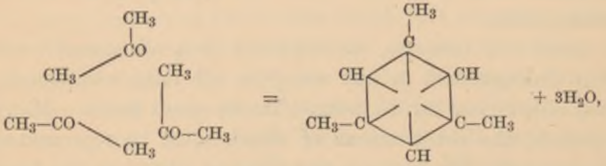
---

[*] The terms 'open-chain' and 'closed-chain' originated in the chain-like appearance of the graphic formulæ as usually written, and are not intended to convey the idea that the atoms are joined together by any form of matter, or that they are all arranged in straight lines.

of the fatty series by simple reactions, and, conversely, many aromatic compounds may be converted into those of the fatty series.

Some examples of the production of aromatic from fatty compounds have already been given—namely, the formation of benzene by the polymerisation of acetylene, and that of mesitylene by the condensation of acetone; these two changes may be expressed graphically in the following manner:





and may be regarded as typical reactions, because many other substances, similar in constitution to acetylene and acetone respectively, may be caused to undergo analogous transformations. Bromacetylene, CBr⋮CH, for example, may be converted into (symmetrical) tribromobenzene, simply by leaving it exposed to direct sunlight,

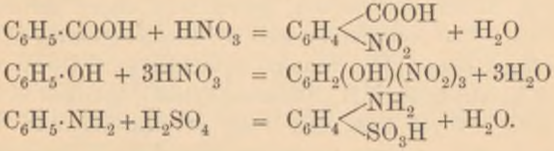
$$3C_2HBr = C_6H_3Br_3;$$

and methylethyl ketone (a homologue of acetone) is transformed into symmetrical triethylbenzene (a homologue of mesitylene) by distilling it with sulphuric acid,

$$3CH_3{\cdot}CO{\cdot}C_2H_5 = C_6H_3(C_2H_5)_3 + 3H_2O.$$

General Character of Aromatic Compounds.—Although, then, it is impossible to draw any sharp line between fatty and aromatic compounds, and many substances are known which form a connecting link between the two divisions, the great majority of aromatic substances differ materially from those of the fatty division in constitution, and consequently also in properties.

Speaking generally, aromatic compounds contain a larger percentage of carbon than those of the fatty division, and probably for this reason, they are more frequently crystalline at ordinary temperatures. They are, as a rule, less readily resolved into simple substances than are the members of the fatty series, although in most cases they are more easily converted into substitution products. Their behaviour with nitric acid and with sulphuric acid is very characteristic, and distinguishes them from nearly all fatty compounds, inasmuch as they are, as a rule, readily converted into nitro- and sulphonic-derivatives respectively by the displacement of hydrogen atoms of the nucleus,



$$\begin{aligned} C_6H_5{\cdot}COOH + HNO_3 &= C_6H_4{<}\begin{smallmatrix}COOH\\NO_2\end{smallmatrix} + H_2O \\ C_6H_5{\cdot}OH + 3HNO_3 &= C_6H_2(OH)(NO_2)_3 + 3H_2O \\ C_6H_5{\cdot}NH_2 + H_2SO_4 &= C_6H_4{<}\begin{smallmatrix}NH_2\\SO_3H\end{smallmatrix} + H_2O. \end{aligned}$$

Fatty compounds rarely give sulphonic- or nitro-derivatives under the same conditions, but are acted on in such a way that they are resolved into two or more simpler substances.

When aromatic nitro-compounds are treated with reducing agents, they are converted into amido-compounds,

$$\begin{aligned} C_6H_5{\cdot}NO_2 + 6H &= C_6H_5{\cdot}NH_2 + 2H_2O \\ C_6H_4(NO_2)_2 + 12H &= C_6H_4(NH_2)_2 + 4H_2O. \end{aligned}$$

These amido-compounds differ from the fatty amines in at least one very important respect, inasmuch as they are converted into diazo-compounds (p. 370) on treatment with nitrous acid in the cold; this behaviour is highly characteristic, and the diazo-compounds form one of the most interesting and important classes of aromatic substances.

It has already been pointed out that benzene does not show the ordinary behaviour of unsaturated fatty compounds, although under certain conditions both the hydrocarbon and its derivatives are capable of forming additive compounds by direct combination with two, four, or six (but not with one, three, or five) monovalent atoms. This fact proves that benzene is not really a saturated compound like methane, or ethane, for example, both of which are quite incapable of yielding derivatives except by substitution. Nevertheless, the conversion of benzene and its derivatives into additive products, is, as a rule, much less readily accomplished than in the case of fatty, unsaturated compounds; the halogen acids, for example, which unite directly with so many unsaturated fatty compounds, have no such action on benzene and its derivatives, and even in the case of the halogens and nascent hydrogen, direct combination occurs only under particular conditions. The compounds, such as dihydrobenzene, C_6H_8, tetrahydrobenzene, C_6H_{10}, benzene hexachloride, $C_6H_6Cl_6$, and benzene hexahydride, C_6H_{12} (hexamethylene), obtained in this way, have not yet been very fully investigated, but from what is known of their properties, they form a connecting link between the members of the aromatic and fatty divisions (compare p. 309).

When the hydrogen atoms in benzene are displaced by groups or radicles which are composed of several atoms, these groups are spoken of as *side-chains;* ethylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_3$, benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$, and methyl aniline, $C_6H_5 \cdot NH \cdot CH_3$, for example, would each be said to contain a side-chain, whereas the term would not, as a rule, be applied in the case of phenol, $C_6H_5 \cdot OH$, nitrobenzene, $C_6H_5 \cdot NO_2$, &c., where the substituting groups are comparatively simple, and do not contain carbon atoms.

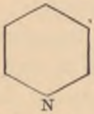
Now the character of any particular atom or group in the side-chain, although influenced to some extent by the fact that the group is united with the benzene nucleus, is on the whole very similar to that which it possesses in fatty compounds. The consequence is that aromatic compounds containing side-chains of this kind have not only the properties already referred to, as characteristic of the derivatives of benzene, but show also, to a certain extent, the behaviour of fatty compounds. Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, for example, may be directly converted into the nitro-derivative, $C_6H_4(NO_2){\cdot}CH_2Cl$, and the sulphonic acid, $C_6H_4(SO_3H){\cdot}CH_2Cl$, reactions characteristic of aromatic compounds; on the other hand, the $-CH_2Cl$ group may be transformed into $-CH_2{\cdot}OH$, $-CHO$, $-COOH$, and so on, just as may the same group in ethyl chloride, $CH_3{\cdot}CH_2Cl$, and similar fatty compounds, and in all cases the products retain, to some extent, the properties of fatty substances as long as the side-chain remains. The groups forming the side-chains, however, are more easily attacked and removed than the closed-chain or nucleus; when ethylbenzene, $C_6H_5{\cdot}CH_2{\cdot}CH_3$, or propylbenzene, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, for example, is boiled with chromic acid, the side-chain undergoes oxidation, carbon dioxide is evolved, and benzoic acid, $C_6H_5{\cdot}COOH$, is produced in both cases, the six atoms of carbon in the nucleus being unchanged (p. 417).

Although the compounds derived from benzene by direct substitution are very numerous, the aromatic group also contains a great many other substances which are more distantly related to benzene, and which can only be regarded as derived from it indirectly. The hydrocarbon *diphenyl*, $C_6H_5{-}C_6H_5$, for example, which, theoretically, is formed by the union of two *phenyl* or $C_6H_5{-}$ groups, just as dimethyl or ethane, $CH_3{-}CH_3$, is produced by the combination of two methyl-groups, is an important member of the aromatic division, and, like benzene, is capable of yielding a very large number of substitution products. Other hydrocarbons are known in which the presence of two or more closed carbon chains, combined in different ways, must be assumed, as, for example, in the cases of naphthalene (p. 442) and anthracene (p. 437),

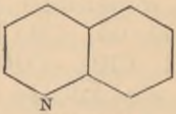
Naphthalene.

Anthracene.

and there are also substances, such as pyridine (p. 472) and quinoline (p. 480), in which a nitrogen atom occupies the position of one of the $CH\equiv$ groups in the closed-chain.



Pyridine.



Quinoline.

All these, and many other compounds and their derivatives, are classed as aromatic, because they show the general behaviour already referred to, and resemble benzene more or less closely in constitution.

CHAPTER XX.

HOMOLOGUES OF BENZENE.

Benzene, the simplest hydrocarbon of the aromatic group, is also the first member of a homologous series of the general formula C_nH_{2n-6}; the hydrocarbons of this series are derived from benzene by the substitution of alkyl-groups for hydrogen atoms, just as the homologous series of paraffins is derived from marsh-gas. The second member, toluene or methylbenzene, $C_6H_5{\cdot}CH_3$, like benzene itself, exists in only one form, but the next higher homologue, which has the molecular composition C_8H_{10}, occurs in four isomeric forms—namely, as ethylbenzene, $C_6H_5{\cdot}C_2H_5$, and as ortho-, meta-, and para-dimethylbenzene, $C_6H_4(CH_3)_2$; on passing up the series, the number of theoretically possible isomerides rapidly increases.

By substituting a methyl-group for one atom of hydrogen in the hydrocarbon C_8H_{10}, for example, eight isomerides of the composition C_9H_{12} may theoretically be obtained, and are, in fact, known; of these isomerides, five—namely, propylbenzene and isopropylbenzene, $C_6H_5{\cdot}C_3H_7$, and *o*-, *m*-, and *p*-methylethylbenzene, $C_6H_4(CH_3){\cdot}C_2H_5$, are derived from ethylbenzene, the other three—namely, symmetrical, adjacent, and asymmetrical trimethylbenzene, $C_6H_3(CH_3)_3$, being derived from the dimethylbenzenes.

Most of the hydrocarbons of this series, and others which will be mentioned later, occur in coal-tar, from which they are extracted in much the same way as benzene; it is, however, exceedingly difficult to obtain any of them in a pure state directly from this source by fractional distillation, as the boiling-points of some of the compounds lie very close together; nevertheless, the process is now carried out on the large scale with such care and with such perfect apparatus that the purified compounds contain, in some cases, only traces of foreign substances.

The homologues of benzene may be obtained by the following general methods:

(1) By treating benzene or its homologues with alkyl halogen compounds in presence of anhydrous aluminium chloride (Friedel and Craft's reaction); under these conditions the hydrogen atoms of the nucleus are displaced by alkyl-groups, benzene and methyl chloride, for example, giving toluene, $C_6H_5{\cdot}CH_3$, xylene, $C_6H_4(CH_3)_2$, trimethylbenzene, $C_6H_3(CH_3)_3$, &c.; whereas ethylbenzene, with the same alkyl compound, yields methylethylbenzene, $C_6H_4(CH_3){\cdot}C_2H_5$, dimethylethylbenzene, $C_6H_3(CH_3)_2{\cdot}C_2H_5$, and so on. These syntheses may be expressed by equations such as the following, but the exact nature of the interaction is not known:

$$C_6H_6 + CH_3Cl = C_6H_5{\cdot}CH_3 + HCl$$
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl$$
$$C_6H_5{\cdot}C_2H_5 + CH_3Cl = C_6H_4(CH_3){\cdot}C_2H_5 + HCl.$$

It is probable that an aluminium compound, such as

$C_6H_5{\cdot}Al_2Cl_5$, is first formed with evolution of hydrogen chloride, this substance then interacting with the alkyl halogen compound to form the hydrocarbon, aluminium chloride being regenerated,

$$C_6H_5{\cdot}Al_2Cl_5 + CH_3Cl = C_6H_5{\cdot}CH_3 + Al_2Cl_6;$$

an alkyl bromide may be used instead of the chloride, and anhydrous ferric or zinc chloride may be employed in the place of aluminium chloride, but, as a rule, not so successfully.

Anhydrous benzene, or one of its homologues, is placed in a flask connected with a reflux condenser, and about one-third of its weight of anhydrous aluminium chloride added; the alkyl chloride or bromide is then passed into the liquid if a gas, or poured in, if a liquid, and the mixture heated on a water-bath until the evolution of hydrogen chloride or bromide is at an end; the apparatus and materials must be dry. In some cases ether, carbon bisulphide, or petroleum is previously mixed with the hydrocarbon in order to dilute it, experience having shown this to be advantageous. When quite cold, water is gradually added to dissolve the aluminium compounds, and after having been separated and dried with calcium chloride, the mixture of hydrocarbons is submitted to fractional distillation; in some cases a preliminary distillation in steam is advisable.*

(2) By treating a mixture, consisting of a halogen derivative of benzene or of one of its homologues, and an alkyl halogen compound, with sodium or potassium (Fittig's reaction); this method of formation is similar to that by which the higher paraffins may be synthetically produced from methane, and has the advantage over Friedel and Craft's method that the constitution of the product is known. Bromobenzene and methyl iodide, for example, give toluene, whereas *o*-, *m*-, or *p*-bromotoluene and ethyl iodide yield *o*-, *m*-, or *p*-ethylmethylbenzene,

$$C_6H_5Br + CH_3I + 2Na = C_6H_5{\cdot}CH_3 + NaI + NaBr$$

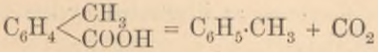
$$C_6H_4Br{\cdot}CH_3 + C_2H_5I + 2K = C_6H_4{<}\begin{matrix}CH_3\\C_2H_5\end{matrix} + KBr + KI.$$

---

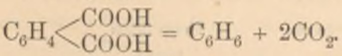
* In most cases the detailed description of the preparation of substances is given in small print.

The bromo-derivatives of the aromatic hydrocarbons are usually employed in such cases because the chloro-derivatives are not so readily acted on, and the iodo-compounds are not so easily prepared; the alkyl iodides are also used in preference to the chlorides or bromides because they interact more readily.

(3) By heating carboxy-derivatives of benzene and its homologues with soda-lime, a method analogous to that employed in converting the fatty acids into paraffins,



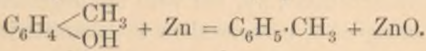
$$C_6H_4\left\langle\begin{matrix}CH_3\\COOH\end{matrix}\right. = C_6H_5{\cdot}CH_3 + CO_2$$



$$C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. = C_6H_6 + 2CO_2.$$

(4) By passing the vapour of hydroxy-derivatives of benzene and its homologues over heated zinc-dust, which acts as a powerful reducing agent by combining with the oxygen in the compound,

$$C_6H_5{\cdot}OH + Zn = C_6H_6 + ZnO$$



$$C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right. + Zn = C_6H_5{\cdot}CH_3 + ZnO.$$

(5) By the destructive distillation of coal, wood, peat, &c., and by passing the vapour of many fatty compounds through red-hot tubes (compare p. 300).

General Properties.—Most of the homologues of benzene are colourless, mobile liquids, resembling benzene in smell and in ordinary physical properties; one or two, however, are crystalline at ordinary temperatures. They all distil without decomposition, are volatile in steam, and burn with a smoky flame; they are insoluble in water, but miscible with alcohol, ether, petroleum, &c., in all proportions; they dissolve fats and many other substances which are insoluble in water.

Just as in other homologous series, the homologues of benzene show a gradual variation in physical properties with increasing molecular weight; an example of this is afforded by the following *mono*-substitution products of benzene, only the last of which occurs in two isomeric forms:

	Benzene, C_6H_6.	Toluene, C_7H_8.	Ethylbenzene, C_8H_{10}.	Propylbenzene, C_9H_{12}.	
				Normal.	Iso.
Sp. gr. at 0°	0·899	0·882	0·866 (at 20°)	0·881	0·879
B.p.	80·5°	110·3°	134°	157°	153°.

In the case of the *di*-substitution products the gradual variation in physical properties is obscured by the existence of the three (or more) isomeric forms, which themselves show considerable differences, as illustrated by the three isomeric xylenes, $C_6H_4(CH_3)_2$,

	Orthoxylene.	Metaxylene.	Paraxylene.
Sp. gr. at 0°	0·893	0·881	0·880
B.p.	142–143°	139°	136–137° (M.p. 15°).

As a general rule, to which, however, there are some exceptions, para-compounds melt at a higher temperature than the corresponding meta-compounds, and the latter usually at a higher temperature than the corresponding ortho-compounds; the boiling-points also vary, but with less regularity.

The homologues of benzene show the characteristic chemical behaviour of the simplest hydrocarbon, inasmuch as they readily yield nitro- and sulphonic-derivatives; toluene, for example, gives nitrotoluene, $C_6H_4(CH_3)\cdot NO_2$, and toluenesulphonic acid, $C_6H_4(CH_3)\cdot SO_3H$, xylene yielding nitroxylene, $C_6H_3(CH_3)_2\cdot NO_2$, and xylenesulphonic acid,

$$C_6H_3(CH_3)_2\cdot SO_3H.$$

In these, and in all similar reactions, the product invariably consists of a mixture of isomerides, the course of the reaction depending both on the nature of the interacting compounds and on the conditions of the experiment (compare p. 351); as a rule, the greater the number of alkyl-groups in the hydrocarbon, the more readily it yields nitro- and sulphonic-derivatives.

The fact that benzene and its homologues gradually dissolve in concentrated sulphuric acid, especially on warming, is sometimes made use of in separating these aromatic hydrocarbons from the paraffins, as, for example, in the analysis of coal-gas; their separation from unsaturated fatty hydrocarbons could not of course be accomplished in this way, as the latter are also dissolved by concentrated sulphuric acid.

All the homologues of benzene are very stable, and are with difficulty resolved into compounds containing a smaller number of carbon atoms; powerful oxidising agents, however, such as chromic acid, potassium permanganate, and *dilute* nitric acid, act on them slowly, the alkyl-groups or side-chains being attacked, and as a rule converted into carboxyl-groups; toluene and ethylbenzene, for example, give benzoic acid, whereas the xylenes yield dicarboxylic acids (p. 424),

$$C_6H_5{\cdot}CH_3 + 3O = C_6H_5{\cdot}COOH + H_2O$$
$$C_6H_5{\cdot}CH_2{\cdot}CH_3 + 6O = C_6H_5{\cdot}COOH + CO_2 + 2H_2O$$
$$C_6H_4(CH_3)_2 + 6O = C_6H_4(COOH)_2 + 2H_2O.$$

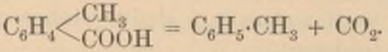
Although in most cases oxidation leads to the formation of a carboxy-derivative of benzene, the stable nucleus of six carbon atoms remaining unchanged, some of the homologues are completely oxidised to carbon dioxide (compare p. 337), and benzene itself undergoes a similar change on prolonged and vigorous treatment.

Aromatic hydrocarbons, like those of the fatty series, may be regarded as hydrides of hypothetical *radicles;* in other words, radicles may theoretically be derived from aromatic hydrocarbons by taking away atoms of hydrogen. These radicles have no actual existence, but the assumption is useful in naming aromatic compounds; the mono- and di-substitution products of benzene, for example, may be regarded as compounds of the monovalent radicle *phenyl*, C_6H_5-, or of the divalent radicle *phenylene*, $C_6H_4<$, respectively, as in phenylamine (aniline), $C_6H_5{\cdot}NH_2$, and in *o*-, *m*- and *p*-phenylenediamine, $C_6H_4(NH_2)_2$. Toluene derivatives, again, may be named as if they were derived from the radicle *toluyl*, $CH_3{\cdot}C_6H_4-$, or from the radicle *benzyl*, $C_6H_5{\cdot}CH_2-$, according as hydrogen of the nucleus, or of the side-chain, has been displaced. The compound $C_6H_5 \cdot CH_2 \cdot OH$, for example, is called benzyl alcohol. The isomeric hydroxy-compounds, $C_6H_4(CH_3) \cdot OH$, however, are usually known as the (*o.m.p.*) cresols (p. 396). Other hypothetical radicles, such as *xylyl*, $C_6H_3(CH_3)_2-$, and *xylylene*, $C_6H_4 < \begin{smallmatrix} CH_2- \\ CH_2- \end{smallmatrix}$, are also made use of.

Toluene, methylbenzene, or phenylmethane, $C_6H_5 \cdot CH_3$, although always prepared from the '90 per cent. benzol' separated from coal-tar (p. 297), can be obtained by any of the general reactions given above, and also by the dry distillation of balsam of Tolu and other resins.

The commercial substance is invariably impure, and when shaken with concentrated sulphuric acid it colours the acid brown or black. It may be purified by repeated fractional distillation, but even then it will contain *thiotolene*, C_5H_6S, a homologue of thiophene (p. 300), and will show the indophenin reaction (with isatin and concentrated sulphuric acid).

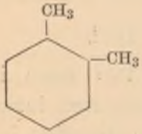
Pure toluene is most conveniently prepared from balsam of Tolu, or by distilling pure toluic acid with lime,



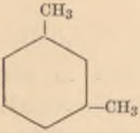
$$C_6H_4 < \begin{matrix} CH_3 \\ COOH \end{matrix} = C_6H_5 \cdot CH_3 + CO_2.$$

It is a colourless, mobile liquid of sp. gr. 0·882 at 0°, and boils at 110°; it does not solidify even at −28°, and cannot, therefore, like benzene, be purified by freezing. It resembles benzene very closely in most respects, differing from it principally in those properties which are due to the presence of the methyl-group. Its behaviour with nitric acid and with sulphuric acid, for example, is similar to that of benzene, inasmuch as it yields nitro- and sulphonic-derivatives; these compounds, moreover, exist in three isomeric (*o.m.p.*) forms, since they are di-substitution products of benzene. The presence of the methyl-group, on the other hand, causes toluene to show in some respects the properties of a paraffin. The hydrogen of this methyl-group may be displaced by chlorine, for example, and the latter by a hydroxyl- or amido-group, by methods exactly similar to those employed in bringing about similar changes in fatty compounds, substances such as $C_6H_5{\cdot}CH_2Cl$, $C_6H_5{\cdot}CH_2{\cdot}OH$, and $C_6H_5{\cdot}CH_2{\cdot}NH_2$ being obtained. This behaviour was of course to be expected, since toluene or phenylmethane is a mono-substitution product of marsh-gas just as much as a derivative of benzene.

The next homologue of toluene—namely, the hydrocarbon of the molecular formula C_8H_{10}, exists in the following four isomeric forms, of which the three *xylenes* or dimethylbenzenes are the most important.

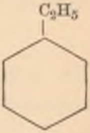


Orthoxylene.



Metaxylene.

Paraxylene.



Ethylbenzene.

The three **xylenes** occur in coal-tar, and may be partially separated from the other constituents of '50 per cent. benzol' (p. 297) by fractional distillation. The portion boiling at 136–141°, after repeated distillation contains a large quantity (up to 85 per cent.) of *m*-xylene and smaller quantities of the *o*- and *p*-compounds; the three isomerides cannot be separated from one another or from all impurities by further distillation, or by any simple means, although it is possible to obtain a complete separation by taking advantage of differences in chemical behaviour.

m-Xylene is readily separated from the other isomerides by digesting with dilute nitric acid, which oxidises *o*- and *p*-xylene to the corresponding toluic acids, $C_6H_4(CH_3){\cdot}COOH$, but does not attack *m*-xylene; the product is rendered alkaline by the addition of potash, and the unchanged hydrocarbon purified by distillation in steam and fractionation. The isolation of *o*- and *p*-xylene depends on the following facts: (1) When crude xylene is agitated with concentrated sulphuric acid, *o*- and *m*-xylene are converted into sulphonic acids, $C_6H_3(CH_3)_2{\cdot}SO_3H$; *p*-xylene remains unchanged, as it is only acted on by fuming sulphuric acid. (2) The sodium salt of *o*-xylenesulphonic acid is less soluble in water than the sodium salt of *m*-xylenesulphonic acid; it is purified by recrystallisation, and converted into *o*-xylene by heating with hydrochloric acid under pressure (p. 381).

The three xylenes may all be prepared by one or other of the general methods: when, for example, methyl chloride is passed into benzene in presence of aluminium chloride, *o*-xylene and a small quantity of the *p*-compound are obtained,

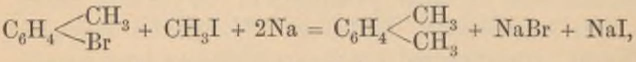
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl;$$

toluene, under the same conditions, yields the same two compounds,

$$C_6H_5{\cdot}CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl.$$

The non-formation of *m*-xylene in these two cases is accounted for by assuming that the methyl-group first introduced into the benzene molecule exerts some directing influence on the position taken up by the second one (p. 351).

Orthoxylene is obtained in a state of purity by treating *o*-bromotoluene with methyl iodide and sodium,

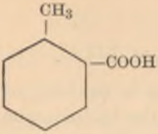


$$C_6H_4{<}\begin{matrix}CH_3\\Br\end{matrix} + CH_3I + 2Na = C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix} + NaBr + NaI,$$

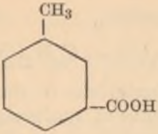
pure *paraxylene* being produced in a similar manner from *p*-bromotoluene; *metaxylene* cannot be prepared by treating *m*-bromotoluene with methyl iodide and sodium, but is easily obtained in a pure condition by distilling mesitylenic acid (p. 338) with lime,

$$C_6H_3(CH_3)_2{\cdot}COOH = C_6H_4(CH_3)_2 + CO_2.$$

The three xylenes are very similar in physical properties (compare p. 332), being all colourless, mobile, rather pleasant-smelling, inflammable liquids (*p*-xylene melts at 15°), which distil without decomposition, and are readily volatile in steam. They also resemble one another in chemical properties, although in some respects they show important differences, which must be ascribed to their difference in constitution. On oxidation, under suitable conditions, they are all converted in the first place into monocarboxylic acids which are represented by the formulæ



Orthotoluic Acid.



Metatoluic Acid.

Paratoluic Acid

On further oxidation the second methyl-group undergoes a like change, and the three corresponding dicarboxylic acids, $C_6H_4(COOH)_2$, are formed (p. 424).

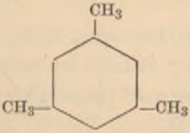
The three hydrocarbons show, however, slight differences in behaviour on oxidation, one being more easily acted on than another by a particular oxidising agent. With chromic acid, for example, *o*-xylene is completely oxidised to carbon dioxide, whereas *m*-xylene and *p*-xylene yield the dicarboxylic acids (see above); with dilute nitric acid *o*-xylene gives *o*-toluic acid, and *p*-xylene *p*-toluic acid, but *m*-xylene is not acted on. Their behaviour with sulphuric acid is also different (p. 335).

Ethylbenzene, or *phenylethane*, $C_6H_5{\cdot}C_2H_5$, an isomeride of the xylenes, is not of much importance; it occurs in coal-tar, and may be obtained by the general methods. It is a colourless liquid, boiling at 134°, and on oxidation with dilute nitric acid or chromic acid it is converted into benzoic acid,

$$C_6H_5{\cdot}CH_2{\cdot}CH_3 + 6O = C_6H_5{\cdot}COOH + CO_2 + 2H_2O.$$

The next member of the series has the molecular formula C_9H_{12}, and exists, as already pointed out (p. 329), in eight isomeric forms, of which the three trimethylbenzenes and isopropylbenzene are the most important.

Mesitylene, or symmetrical trimethylbenzene,



occurs in small quantities in coal-tar, but is most conveniently prepared by distilling a mixture of acetone (2 vols.), concentrated sulphuric acid (2 vols.), and water (1 vol.), sand being added to prevent frothing,

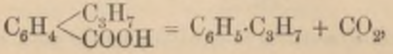
$$3(CH_3)_2CO = C_6H_3(CH_3)_3 + 3H_2O.$$

The formation of mesitylene in this way is not only of interest because it affords a means of synthesising the hydrocarbon from its elements, but also because it throws light on the constitution of the compound. Although the change is a process of condensation, and is most simply expressed by the graphic equation already given (p. 324), it might be assumed that the acetone is first converted into $CH_3{\cdot}C{\vdots}CH$, or into $CH_3{\cdot}C(OH){:}CH_2$ (by intramolecular change), and that mesitylene is then produced by a secondary reaction; whatever view, however, is adopted as to the actual course of the reaction (unless, indeed, highly improbable assumptions be made), the final result is always the same, and the constitution of the product must be expressed by a symmetrical formula; for this, and other reasons, mesitylene is regarded as *symmetrical* or 1:3:5-trimethylbenzene.

Mesitylene is a colourless, mobile, pleasant-smelling liquid, boiling at 163°, and volatile in steam; when treated with concentrated nitric acid it yields mono- and di-nitromesitylene, whereas with a mixture of nitric and sulphuric acids it is converted into *trinitromesitylene*, $C_6(NO_2)_3(CH_3)_3$. On oxidation with dilute nitric acid it yields *mesitylenic acid*, $C_6H_3(CH_3)_2{\cdot}COOH$, *uvitic acid*, $C_6H_3(CH_3)(COOH)_2$, and *trimesic acid*, $C_6H_3(COOH)_3$, by the successive transformation of the methyl- into carboxyl-groups.

Pseudocumene, or asymmetrical trimethylbenzene, $C_6H_3(CH_3)_3$ [$3CH_3 = 1{:}2{:}4$], and *hemimellitene*, or adjacent trimethylbenzene [$3CH_3 = 1{:}2{:}3$], also occur in small quantities in coal-tar, and are very similar to mesitylene in properties; on oxidation, they yield various acids by the conversion of one or more methyl- into carboxyl-groups.

Cumene, or isopropylbenzene, $C_6H_5{\cdot}CH(CH_3)_2$, is usually obtained from coal-tar; it may be prepared in a pure condition by distilling *cumic acid* (*isopropylbenzoic acid*) with lime,



$$C_6H_4{<}\begin{matrix}C_3H_7\\COOH\end{matrix} = C_6H_5{\cdot}C_3H_7 + CO_2,$$

by treating a mixture of isopropyl bromide and benzene with aluminium chloride,

$$C_6H_6 + C_3H_7Br = C_6H_5{\cdot}C_3H_7 + HBr,$$

and by the action of sodium on a mixture of bromobenzene and isopropyl bromide,

$$C_6H_5Br + C_3H_7Br + 2Na = C_6H_5{\cdot}C_3H_7 + 2NaBr.$$

It is a colourless liquid, boiling at 153°, and on oxidation with dilute nitric acid it is converted into benzoic acid.

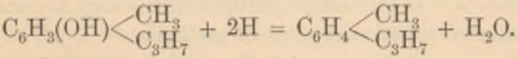
Cymene, or *para*-methylisopropylbenzene, $C_6H_4(CH_3){\cdot}C_3H_7$, is a hydrocarbon of considerable importance, as it occurs in the ethereal oils or essences of many plants; it is easily prepared in many ways, as, for example, by heating camphor with phosphorus pentoxide or phosphorus pentasulphide,

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O,$$

by heating turpentine with concentrated sulphuric acid or with iodine (both of which, in this case, act as oxidising agents),

$$C_{10}H_{16} + O = C_{10}H_{14} + H_2O,$$

and by heating thymol (p. 397), or carvacrol (p. 397), with phosphorus pentasulphide (which acts as a reducing agent),



$$C_6H_3(OH){<}\begin{matrix}CH_3\\C_3H_7\end{matrix} + 2H = C_6H_4{<}\begin{matrix}CH_3\\C_3H_7\end{matrix} + H_2O.$$

Cymene is a pleasant-smelling liquid of sp. gr. 0·8722 at 0°, and boils at 175–176°; on oxidation with dilute nitric acid it yields *p-toluic acid*, $C_6H_4(CH_3){\cdot}COOH$, and *terephthalic acid*, $C_6H_4(COOH)_2$.

Diphenyl, Diphenylmethane, and Triphenylmethane.

All the hydrocarbons hitherto described contain only *one* benzene nucleus, and may be regarded as derived from benzene by the substitution of fatty alkyl-groups for atoms of hydrogen; there are, however, several other series of aromatic hydrocarbons, which include compounds of very considerable importance.

Diphenyl, $C_6H_5–C_6H_5$, contains *two* benzene nuclei, and is the hydrocarbon in the aromatic series which corresponds with dimethyl in the fatty series, although it is not a homologue of benzene. It is formed on treating bromobenzene in ethereal solution with sodium,

$$2C_6H_5Br + 2Na = C_6H_5{\cdot}C_6H_5 + 2NaBr,$$

the reaction being analogous to the formation of dimethyl from methyl bromide by the action of sodium.

Diphenyl is prepared by passing benzene vapour through a red-hot tube filled with pieces of pumice,

$$2C_6H_6 = C_6H_5{\cdot}C_6H_5 + H_2.$$

The dark-coloured distillate is fractionated, and the diphenyl purified by recrystallisation from alcohol.

Diphenyl is a colourless, crystalline substance, melts at 71°, and boils at 254°; when oxidised with chromic acid, it yields benzoic acid, one of the benzene nuclei being destroyed. Its behaviour with halogens, nitric acid, and sulphuric acid is similar to that of benzene, substitution products being formed.

Diphenylmethane, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$, also contains *two* benzene nuclei; it may be regarded as derived from marsh-gas by the substitution of two phenyl-groups for two atoms of hydrogen, just as toluene or phenylmethane may be considered as a mono-substitution product of methane.

Diphenylmethane may be prepared by treating benzene with benzyl chloride (p. 348) in presence of aluminium chloride,

$$C_6H_6 + C_6H_5{\cdot}CH_2Cl = C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + HCl.$$

It is a crystalline substance, and melts at 26·5°; when treated with nitric acid, it yields nitro-derivatives in the usual way, and on oxidation with chromic acid, it is converted into diphenyl ketone or benzophenone, $C_6H_5{\cdot}CO{\cdot}C_6H_5$ (p. 412).

Triphenylmethane, $(C_6H_5)_3CH$, is by far the most important member of another series, the members of which contain *three* benzene nuclei. It is formed when benzal chloride (p. 349) is treated with benzene in presence of aluminium chloride,

$$C_6H_5{\cdot}CHCl_2 + 2C_6H_6 = (C_6H_5)_3CH + 2HCl,$$

but it is usually prepared by heating a mixture of chloroform and benzene with aluminium chloride,

$$CHCl_3 + 3C_6H_6 = (C_6H_5)_3CH + 3HCl.$$

Aluminium chloride (5 parts) is gradually added to a mixture of chloroform (1 part) and benzene (5 parts), which is then heated at about 60° until the evolution of hydrogen chloride ceases, an operation occupying about thirty hours; after cooling and adding water, the oily product is separated and submitted to fractional distillation; those portions of the distillate which solidify on cooling, consist of crude triphenylmethane, which is further purified by recrystallisation from benzene and then from ether.

Triphenylmethane is a colourless, crystalline compound, which melts at 93°, and boils at 355°; it is readily soluble in ether and benzene, but only sparingly so in cold alcohol. When treated with fuming nitric acid, it is converted into a yellow, crystalline *trinitro*-derivative, $CH(C_6H_4{\cdot}NO_2)_3$, which, like other nitro-compounds, is readily transformed into the corresponding *triamido*-compound,

$$CH(C_6H_4{\cdot}NH_2)_3,$$

on reduction; the last-named substance is of considerable importance, as many of its derivatives are largely employed as dyes (p. 508).

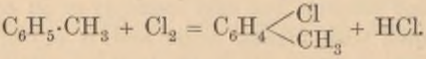
On oxidation with chromic acid, triphenylmethane is converted into triphenyl carbinol, $(C_6H_5)_3C{\cdot}OH$.

CHAPTER XXI.

HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.

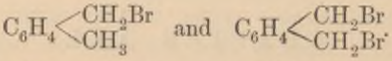
The action of halogens on benzene has already been referred to (p. 302), and it has been pointed out that the hydrocarbon yields either additive or substitution products according to the conditions of the experiment; at ordinary temperatures, in absence of direct sunlight, substitution products are formed, the action being greatly hastened by the presence of a halogen carrier, such as iodine, ferric chloride, or antimony chloride;* at its boiling-point, however, or in presence of direct sunlight, the hydrocarbon yields additive compounds by direct combination with (two, four, or) six atoms of the halogen.

The homologues of benzene also show a curious behaviour; when treated with chlorine or bromine at ordinary temperatures in absence of direct sunlight, they are converted into substitution products by the displacement of hydrogen of the *nucleus*, and, as in the case of benzene itself, interaction is greatly promoted by the presence of a halogen carrier; under these conditions toluene, for example, gives a mixture of *o*- and *p*-chlorotoluenes or bromotoluenes,



$$C_6H_5{\cdot}CH_3 + Cl_2 = C_6H_4{<}\substack{Cl\\ CH_3} + HCl.$$

When, on the other hand, no halogen carrier is present, and the hydrocarbons are treated with chlorine or bromine at their boiling-points, or in direct sunlight, they yield derivatives by the substitution of hydrogen of the *side-chain;* when, for example, chlorine is passed into *boiling* toluene, the three hydrogen atoms of the methyl-group are successively displaced, benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, benzal chloride, $C_6H_5{\cdot}CHCl_2$, and benzotrichloride, $C_6H_5{\cdot}CCl_3$, being formed; xylene, again, when treated with bromine at its boiling-point, gives the compounds



$$C_6H_4{<}\substack{CH_2Br\\ CH_3} \quad \text{and} \quad C_6H_4{<}\substack{CH_2Br\\ CH_2Br}.$$

---

* The action of iodine has been explained in part i. (p. 163); ferric chloride, antimony pentachloride, molybdenum pentachloride, and other metallic chlorides, act as halogen carriers, probably because they readily dissociate, yielding *nascent* halogen and lower chlorides ($FeCl_2$, $SbCl_3$, $MoCl_3$); the latter then combine again with a fresh quantity of the halogen, and thus the process is repeated.

Although these statements are true in the main, it must not be supposed that substitution takes place exclusively either in the nucleus or side-chain, as the case may be, because this is not so; in presence of a halogen carrier traces of a halogen derivative are formed by substitution of hydrogen of the side-chain, and at the boiling-point of the hydrocarbon, or in direct sunlight, traces of a substitution product, formed by displacement of hydrogen of the nucleus, are obtained.

Iodine seldom acts on benzene and its homologues under any of the above-mentioned conditions, partly because of the slight affinity of iodine for hydrogen, partly because the hydrogen iodide which is produced interacts with the iodo-derivative, and reconverts it into the hydrocarbon

$$C_6H_6 + I_2 = C_6H_5I + HI$$
$$C_6H_5I + HI = C_6H_6 + I_2;$$

if, however, iodic acid, or some other substance which decomposes hydriodic acid, be present, iodo-derivatives may sometimes be prepared by direct treatment with the halogen.*

Preparation.—As a rule, chloro- and bromo-derivatives of benzene and its homologues are prepared by direct '*chlorination*' or '*bromination*,' the conditions employed depending on whether hydrogen of the nucleus or of the side-chain is to be displaced; if, for example, it were desired to convert toluene into *p-chlorobenzyl chloride*, $C_6H_4Cl{\cdot}CH_2Cl$, the hydrocarbon might be first treated with chlorine at ordinary temperatures in presence of iodine, and the *p-chlorotoluene*, $C_6H_4Cl{\cdot}CH_3$, after having been separated from the accompanying ortho-compound, would then be heated to boiling in

---

* $HIO_3 + 5HI = 3I_2 + 3H_2O$. Iodo-substitution products are also frequently formed on employing $FeCl_3$, or $AlCl_3$, as a carrier, because the ICl which is formed has a much more energetic substituting action than the iodine itself, owing to the simultaneous formation of HCl,

$$C_6H_6 + ICl = C_6H_5I + HCl.$$

a flask connected with a reflux condenser, and a stream of dry chlorine led into it.

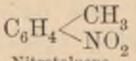
In all operations of this kind the theoretical quantity, or a slight excess of halogen, is employed; the bromine is weighed directly, but the weight of the chlorine is usually ascertained indirectly by continuing the process until the theoretical gain in weight has taken place; the halogen should be dry, as in presence of water oxidation products of the hydrocarbon may be formed. The fumes of hydrogen chloride or bromide evolved during such operations are conveniently absorbed by passing them to the bottom of a deep vessel containing damp coke.

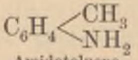
A very important general method for the preparation of aromatic halogen derivatives, *containing the halogen in the nucleus*, consists in the decomposition of the diazo-compounds. As the properties and decompositions of the last-named substances are described later (p. 370), it is only necessary to state here that this method is used in the preparation of nearly all iodo-compounds, and that it affords a means of indirectly substituting any of the halogens, not only for hydrogen, but also for nitro- or amido-groups.

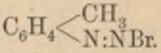
The conversion of benzene or toluene, for example, into a mono-halogen derivative by this method involves the following steps:

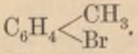
C_6H_6	$C_6H_5{\cdot}NO_2$	$C_6H_5{\cdot}NH_2$	$C_6H_5{\cdot}N{:}NCl$	C_6H_5Cl
Benzene.	Nitrobenzene.	Amidobenzene.	Diazobenzene Chloride.	Chlorobenzene.

$C_6H_5{\cdot}CH_3$
Toluene.


$$C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix}$$
Nitrotoluene.


$$C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix}$$
Amidotoluene.

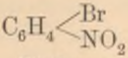

$$C_6H_4{<}\begin{matrix}CH_3\\N{:}NBr.\end{matrix}$$
Diazotoluene Bromide.


$$C_6H_4{<}\begin{matrix}CH_3\\Br\end{matrix}.$$
Bromotoluene.

The preparation of a *di*-halogen derivative may sometimes be carried out in a similar manner, the hydrocarbon being first converted into the *di*-nitro-derivative; in most cases, however, it is necessary to prepare the *mono*-halogen derivative by the reactions given above, and after converting it into the nitro-compound, the nitro-group is displaced by a second atom of halogen by repeating the series of operations.

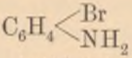
C_6H_5Br

Bromobenzene.



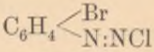
$C_6H_4{<}\genfrac{}{}{0pt}{}{Br}{NO_2}$

Nitrobromobenzene.



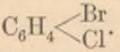
$C_6H_4{<}\genfrac{}{}{0pt}{}{Br}{NH_2}$

Amidobromobenzene.



$C_6H_4{<}\genfrac{}{}{0pt}{}{Br}{N:NCl}$

Diazobromobenzene Chloride.

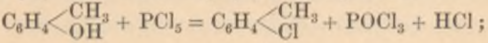


$C_6H_4{<}\genfrac{}{}{0pt}{}{Br}{Cl}\cdot$

Bromochlorobenzene.

Halogen derivatives of benzene and its homologues are sometimes prepared by treating hydroxy-compounds with pentachloride or pentabromide of phosphorus, the changes being similar to those which occur in the case of fatty hydroxy-compounds; if the hydroxyl-group be present in the nucleus, the halogen naturally takes up the same position, phenol, for example, giving chlorobenzene, and cresol, chlorotoluene,

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$

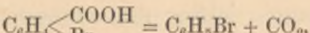


$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{OH} + PCl_5 = C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{Cl} + POCl_3 + HCl\,;$$

an aromatic alcohol (p. 402), such as benzyl alcohol, also yields the corresponding halogen derivative (benzyl chloride), containing the halogen in the side-chain,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl.$$

Halogen derivatives may also be obtained by distilling halogen acids with lime,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{COOH}{Br} = C_6H_5Br + CO_2,$$

by heating sulphonic chlorides (p. 381) with phosphorus pentachloride,

$$C_6H_5{\cdot}SO_2Cl + PCl_5 = C_6H_5Cl + POCl_3 + SOCl_2,$$

and by several other methods of less importance.

Properties.—At ordinary temperatures, some of the halogen derivatives of benzene and its homologues are colourless liquids; the majority, however, are crystalline solids. They are all insoluble, or nearly so, in water, but readily soluble in alcohol, ether, &c. Many are readily volatile in steam, and distil without decomposition, the boiling-point being higher and the specific gravity greater than that of the parent hydrocarbon, and rising also on substituting bromine for chlorine, or iodine for bromine.

	Benzene.	Chlorobenzene.	Bromobenzene.	Iodobenzene.
B.p.	80·5°	132°	155°	185°
Sp. gr. at 0°	0·899	1·128	1·521	1·857.

They are not so inflammable as the hydrocarbons, and the vapours of many of them have a very irritating action on the eyes and respiratory organs.

When the halogen is united with carbon of the benzene nucleus, it is, as a rule, very firmly combined, and cannot, as in the case of the halogen derivatives of the fatty series, be displaced by the hydroxyl- or amido-group with the aid of aqueous potash or ammonia; such halogen derivatives, moreover, are not acted on by alcoholic potash, and cannot be converted into less saturated compounds in the same way as ethyl bromide, for example, may be converted into ethylene; in fact, no derivative of benzene, containing less than six monovalent atoms, or their valency equivalent, is known. If, however, hydrogen of the nucleus has been displaced by one or more nitro-groups, as well as by a halogen, the latter often becomes much more open to attack; *o-* and *p*-chloronitrobenzene, $C_6H_4Cl{\cdot}NO_2$, for example, are moderately easily acted on by alcoholic potash and by alcoholic ammonia at high temperatures, yielding the corresponding nitrophenols, $C_6H_4(OH){\cdot}NO_2$, and nitranilines, $C_6H_4(NH_2){\cdot}NO_2$; *m*-chloronitrobenzene, however, is not acted on under these conditions, a fact which shows that compounds closely related in constitution and identical in composition sometimes differ very considerably in properties.

Halogen atoms in the side-chains are very much less firmly combined than those in the nucleus, and may be displaced by hydroxyl- or amido-groups just as in fatty compounds; benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, for example, is converted into benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, by boiling sodium carbonate solution, and when heated with alcoholic ammonia it yields benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$ (p. 368).

Halogen atoms in the nucleus, as well as those in the side-chain, are displaced by hydrogen on treatment with hydriodic acid and amorphous phosphorus at high temperatures, or with sodium amalgam in alcoholic solution; the former, however, are much less readily displaced than the latter.

Chlorobenzene, or phenyl chloride, C_6H_5Cl, may be described as a typical example of those halogen derivatives in which the halogen is combined with carbon of the benzene nucleus. It may be obtained (together with dichlorobenzene, $C_6H_4Cl_2$, trichlorobenzene, $C_6H_3Cl_3$, &c.) by chlorinating benzene; also by treating phenol (p. 391) with phosphorus pentachloride, just as ethyl chloride may be produced from alcohol,

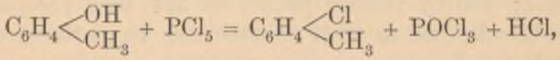
$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

It is usually prepared by Sandmeyer's reaction (p. 372)—that is to say, by warming an aqueous solution of diazobenzene chloride with cuprous chloride; this method, therefore, affords a means of preparing chlorobenzene, not only from the diazo-compound, but also indirectly from amidobenzene (aniline), nitrobenzene, and benzene, the changes being those given above (p. 344). Chlorobenzene is a colourless, mobile, pleasant-smelling liquid, specifically heavier than water; it boils at 132°, and is readily volatile in steam. Like benzene, it is capable of yielding nitro-, amido-, and other derivatives by the displacement of one or more hydrogen atoms; it differs from ethyl chloride and from other fatty alkyl halogen compounds in being unacted on by water and alkalies, or by metallic salts; it is impossible, for example, to prepare phenyl acetate, $CH_3{\cdot}COOC_6H_5$, by treating silver acetate with chlorobenzene, although ethyl acetate is easily obtained from ethyl chloride in this way.

Bromobenzene, or phenyl bromide, C_6H_5Br, may be obtained by brominating benzene, but is usually prepared from diazobenzene bromide by Sandmeyer's method; it is a colourless liquid, boiling at 155°, and closely resembles chlorobenzene in all respects. As a rule, however, the bromo-derivatives crystallise more readily, and have a higher melting-point than the corresponding chloro-compounds.

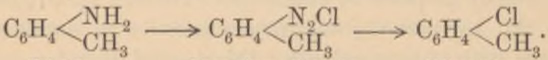
Iodobenzene, or phenyl iodide, boils at 185°.

Chlorotoluene, or toluyl chloride, $C_6H_4Cl{\cdot}CH_3$, being a di-substitution product of benzene, exists in three isomeric modifications, only two of which—namely, the *o*- and *p*-compounds, are formed on treating *cold* toluene with chlorine in presence of iodine or ferric chloride; the three isomerides may be separately prepared by treating the corresponding cresols (p. 396) with phosphorus pentachloride,



$$C_6H_4{<}\begin{matrix}OH\\CH_3\end{matrix} + PCl_5 = C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix} + POCl_3 + HCl,$$

but they are best prepared from the corresponding toluidines by Sandmeyer's method,



$$C_6H_4{<}\begin{matrix}NH_2\\CH_3\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}N_2Cl\\CH_3\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix}.$$

Toluidine. Diazotoluene Chloride. Chlorotoluene.

Orthochlorotoluene boils at 156°, *metachlorotoluene* at 150°, and *parachlorotoluene* at 160°; they resemble chlorobenzene in most respects, but, since they contain a methyl-group, they have also some of the properties of fatty compounds; on oxidation, they are converted into the corresponding *chlorobenzoic acids*, $C_6H_4Cl{\cdot}COOH$, just as toluene is transformed into benzoic acid.

Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, although isomeric with the three chlorotoluenes, differs from them very widely, and may be taken as an example of the class of halogen-compounds in which the halogen is present in the side-chain. It can be obtained by treating benzyl alcohol (p. 403) with phosphorus pentachloride,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl,$$

but is always prepared by passing chlorine into boiling toluene,

$$C_6H_5{\cdot}CH_3 + Cl_2 = C_6H_5{\cdot}CH_2Cl + HCl.$$

The toluene is contained in a flask which is heated on a sand-bath and connected with a reflux condenser; a stream of dry chlorine is then passed into the boiling liquid until the theoretical gain in weight has taken place and the product is purified by fractional distillation; the action takes place most rapidly in strong sunlight.

Benzyl chloride is a colourless, unpleasant-smelling liquid, boiling at 176°; it is insoluble in water, but miscible with alcohol, ether, benzene, &c. It behaves like other aromatic compounds towards nitric acid, by which it is converted into a mixture of isomeric nitro-compounds, $C_6H_4(NO_2)\cdot CH_2Cl$. At the same time, however, it has many properties in common with the alkyl halogen compounds; like ethyl chloride, it is slowly decomposed by boiling water, yielding the corresponding hydroxy-compound, benzyl alcohol (p. 403),

$$C_6H_5\cdot CH_2Cl + H_2O = C_6H_5\cdot CH_2\cdot OH + HCl,$$

and just as ethyl chloride interacts with silver acetate, giving ethyl acetate, so benzyl chloride, under the same conditions, yields the ethereal salt, *benzyl acetate*,

$$C_6H_5\cdot CH_2Cl + CH_3\cdot COOAg = CH_3\cdot COOCH_2\cdot C_6H_5 + AgCl.$$

Benzyl chloride is a substance of considerable commercial importance, inasmuch as it is used for the preparation of benzaldehyde (p. 406).

Benzal chloride, $C_6H_5\cdot CHCl_2$, may be obtained by treating benzaldehyde with phosphorus pentachloride,

$$C_6H_5\cdot CHO + PCl_5 = C_6H_5\cdot CHCl_2 + POCl_3,$$

but it is prepared by chlorinating toluene just as described in the case of benzyl chloride, except that the process is continued until twice as much chlorine has been absorbed. It is a colourless liquid, boiling at 206°, and is extensively used for the preparation of benzaldehyde.

Benzotrichloride, or phenylchloroform, $C_6H_5\cdot CCl_3$, is also prepared by chlorinating boiling toluene; it boils at 213°, and when heated with water it is converted into benzoic acid,

$$C_6H_5\cdot CCl_3 + 2H_2O = C_6H_5\cdot COOH + 3HCl.$$

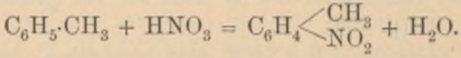
CHAPTER XXII.

NITRO-COMPOUNDS.

It has already been stated that one of the most characteristic properties of aromatic compounds is the readiness with which they may be converted into nitro-derivatives by the substitution of nitro-groups for hydrogen of the nucleus; the compounds formed in this way are of the greatest importance, more especially because it is from them that the amido- and diazo-compounds are prepared.

Preparation.—Many aromatic compounds may be '*nitrated*'—that is to say, converted into their nitro-derivatives, by dissolving them in concentrated nitric acid (sp. gr. 1·3 to 1·5), in the cold or at ordinary temperatures, and under such conditions a mononitro-compound is usually produced; benzene, for example, yields nitrobenzene, and toluene, a mixture of *o*- and *p*-nitrotoluenes,

$$C_6H_6 + HNO_3 = C_6H_5{\cdot}NO_2 + H_2O$$



$$C_6H_5{\cdot}CH_3 + HNO_3 = C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix} + H_2O.$$

Some aromatic compounds, however, are insoluble in nitric acid, and are then only very slowly acted on; in such cases, a mixture of concentrated nitric and sulphuric acids is used. This mixture is also used in many cases, even when the substance is soluble in nitric acid, because the sulphuric acid combines with the water which is produced during the interaction, and thus its presence favours nitration, just as the presence of dehydrating agents favours the formation of ethereal salts from a mixture of an acid and an alcohol. When a large excess of nitric and sulphuric acids is employed, and especially when heat is applied, the aromatic compound is usually converted into (a mixture of isomeric) dinitro- or trinitro-derivatives; benzene, for instance, yields a mixture of three dinitro-benzenes, the principal product, however, being the meta-compound,

$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O.$$

As soon as nitration is complete (portions of the product may be tested from time to time), the solution or mixture, having been cooled if necessary, is poured on to ice or into a large volume of water, and the product, which is usually precipitated in crystals, separated by filtration, or if an oil, by extraction with ether, or in some other manner.

Generally speaking, the number of hydrogen atoms displaced by nitro-groups is greater the higher the temperature and the more concentrated the acid, or acid mixture, employed, but depends to an even greater extent on the nature of the substance undergoing nitration, because the introduction of nitro-groups is facilitated when other atoms or groups, especially alkyl radicles, have already been substituted for hydrogen of the nucleus. The nature of these atoms or groups determines, moreover, the position taken up by the entering nitro-group; if the former be strongly negative or acid in character, as, for example, $-NO_2$, $-COOH$, and $-SO_3H$, a *m*-nitro-derivative is formed, whereas, when the atom or group in question is a halogen, an alkyl, or an amido- or hydroxyl-group, a mixture of the *o*- and *p*-nitro-derivatives is produced.

This directing influence of an atom or group already combined with the nucleus, on the position which is taken up by a second atom or group, is by no means restricted to the case of nitro-compounds, but is observed in the formation of all benzene substitution derivatives, except, of course, in that of the mono-substitution products; so regularly, in fact, is this influence exercised, that it is possible to summarise the course of those reactions which take place in the formation of the best-known di-derivatives in the following statements:

The relative position taken up by an atom or group, B, depends on its nature, and on that of the atom or group, A, already united with the nucleus.

When A = Cl, Br, I, NH_2, OH, CH_3,
and B = Cl, Br, NO_2, SO_3H,
a *para*-compound is the principal product, but it is usually accompanied by smaller and varying quantities of the ortho-compound.

When, on the other hand,
A = NO_2, COOH, SO_3H, CHO, $CO{\cdot}CH_3$,
and B = Cl, Br, NO_2, SO_3H,
a *meta*-derivative is the principal product, and only very small quantities of the ortho- and para-compounds are formed.

These statements also hold good when two identical atoms or groups are introduced in one operation, since the change really takes place in two stages; when benzene, for example, is treated with nitric acid, meta-dinitrobenzene is the principal product, whereas with bromine it yields para-dibromobenzene.

Properties.—As a rule, aromatic nitro-compounds are yellowish, well-defined crystalline substances, and are, therefore, of great service in identifying hydrocarbons and other liquids; many of them are volatile in steam, but, with the exception of certain mono-nitro-derivatives, cannot be distilled under ordinary pressure, as when heated strongly they undergo decomposition, sometimes with explosive violence; they are generally insoluble in water, but soluble in benzene, ether, alcohol, &c. As in the case of the nitro-paraffins (part i. p. 181), the nitro-group is very firmly combined, and is not, as a rule, displaced by the hydroxyl-group on treatment with potash even at high temperatures.

The most important reaction of the nitro-compounds—namely, their behaviour on reduction, is described later (p. 356).

Nitrobenzene, $C_6H_5{\cdot}NO_2$, is usually prepared in the laboratory by slowly adding to benzene (10 parts) a mixture of nitric acid of sp. gr. 1·45 (12 parts), and concentrated sulphuric acid (16 parts), the temperature being kept below about 40° by cooling in water, and the mixture being constantly shaken; the benzene dissolves in the acids, although it does not appear to do so, because it is quickly converted into the nitro-compound, which separates again as a yellowish-brown oil. As soon as all the benzene has been added, the mixture is heated at about 80° for half an hour, then cooled, and poured into a large volume of water; the nitrobenzene, which collects at the bottom of the vessel, is separated with the aid of a funnel, washed with a little water or dilute soda until free from acid, dried with calcium chloride, and fractionated, in order to separate it from unchanged benzene and from small quantities of dinitrobenzene which may have been produced; this is very easily accomplished, as the boiling-points of the three compounds are widely different.

On the large scale, nitrobenzene is prepared in a similar manner, but the operation is carried out in iron vessels provided with an arrangement for stirring, and the product is distilled from iron retorts, or, better, in a current of steam.

Nitrobenzene is a pale-yellow oil of sp. gr. 1·2 at 0°, and has a strong smell which is very like that of benzaldehyde (p. 406); it boils at 205°, is volatile in steam, and is miscible with organic liquids, but practically insoluble in water; in spite of the fact that it is poisonous, it is often employed instead of oil of bitter almonds for flavouring and perfuming purposes, under the name of 'essence of mirbane;' its principal use, however, is for the manufacture of aniline (p. 361).

Meta-dinitrobenzene, $C_6H_4(NO_2)_2$, is obtained, together with small quantities of the *o*- and *p*-dinitro-compounds, when benzene is gradually added to a mixture of nitric acid (sp. gr. 1·5) and concentrated sulphuric acid, and the whole then heated on a sand-bath, until a portion of the oil, which floats on the surface, solidifies completely when dropped into water; after cooling, the mixture is poured into a large volume of water, the solid product separated by filtration, washed with water, and recrystallised from hot alcohol until its melting-point is constant; the *o*- and *p*-compounds, formed only in very small quantities, remain dissolved in the mother-liquors.

Meta-dinitrobenzene crystallises in pale-yellow needles, melts at 90°, and is volatile in steam; it is only sparingly soluble in boiling water, but dissolves freely in most organic liquids. On reduction with alcoholic ammonium sulphide (p. 357) it is first converted into *m*-nitraniline (p. 363), and then into *m*-phenylenediamine or meta-diamidobenzene, $C_6H_4(NH_2)_2$ (p. 364).

o-Dinitrobenzene and *p-dinitrobenzene* are colourless, crystalline compounds, melting at 118° and 173° respectively; they resemble the corresponding *m*-compound in their behaviour on reduction, and in most other respects. *o*-Dinitrobenzene, however, differs notably from the other two isomerides, inasmuch as it interacts with boiling soda, yielding *o*-nitrophenol (p. 393), and, with alcoholic ammonia at moderately high temperatures, giving *o*-nitraniline (p. 363). A similar behaviour is observed in the case of other *o*-dinitro-compounds, the presence of the one nitro-group rendering the other more easily displaceable.

Symmetrical *trinitrobenzene*, $C_6H_3(NO_2)_3$, is formed when the *m*-dinitro-compound is heated with a mixture of nitric and anhydrosulphuric acids; it crystallises in colourless plates and needles, melting at 121–122°.

The halogen derivatives of benzene are readily nitrated, yielding, however, the *o*- and *p*-mononitro-derivatives only, according to the general rule; the *m*-nitro-halogen compounds are therefore prepared by chlorinating or brominating nitrobenzene. All these nitro-halogen derivatives are crystalline, and, as will be seen from the following table, their melting-points exhibit the regularity mentioned above (p. 332), except in the case of *m*-iodonitrobenzene:

		Ortho.	Meta.	Para.
Chloronitrobenzene,	$C_6H_4Cl{\cdot}NO_2$,	32·5°	44·4°	83°
Bromonitrobenzene,	$C_6H_4Br{\cdot}NO_2$,	41·5	56	126
Iodonitrobenzene,	$C_6H_4I{\cdot}NO_2$,	49	33	171

They are, on the whole, very similar in chemical properties, except that, as already pointed out (p. 346), the *o*- and *p*-compounds differ from the *m*-compounds in their behaviour with alcoholic potash and ammonia, a difference which recalls that shown by the three dinitrobenzenes.

The **nitrotoluenes,** $C_6H_4(CH_3)·NO_2$, are important, because they serve for the preparation of the toluidines (p. 364). The *o*- and *p*-compounds are prepared by nitrating toluene, and may be partially separated by fractional distillation; *o-nitrotoluene* is liquid at ordinary temperatures, and boils at 223°, whereas *p-nitrotoluene* is crystalline, and boils at 237°, its melting-point being 54°. *m-Nitrotoluene* is not easily prepared; it melts at 16°, and boils at 230°.

Many other nitro-compounds are mentioned later.

CHAPTER XXIII.

AMIDO-COMPOUNDS AND AMINES.

The hydrogen atoms in ammonia may be displaced by aromatic radicles, bases, such as aniline, $C_6H_5·NH_2$, benzylamine, $C_6H_5·CH_2·NH_2$, and diamidobenzene, $C_6H_4(NH_2)_2$, which are analogous to, and have many properties in common with the fatty amines, being produced; as, however, those compounds which contain the amido-group directly united with carbon of the nucleus differ in many important respects from those in which this group is present in the side-chain, the former are usually called *amido-compounds*, whereas the latter are classed as *aromatic amines*, because they are the true analogues of the fatty amines.

Amido-compounds.

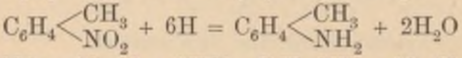
The amido-compounds may, therefore, be regarded as derived from benzene and its homologues by the substitution of one or more amido-groups for hydrogen atoms of the *nucleus;* they may be classed as mono-, di-, tri-, &c., amido-compounds, according to the number of such groups which they contain.

$C_6H_5{\cdot}NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.
Amidobenzene (Aniline).	Diamidobenzene.	Triamidobenzene.

With the exception of aniline, all amido-compounds exist in three or more isomeric modifications; there are, for example, three isomeric (*o.m.p.*) diamidobenzenes, and three isomeric (*o.m.p.*) amidotoluenes, or toluidines, $C_6H_4(CH_3){\cdot}NH_2$, a fourth isomeride of the toluidines—namely, benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$ (p. 368), being also known.

Preparation.—The amido-compounds are almost always prepared by the reduction of the nitro-compounds; various reducing agents, such as tin, zinc, or iron, and hydrochloric or acetic acid, are employed, but perhaps the most common one is a solution of stannous chloride in hydrochloric acid,

$$C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}NH_2 + 2H_2O$$



$$C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix} + 6H = C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix} + 2H_2O$$

$$C_6H_5{\cdot}NO_2 + 3SnCl_2 + 6HCl = C_6H_5{\cdot}NH_2 + 3SnCl_4 + 2H_2O.$$

Reduction is usually effected by simply treating the nitro-compound with the reducing mixture without a special solvent, when a vigorous reaction often ensues, heating being seldom necessary except towards the end of the operation. The solution contains the amido-compound, combined as a salt with the acid which has been employed; when, however, tin or stannous chloride and hydrochloric acid have been used, a double salt of the hydrochloride of the base and stannic chloride is produced; in the reduction of nitrobenzene, for example, the double salt, *aniline stannichloride*, has the composition

$$(C_6H_5{\cdot}NH_2,\ HCl)_2,\ SnCl_4.$$

In any case, the salt is decomposed by the addition of excess of caustic soda or lime, and the liberated base either distilled with steam or extracted with ether, or isolated in some other manner suitable to the special case. Recent researches show that the reduction of nitro-compounds may take place in two stages: in the first place, a derivative of hydroxylamine is produced,

$$C_6H_5{\cdot}NO_2 + 4H = \underset{\text{Phenylhydroxylamine,}}{C_6H_5{\cdot}NH{\cdot}OH} + H_2O,$$

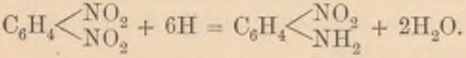
and this, by the further action of the reducing agent, is converted into the amido-compound.

Nitro-compounds may also be reduced to amido-compounds by employing sulphuretted hydrogen in alkaline solution, or, more conveniently, an alcoholic solution of ammonium sulphide,

$$C_6H_5\cdot NO_2 + 3SH_2 = C_6H_5\cdot NH_2 + 2H_2O + 3S.$$

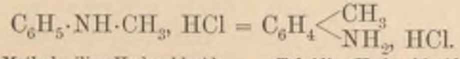
The nitro-compound is dissolved in alcohol, concentrated ammonia added, and a stream of sulphuretted hydrogen passed into the solution, until reduction is complete, heat being applied if necessary. The solution is then filtered from precipitated sulphur, the alcohol distilled off, and the residue acidified with hydrochloric acid; the filtered solution of the hydrochloride of the base is now evaporated to a small bulk and treated with soda, when the base separates as an oil or solid, and may then be purified by distillation, recrystallisation, &c.

When there are two or more nitro-groups in a compound, partial reduction may be accomplished either by treating its alcoholic solution with the calculated quantity of stannous chloride and hydrochloric acid, or by adding strong ammonia and passing sulphuretted hydrogen; in the latter, as in the former case, one nitro-group is reduced before a second is attacked, so that by stopping the current of gas at the right time (usually ascertained by weighing the sulphuretted hydrogen absorbed), only partial reduction takes place. Dinitrobenzene, for example, can be converted into nitraniline by either of these methods, the latter being the more convenient,



$$C_6H_4{<}\begin{matrix}NO_2\\ NO_2\end{matrix} + 6H = C_6H_4{<}\begin{matrix}NO_2\\ NH_2\end{matrix} + 2H_2O.$$

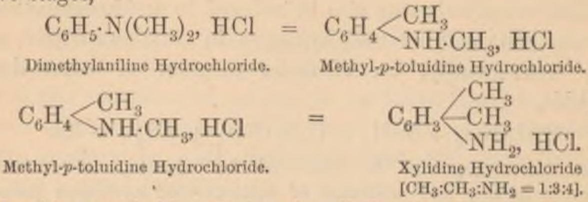
The amido-derivatives of toluene, xylene, &c., are commercially prepared by heating the hydrochlorides of the isomeric alkylanilines, such as methylaniline and dimethylaniline, at 280–300°, when the alkyl-group leaves the nitrogen atom and enters the nucleus (compare p. 365),



$$C_6H_5\cdot NH\cdot CH_3,\ HCl = C_6H_4{<}\begin{matrix}CH_3\\ NH_2\end{matrix},\ HCl.$$

Methylaniline Hydrochloride. p-Toluidine Hydrochloride.

In the case of dimethylaniline this change takes place in two stages,



$$C_6H_5\cdot N(CH_3)_2,\ HCl \quad = \quad C_6H_4\left<\begin{matrix}CH_3\\ NH\cdot CH_3,\ HCl\end{matrix}\right.$$

Dimethylaniline Hydrochloride. Methyl-*p*-toluidine Hydrochloride.

$$C_6H_4\left<\begin{matrix}CH_3\\ NH\cdot CH_3,\ HCl\end{matrix}\right. \quad = \quad C_6H_3\left<\begin{matrix}CH_3\\ CH_3\\ NH_2,\ HCl.\end{matrix}\right.$$

Methyl-*p*-toluidine Hydrochloride. Xylidine Hydrochloride $[CH_3{:}CH_3{:}NH_2 = 1{:}3{:}4]$.

In this remarkable reaction the alkyl-group displaces hydrogen from the ortho-, and from the para-position to the amido-group, but principally the latter; meta-derivatives cannot be prepared in this way.

This method is used, on the large scale, for preparing toluidine, xylidine, &c.; aniline is heated with methyl alcohol and hydrochloric acid at a high temperature, when the methyl- and dimethylanilines first produced (p. 365) undergo intramolecular change as explained above.

The diamido-compounds, such as the *o*-, *m*-, and *p*-diamidobenzenes or phenylenediamines, $C_6H_4(NH_2)_2$, are prepared by reducing either the corresponding dinitrobenzenes, $C_6H_4(NO_2)_2$, or the nitranilines, $C_6H_4(NO_2)\cdot NH_2$, generally with tin and hydrochloric acid.

Properties.—The *monamido*-compounds are mostly colourless liquids, which distil without decomposition, and are specifically heavier than water; they have a faint but characteristic odour, and dissolve freely in alcohol, ether, and other organic solvents, but they are only sparingly soluble in water; on exposure to light they rapidly darken, and ultimately become brown or black.

They are comparatively weak bases, which are neutral to litmus, and although they combine with acids to form salts such as aniline hydrochloride, $C_6H_5\cdot NH_2, HCl$, these salts are readily decomposed by weak alkalies or alkali carbonates, with liberation of the bases; in these respects, then, the amido-compounds differ in a marked manner from the strongly basic fatty amines and from the true aromatic amines, such as benzylamine (p. 368).

The feebly basic character of the amido-compounds is due to the fact that the phenyl radicle, C_6H_5-, has a marked negative or acid character, and its substitution for one of the hydrogen atoms in ammonia has the effect of diminishing or neutralising the basic character of the latter, a result which is directly the opposite of that arrived at by displacing the hydrogen atoms of ammonia by an alkyl (or positive) group, since the amines are stronger bases than ammonia.

When two hydrogen atoms in ammonia are displaced by phenyl-groups, as in diphenylamine, $(C_6H_5)_2NH$ (p. 367), a still feebler base is produced, the salts of which are decomposed by water. Triphenylamine, $(C_6H_5)_3N$ (p. 368), moreover, does not form salts at all.

For the same reason the hydroxy-, nitro-, and halogen-derivatives of the amido-compounds, such as amido-phenol, $C_6H_4(OH)\cdot NH_2$, nitraniline, $C_6H_4(NO_2)\cdot NH_2$, chloraniline, $C_6H_4Cl\cdot NH_2$, &c., are even weaker bases than the amido-compounds themselves, because the presence of the negative groups or atoms, HO–, NO_2-, Cl–, &c., enhances the acid character of the phenyl radicle.

The amido-compounds also differ from the fatty primary amines and from the true aromatic primary amines in their behaviour with nitrous acid. Although when warmed with nitrous acid in aqueous solution they yield phenols by the substitution of hydroxyl for the amido-group, just as the fatty amines under similar treatment are converted into alcohols (part i. p. 202),

$$C_6H_5\cdot NH_2 + NO_2H = C_6H_5\cdot OH + N_2 + H_2O$$
$$C_2H_5\cdot NH_2 + NO_2H = C_2H_5\cdot OH + N_2 + H_2O,$$

yet when treated with nitrous acid in cold aqueous solution, they are converted into diazo-compounds (p. 370), substances which cannot be produced from the primary amines.

It will be evident from the above statements that there are several important differences between the amido-compounds and the true primary amines, the character of an amido-group in the nucleus being influenced by its state of combination; nevertheless, except as regards those points already mentioned, amido-compounds have, on the whole, properties very similar to those of the true primary amines.

The amido-compounds, like the primary amines, interact readily with alkyl halogen compounds, yielding alkyl-derivatives, such as methylaniline, $C_6H_5{\cdot}NH{\cdot}CH_3$, dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, &c., and also compounds such as phenyltrimethylammonium iodide, $C_6H_5{\cdot}N(CH_3)_3I$, which correspond with the quaternary ammonium salts (part i. p. 205).

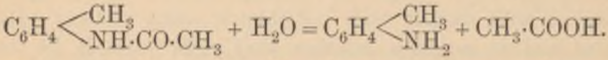
They are also readily acted on by anhydrides and acid chlorides, and even by acids on prolonged heating, yielding substances such as acetanilide and acetotoluidide, which are closely allied to the fatty amides (part i. p. 161), and from which they may be regarded as derived,

$$C_6H_5{\cdot}NH_2 + CH_3{\cdot}COOH = C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + H_2O$$

$$\underset{p\text{-Toluidine.}}{C_6H_4(CH_3){\cdot}NH_2} + (CH_3{\cdot}CO)_2O =$$

$$\underset{\text{Aceto-}p\text{-toluidide.}}{C_6H_4(CH_3){\cdot}NH{\cdot}CO{\cdot}CH_3} + CH_3{\cdot}COOH\,;$$

these compounds, like the amides, are readily resolved into their constituents on boiling with acids or alkalies,



$$C_6H_4{<}\begin{matrix}CH_3\\NH{\cdot}CO{\cdot}CH_3\end{matrix} + H_2O = C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix} + CH_3{\cdot}COOH.$$

The amido-compounds, like the fatty primary amines, give the carbylamine reaction; when a trace of aniline, for example, is heated with alcoholic potash and chloroform, an intensely nauseous smell is observed, due to the formation of phenylcarbylamine (part i. pp. 173, 202),

$$C_6H_5{\cdot}NH_2 + CHCl_3 + 3KOH = C_6H_5{\cdot}N{\vdots}C + 3KCl + 3H_2O.$$

Aqueous solutions of amido-compounds are coloured intensely violet on the addition of a solution of bleaching-powder or sodium hypochlorite, a behaviour which, as well as the carbylamine reaction, is made use of in their detection.

Diamido- and *triamido-compounds*, such as the three (*o. m. p.*) phenylenediamines or diamidobenzenes, $C_6H_4(NH_2)_2$, and the triamidobenzenes, $C_6H_3(NH_2)_3$, are very similar to the monamido-compounds in chemical properties, but differ from them usually in being solid, more readily soluble in water, and less volatile; since, moreover, they contain two and three amido-groups respectively, they neutralise two or three equivalents of an acid, yielding salts such as $C_6H_4(NH_2)_2, 2HCl$ and $C_6H_3(NH_2)_3, 3HCl$.

Aniline and its Derivatives.

Aniline, amidobenzene, or phenylamine, $C_6H_5 \cdot NH_2$, was first prepared by Unverdorben in 1826 by distilling indigo, the name aniline being derived from 'anil,' the Spanish for indigo. Runge in 1834 showed that aniline is contained in small quantities in coal-tar, but its preparation from nitrobenzene was first accomplished by Zinin in 1841.

Aniline is manufactured on a very large scale by the reduction of nitrobenzene with scrap iron and crude hydrochloric acid; but in preparing small quantities in the laboratory, the most convenient reducing agent is tin and hydrochloric acid,

$$C_6H_5 \cdot NO_2 + 6H = C_6H_5 \cdot NH_2 + 2H_2O,$$
$$2C_6H_5 \cdot NO_2 + 3Sn + 12HCl = 2C_6H_5 \cdot NH_2 + 3SnCl_4 + 4H_2O.$$

Nitrobenzene (50 grams) and granulated tin (80 grams) are placed in a flask, and concentrated hydrochloric acid (290 grams) added in small quantities at a time; at first the mixture must be cooled if the reaction be too violent, but when all the acid has been added, the product is carefully heated on a water-bath for about half an hour. The solution of aniline stannichloride is now treated with soda until strongly alkaline, the liberated aniline distilled in steam, and the distillate extracted with ether. The ethereal extract is then dried over solid potash, the ether distilled off, and the aniline purified by distillation.

Aniline is a colourless oil, boiling at 183°; it has a faint, characteristic odour, and is sparingly soluble in water, but readily in alcohol and ether; it gradually turns yellow when exposed to light and air, becoming ultimately almost black. Although neutral to litmus, aniline has very decided basic properties, and neutralises acids, forming soluble salts, such as aniline *hydrochloride*, $C_6H_5{\cdot}NH_2$, HCl, and the rather sparingly soluble *sulphate*, $(C_6H_5{\cdot}NH_2)_2$, H_2SO_4. The former, like the hydrochlorides of ethylamine, &c., forms double salts with platinum chloride and gold chloride ; on treating a moderately concentrated solution of the hydrochloride with platinum chloride, for example, the *platinochloride*,

$$(C_6H_5{\cdot}NH_2)_2,\ H_2PtCl_6,$$

is precipitated in yellow plates, which are moderately soluble in water.

When aniline is heated with chloroform and alcoholic potash, it yields phenylcarbylamine, $C_6H_5{\cdot}N{:}C$, a substance readily recognised by its penetrating and very disagreeable odour ; the presence of aniline may also be detected by treating its aqueous solution with bleaching-powder solution or sodium hypochlorite, when an intense purple colouration is produced.

When solutions of the salts of aniline are treated with nitrous acid, at ordinary temperatures, salts of diazo-compounds (p. 370) are formed, but on warming, the latter are decomposed with formation of phenol (p. 391).

Aniline is very largely employed in the manufacture of dyes, and in the preparation of a great number of benzene derivatives.

Acetanilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, is readily prepared by boiling aniline with excess of glacial acetic acid on a reflux apparatus for several hours, when the aniline acetate first formed is slowly converted into acetanilide, with elimination of water. The product is purified by fractionation or simply by recrystallisation from boiling water,

$$C_6H_5{\cdot}NH_2,\ CH_3{\cdot}COOH = C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + H_2O.$$

It crystallises in glistening plates, melts at 115°, and is sparingly soluble in cold water, but readily in alcohol ; when treated with acids or alkalies, it is rapidly hydrolysed into aniline and acetic acid. It is used in medicine as a febrifuge, under the name of *antifebrin*.

Formanilide, $C_6H_5 \cdot NH \cdot CHO$, the anilide of formic acid, and *oxanilide*, $C_6H_5 \cdot NH \cdot CO \cdot CO \cdot NH \cdot C_6H_5$, the anilide of oxalic acid, may be similarly prepared.

Substitution Products of Aniline.—Aniline and, in fact, all amido-compounds are much more readily attacked by halogens than the hydrocarbons: when aniline, for example, is treated with chlorine or bromine in aqueous solution, it is at once converted into *trichlor-aniline*, $C_6H_2Cl_3 \cdot NH_2$, and *tribromaniline*, $C_6H_2Br_3 \cdot NH_2$, respectively, so that in order to obtain mono- and di-substitution products, indirect methods must be employed.

The *o*- and *p-chloranilines*, $C_6H_4Cl \cdot NH_2$, may be prepared by passing chlorine into acetanilide, the *p*-derivative being obtained in the larger quantity. The two isomerides are first separated by crystallisation, and then decomposed by boiling with an alkali or acid,

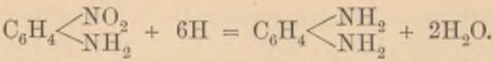
$$\underset{\text{Chloracetanilide.}}{C_6H_4Cl \cdot NH \cdot CO \cdot CH_3} + KOH = \underset{\text{Chloraniline.}}{C_6H_4Cl \cdot NH_2} + CH_3 \cdot COOK.$$

The effect of introducing an acetyl-group into the amido-group is therefore to render aniline less readily attacked; acetanilide, in fact, behaves towards chlorine and bromine more like benzene than aniline. *m*-Chloraniline is most conveniently prepared by the reduction of *m*-chloronitrobenzene, $C_6H_4Cl \cdot NO_2$ (a substance formed by chlorinating nitrobenzene in the presence of antimony chloride). *o*-Chloraniline and *m*-chloraniline are oils boiling at 207° and 230° respectively, but *p*-chloraniline is a solid, which melts at 69°, and boils at 231°.

Nitranilines, $C_6H_4(NO_2) \cdot NH_2$, cannot be obtained by nitrating aniline, as the nitrous acid, produced by the reduction of the nitric acid, converts the amido- into the hydroxyl-group, and nitro-derivatives of phenol are formed.

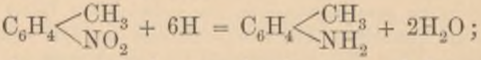
The *o*- and *p*-compounds are prepared by nitrating acetanilide, the *o*- and *p*-nitracetanilides thus obtained being separated by fractional crystallisation, and then converted into the corresponding nitranilines by heating with alkalies. *m*-Nitraniline is very readily prepared by the partial reduction of *m*-dinitrobenzene, $C_6H_4(NO_2)_2$, with ammonium sulphide (p. 357).

o-Nitraniline melts at 71°, *m*- at 114°, and *p*- at 147°; they are all sparingly soluble in water, readily in alcohol, and on reduction they yield the corresponding *o*-, *m*-, and *p*-phenylenediamines,



$$C_6H_4{<}\begin{matrix}NO_2\\NH_2\end{matrix} + 6H = C_6H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix} + 2H_2O.$$

Homologues of Aniline.—The *toluidines*, or amido-toluenes, $C_6H_4(CH_3){\cdot}NH_2$, are prepared by reducing the corresponding *o*-, *m*-, and *p*-nitrotoluenes (p. 355), by means of tin and hydrochloric acid, the details of the process being exactly similar to those already given in the case of the preparation of aniline from nitrobenzene,



$$C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix} + 6H = C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix} + 2H_2O;$$

the *o*- and *p*-compounds may also be prepared from methylaniline (p. 357). Both *o*- and *m*-toluidine are oils boiling at 197°, but *p*-toluidine is crystalline, and melts at 45°, boiling at 198°. When treated with nitrous acid, the toluidines yield diazo-salts, from which the corresponding cresols, $C_6H_4(CH_3){\cdot}OH$, are obtained, and in all other reactions they show the greatest similarity to aniline; *o*- and *p*-toluidine are largely employed in the manufacture of dyes.

Diamidobenzenes.—The *phenylenediamines*, $C_6H_4(NH_2)_2$, are obtained by the reduction of the corresponding dinitrobenzenes, or the nitranilines, and a general description of their properties has already been given (p. 361); *o*-phenylenediamine melts at 103°, the *m*- and *p*-compounds at 63° and 140° respectively. *m*-Phenylenediamine gives an intense yellow colouration with a trace of nitrous acid, and is employed in water-analysis for the estimation of nitrites; both the *m*- and *p*-compounds are largely employed in the manufacture of dyes.

Alkylanilines.

Those derivatives of the amido-compounds, obtained by displacing one or both of the hydrogen atoms of the amido-group by alkyl radicles, are substances of considerable importance, and are usually known as **alkylanilines.** They are prepared by heating the amido-compounds, for some hours, with the alkyl halogen compounds, the reaction being analogous to that which occurs in the formation of secondary and tertiary from primary amines (p. 369),

$$C_6H_5{\cdot}NH_2 + RCl = C_6H_5{\cdot}NHR, HCl$$
$$C_6H_5{\cdot}NH_2 + 2RCl = C_6H_5{\cdot}NR_2, HCl + HCl.$$

Instead of employing the alkyl halogen compounds, a mixture of the corresponding alcohol and halogen acid may be used; methyl- and dimethyl-aniline, for example, are prepared, on the large scale, by heating aniline with methyl alcohol and hydrochloric acid at 200–250°,

$$C_6H_5{\cdot}NH_2, HCl + CH_3{\cdot}OH = C_6H_5{\cdot}NH(CH_3), HCl + H_2O$$
$$C_6H_5{\cdot}NH_2, HCl + 2CH_3{\cdot}OH = C_6H_5{\cdot}N(CH_3)_2, HCl + 2H_2O.$$

In either case the product consists of the salts of the mono- and dialkyl-derivatives, mixed with certain quantities of unchanged substances, but the mono-alkyl derivative is usually present in small quantity only (about 5 per cent.). The three bases are separated as follows: The product is treated with potash, and the free bases (aniline, methylaniline, and dimethylaniline), which separate as an oily layer, are extracted with ether. After distilling off the ether, the mixture is digested for a short time with acetic anhydride, by which treatment the aniline and methylaniline are converted into acetanilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, and methylacetanilide, $C_6H_5{\cdot}N(CH_3){\cdot}CO{\cdot}CH_3$, respectively, whereas the dimethylaniline is not acted on; the whole is then distilled, the portion boiling below 175°, which consists of acetic anhydride, being collected separately. The crystals, which are deposited on standing from the portions passing over above 175°, are separated by filtration and pressure from the oily dimethylaniline, which is then purified by fractionation.

After washing the crystalline anilides with very dilute acetic acid, the mixture is hydrolysed with hydrochloric acid, the liquid diluted considerably with water, cooled, and an excess of sodium nitrite added; the aniline is thus converted into diazobenzene chloride (p. 370), and the methylaniline into nitrosomethylaniline, $C_6H_5{\cdot}N(CH_3){\cdot}NO$. The latter is extracted with ether, reduced with tin and hydrochloric acid (p. 366), and the regenerated methylaniline purified by distillation in steam and fractionation. *Ethyl-* and *diethyl-aniline* may be prepared and isolated in a similar manner.

These mono- and di-alkyl derivatives are stronger bases than the amido-compounds from which they are derived, the presence of the positive alkyl-group counteracting to some extent the action of the negative phenyl-group (compare p. 359); they are, in fact, very similar in properties to the secondary and tertiary amines respectively, and may be regarded as derived from the fatty amines by the substitution of a phenyl-group for a hydrogen atom, just as the secondary and tertiary amines are obtained by displacing hydrogen atoms by alkyl-groups. Methylaniline, for example, is also phenylmethylamine, and its properties are those of a substitution product of methylamine.

The mono-alkylanilines, like the secondary amines, are converted into yellowish nitroso-compounds on treatment with nitrous acid,

$$\underset{\text{Methylaniline.}}{C_6H_5{\cdot}NH{\cdot}CH_3} + HO{\cdot}NO = \underset{\text{Nitrosomethylaniline.}}{C_6H_5{\cdot}N(NO){\cdot}CH_3} + H_2O.$$

$$\underset{\text{Dimethylamine.}}{(CH_3)_2NH} + HO{\cdot}NO = \underset{\text{Nitrosodimethylamine.}}{(CH_3)_2{\cdot}N{\cdot}NO} + H_2O.$$

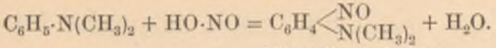
These nitroso-compounds give Liebermann's nitroso-reaction (part i. p. 204), and on reduction they yield ammonia and the original alkylaniline,

$$C_6H_5{\cdot}N(NO){\cdot}CH_3 + 6H = C_6H_5{\cdot}NH{\cdot}CH_3 + NH_3 + H_2O.$$

Methylaniline, $C_6H_5{\cdot}NH{\cdot}CH_3$, prepared as just described, is a colourless liquid which boils at 191°, and, compared with aniline, has strongly basic properties. On adding sodium nitrite to its solution in hydrochloric acid, *nitrosomethylaniline*, $C_6H_5{\cdot}N(NO){\cdot}CH_3$, is precipitated as a light-yellow oil.

Dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, the preparation of which has just been given, is a colourless, strongly basic oil, which boils at 192°; it is largely used in the manufacture of dyes.

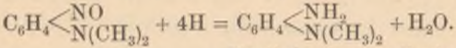
The di-alkylanilines, such as dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, also interact readily with nitrous acid (a behaviour which is not shown by tertiary fatty amines), intensely green (iso)nitroso-compounds being formed, the NO– group displacing hydrogen of the nucleus from the *p*-position to the nitrogen atom,



$$C_6H_5{\cdot}N(CH_3)_2 + HO{\cdot}NO = C_6H_4{<}\substack{NO\\ N(CH_3)_2} + H_2O.$$

Nitrosodimethylaniline.

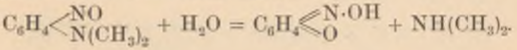
These substances do not give Liebermann's nitroso-reaction, and when reduced they yield derivatives of *p*-phenylenediamine,



$$C_6H_4{<}\substack{NO\\ N(CH_3)_2} + 4H = C_6H_4{<}\substack{NH_2\\ N(CH_3)_2} + H_2O.$$

Dimethyl-*p*-phenylenediamine.

p-Nitrosodimethylaniline, $C_6H_4{<}\substack{NO\\ N(CH_3)_2}$, is prepared by dissolving dimethylaniline (1 part) in water (5 parts), and concentrated hydrochloric acid (2·5 parts), and gradually adding to the well-cooled solution the calculated quantity of sodium nitrite dissolved in a little water. The yellow crystalline precipitate of nitrosodimethylaniline hydrochloride is separated by filtration, dissolved in water, decomposed by potassium carbonate, and the free base extracted with ether. Nitrosodimethylaniline crystallises from ether in dark-green plates, and melts at 85°; it is not a nitrosamine, and does not give Liebermann's nitroso-reaction. When reduced with zinc and hydrochloric acid, it is converted into *dimethyl-p-phenylenediamine* (see above), and when boiled with dilute soda, it is decomposed into quinone monoxime (*p-nitrosophenol*) and dimethylamine,



$$C_6H_4{<}\substack{NO\\ N(CH_3)_2} + H_2O = C_6H_4{\leqslant}\substack{N{\cdot}OH\\ O} + NH(CH_3)_2.$$

Diphenylamine and Triphenylamine.

The hydrogen atoms of the amido-group in aniline may also be displaced by phenyl radicles, the compounds diphenylamine, $(C_6H_5)_2NH$, and triphenylamine, $(C_6H_5)_3N$, being produced. These substances, however, cannot be obtained by treating aniline with chlorobenzene, C_6H_5Cl, a method which would be analogous to that which is employed in the preparation of diethylamine and triethylamine, because the halogen is so firmly bound to the nucleus, that no action takes place even when the substances are heated together.

Diphenylamine is most conveniently prepared by heating aniline hydrochloride with aniline at about 240° in closed vessels,

$$C_6H_5 \cdot NH_2, HCl + C_6H_5 \cdot NH_2 = (C_6H_5)_2 \cdot NH + NH_4Cl.$$

It is a colourless, crystalline substance, which melts at 54°, boils at 310°, and is insoluble in water, but readily soluble in alcohol and ether. It is only a feeble base, and its salts are decomposed by water with separation of the base; its solution in concentrated sulphuric acid gives with a trace of nitrous acid an intense blue colouration, and it therefore serves as a very delicate test for nitrous acid or nitrites. Diphenylamine is largely used in the manufacture of dyes, also for experiments in which a high constant temperature is required, as, for example, in determining the vapour density of substances of high boiling-point by V. Meyer's method. When treated with potassium, diphenylamine yields a solid potassium derivative, $(C_6H_5)_2NK$, the presence of the two phenyl-groups being sufficient to impart to the $>NH$ group a feeble acid character, similar to that of imides (part i. p. 238).

Triphenylamine, $(C_6H_5)_3N$, may be prepared by heating potassium diphenylamine with monobromobenzene at 300°,

$$(C_6H_5)_2NK + C_6H_5Br = (C_6H_5)_3N + KBr.$$

It is a colourless, crystalline substance, melts at 127°, and has no basic properties, as it does not combine even with the strongest acids.

Aromatic Amines.

The true aromatic amines—namely, those compounds in which the amido-group is united with carbon of the *side-chain*, are of far less importance than the amido-compounds, and only a few substances of this class have been thoroughly investigated.

Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$, may, however, be described as a typical aromatic primary amine. It may be obtained by reducing phenyl cyanide (benzonitrile, p. 421) with sodium and alcohol,

$$C_6H_5{\cdot}CN + 4H = C_6H_5{\cdot}CH_2{\cdot}NH_2,$$

by treating the amide of phenylacetic acid (p. 429) with bromine and potash,

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH_2 + Br_2 + 4KOH = C_6H_5{\cdot}CH_2{\cdot}NH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

and by heating benzyl chloride with alcoholic ammonia,

$$C_6H_5{\cdot}CH_2Cl + NH_3 = C_6H_5{\cdot}CH_2{\cdot}NH_2, HCl.$$

All these methods are similar to those employed in the preparation of fatty primary amines.

Benzylamine is a colourless, pungent-smelling, strongly basic liquid, boiling at 185°; it closely resembles the fatty amines in nearly all respects, and differs from the monamido-compounds (aniline, toluidine, &c.) in being readily soluble in water, and in not yielding diazo-compounds when its salts are treated with nitrous acid. Like the fatty primary amines, it gives the carbylamine reaction, and is converted into the corresponding alcohol (benzyl alcohol, p. 403) on treatment with nitrous acid.

Secondary and tertiary aromatic amines are formed when a primary amine is heated with an aromatic halogen compound, containing the halogen in the side-chain; when, for example, benzylamine is heated with benzyl chloride, both *dibenzylamine* and *tribenzylamine* are produced, just as diethylamine and triethylamine are obtained when ethylamine is heated with ethyl bromide,

$$C_6H_5{\cdot}CH_2{\cdot}NH_2 + C_6H_5{\cdot}CH_2Cl = (C_6H_5{\cdot}CH_2)_2NH, HCl$$

$$C_6H_5{\cdot}CH_2{\cdot}NH_2 + 2C_6H_5{\cdot}CH_2Cl = (C_6H_5{\cdot}CH_2)_3N, HCl + HCl.$$

When, therefore, benzyl chloride is heated with ammonia, the product consists of a mixture of the salts of all three amines.

CHAPTER XXIV.

DIAZO-COMPOUNDS AND THEIR DERIVATIVES.

It has already been stated that when the amido-compounds or their salts are treated with nitrous acid in aqueous solution, they yield phenols; this decomposition, however, usually takes place only on warming. If, for example, a well-cooled dilute solution of aniline hydrochloride (1 mol.) be mixed with sodium nitrite (1 mol.), and hydrochloric acid (1 mol.) added to set free the nitrous acid, phenol is not produced, and the solution contains a very unstable substance called *diazobenzene chloride*, the formation of which may be expressed by the equation

$$C_6H_5{\cdot}NH_2{,}HCl + NO_2H = C_6H_5{\cdot}N{:}NCl + 2H_2O.$$

In this respect, then, the amido-compounds differ from the fatty amines; the latter are at once converted into alcohols by nitrous acid in the cold, whereas the former are first transformed into diazo-compounds, which, usually only on warming, decompose more or less readily with formation of phenols (p. 386).

All amido-compounds behave in this way, yielding diazo-salts similarly constituted to diazobenzene chloride.

The diazo-salts were discovered in 1860 by P. Griess; they may be assumed to be salts of diazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}OH$, and its homologues, substances which it has not been found possible to isolate in a pure state and analyse on account of their unstable nature.

The diazo-salts (usually spoken of as the diazo-compounds) may nevertheless be isolated without much difficulty, although, as a matter of fact, they are seldom separated from their aqueous solutions, partly because of their explosive character, partly because for most purposes for which they are prepared this operation is quite unnecessary.

Preparation.—Anhydrous diazo-salts may be obtained by treating a well-cooled solution of an amido-compound in absolute alcohol with amyl nitrite and a mineral acid, in absence of any considerable quantity of water,

$$C_6H_5\cdot NH_2,HCl + C_5H_{11}\cdot O\cdot NO = C_6H_5\cdot N:NCl + C_5H_{11}\cdot OH + H_2O.$$

Diazobenzene sulphate, $C_6H_5\cdot N:N\cdot SO_4H$, for example, is prepared by dissolving aniline (15 parts) in absolute alcohol (10 parts), adding concentrated sulphuric acid (20 parts), and after cooling in a freezing mixture, slowly running in pure amyl nitrite (20 grams); after 10–15 minutes diazobenzene sulphate separates in crystals, which are washed with alcohol and ether, and dried in the air at ordinary temperatures.

Diazobenzene chloride and *diazobenzene nitrate* may be obtained in a similar manner, employing alcoholic solutions of hydrogen chloride and of nitric acid in the place of sulphuric acid.

Diazobenzene nitrate, $C_6H_5\cdot N:N\cdot NO_3$, may also be conveniently isolated as follows: Aniline nitrate is suspended in a small quantity of water, and the liquid saturated with nitrous acid (generated from As_2O_3 and HNO_3), when the crystals gradually dissolve with formation of diazobenzene nitrate; on the addition of alcohol and ether, this salt separates in colourless needles. Special precautions are to be observed in preparing this substance, as, when dry, it is highly explosive, although it may be handled with safety if kept moist.

Aqueous solutions of the diazo-salts are prepared by dissolving the amido-compound in an aqueous mineral acid, and adding the theoretical quantity of a solution of sodium nitrite, after first cooling to 0° (see above, also p. 373).

Properties.—The diazo-salts are colourless, crystalline compounds, very readily soluble in water; in the dry state they are more or less explosive, and should be handled only with the greatest caution. They are of immense value in synthetical chemistry and in the preparation of dyes, as they undergo a number of remarkable reactions, of which the following are some of the more important.

When warmed in aqueous solution they decompose rapidly, with evolution of nitrogen and formation of phenols (p. 386),

$$C_6H_5{\cdot}N{:}N{\cdot}NO_3 + H_2O = C_6H_5{\cdot}OH + N_2 + HNO_3$$

$$\underset{p\text{-Diazotoluene Chloride.}}{C_6H_4(CH_3){\cdot}N{:}NCl} + H_2O = \underset{p\text{-Cresol.}}{C_6H_4(CH_3){\cdot}OH} + N_2 + HCl.$$

When boiled with strong alcohol they yield hydrocarbons, part of the alcohol being oxidised to aldehyde,

$$C_6H_5{\cdot}N{:}NCl + C_2H_5{\cdot}OH = C_6H_6 + N_2 + HCl + CH_3{\cdot}CHO.$$

These two reactions afford a means of obtaining phenols and hydrocarbons from amido-compounds.

The diazo-compounds behave in a very remarkable way when treated with cuprous salts; if, for example, a solution of diazobenzene chloride be warmed with cuprous chloride, nitrogen is evolved, and chlorobenzene is produced. In this reaction, the diazo-salt combines with the cuprous chloride to form an intermediate brownish additive compound, which is decomposed at higher temperatures, cuprous chloride being regenerated; theoretically, therefore, the reaction is continuous,

$$C_6H_5{\cdot}N{:}NCl, Cu_2Cl_2 = C_6H_5Cl + N_2 + Cu_2Cl_2.$$

If, instead of the chloride, cuprous bromide or cuprous iodide be employed, bromobenzene or iodobenzene is produced,

$$\underset{\text{Additive Compound.}}{C_6H_5{\cdot}N{:}NBr, Cu_2Br_2} = \underset{\text{Bromobenzene.}}{C_6H_5Br} + N_2 + Cu_2Br_2,$$

whereas by using cuprous cyanide, a cyanide or nitrile is formed,

$$\underset{\text{Additive Compound.}}{C_6H_5{\cdot}N_2{\cdot}CN, Cu_2(CN)_2} = \underset{\text{Phenyl Cyanide.}}{C_6H_5{\cdot}CN} + N_2 + Cu_2(CN)_2.$$

In this latter reaction a mixture of cupric sulphate and potassium cyanide is generally used instead of the previously prepared cuprous cyanide.

By means of this very important reaction, which was discovered by Sandmeyer in 1884, it is possible to displace the

NH_2– group in amido-compounds by Cl, Br, I, CN, and indirectly by COOH (by the hydrolysis of the CN– group), and indeed by other atoms or groups; as, moreover, the yield is generally good, Sandmeyer's reaction is of great practical value. The amido-compounds being readily obtainable from the nitro-compounds, and the latter from the hydrocarbons, this method affords a means of preparing halogen, cyanogen, and other derivatives indirectly from the hydrocarbons.

Gattermann has shown that the decomposition of the diazo-compounds is, in many cases, best brought about by treating the cold solution of the diazo-salt with copper powder (prepared by the action of zinc-dust on a solution of copper sulphate). Monochlorbenzene, for example, is readily obtained from aniline by the following process: Aniline (31 grams) is dissolved in hydrochloric acid (300 grams) and water (150 grams), the solution well cooled with ice, and *diazotised* by adding gradually a concentrated aqueous solution of sodium nitrite (23 grams). The solution of diazobenzene chloride thus obtained is gradually mixed with copper powder (40 grams), when nitrogen is evolved and chlorobenzene produced, the reaction being complete in about half an hour. The chlorobenzene is then purified by distillation in steam and fractionation.

In preparing cyanobenzene, $C_6H_5{\cdot}CN$, from aniline, aniline sulphate is diazotised, the solution mixed with potassium cyanide, and then copper powder added.

The diazo-compounds also serve for the preparation of an important class of compounds known as the *hydrazines*, these substances being obtained by reducing the diazo-compounds, usually with stannous chloride and hydrochloric acid,

$$\underset{\text{Diazochloride.}}{R{\cdot}N{:}NCl} + 4H = \underset{\text{Hydrazine Hydrochloride.}}{R{\cdot}NH{\cdot}NH_2,HCl}.$$

Constitution of Diazo-compounds.—That diazobenzene salts have the constitution expressed by the formula $C_6H_5{\cdot}\underset{b}{N}{:}\underset{a}{N}R$ (where R = Cl, Br, I, NO_3, HSO_4, &c.) is shown by the following considerations. On reduction they are converted into phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$ (the constitution of which is known, p. 376), a fact which shows that the two nitrogen atoms are united together, and that one of them (*b*) is combined with the benzene nucleus. Diazobenzene chloride interacts readily with dimethylaniline, giving dimethylamidoazobenzene (p. 376),

$$C_6H_5\cdot\underset{b}{N}{:}\underset{a}{N}Cl + C_6H_5\cdot N(CH_3)_2 = C_6H_5\cdot\underset{b}{N}{:}\underset{a}{N}\cdot C_6H_4\cdot N(CH_3)_2 + HCl,$$

and this substance, on reduction, yields aniline and dimethyl-*p*-phenylenediamine (p. 376),

$$C_6H_5\cdot\underset{b}{N}{:}\underset{a}{N}\cdot C_6H_4\cdot N(CH_3)_2 + 4H = C_6H_5\cdot\underset{b}{N}H_2 + \underset{a}{N}H_2\cdot C_6H_4\cdot N(CH_3)_2.$$

These changes can only be explained on the assumption that the acid radicle is attached to the *a*-nitrogen atom, as in the above formula, because if it were united to the other nitrogen atom (*b*), as in the formula $C_6H_5\cdot\underset{b}{N}Cl\,\vdots\,\underset{a}{N}$, for example, such products could not be obtained.

Free diazobenzene is very unstable, and has not been obtained in a pure state, but it probably has the constitution $C_6H_5\cdot N{:}N\cdot OH$.

Diazoamido- and Amidoazo-compounds.

Although some of the more characteristic reactions of diazo-compounds have already been mentioned, there are numerous other changes of great interest and of great commercial importance which these substances undergo.

When, for example, diazobenzene chloride is treated with aniline, a reaction takes place similar to that which occurs when aniline is treated with benzoyl chloride (p. 420), and diazoamidobenzene is formed,

$$C_6H_5\cdot N{:}NCl + NH_2\cdot C_6H_5 = \underset{\text{Diazoamidobenzene.}}{C_6H_5\cdot N{:}N\cdot NH\cdot C_6H_5} + HCl$$

$$C_6H_5\cdot COCl + NH_2\cdot C_6H_5 = \underset{\text{Benzoylamidobenzene or Benzanilide.}}{C_6H_5\cdot CO\cdot NH\cdot C_6H_5} + HCl.$$

As, moreover, other diazo-compounds and other amido-compounds interact in a similar manner, numerous diazoamido-compounds may be obtained.

Diazoamidobenzene, $C_6H_5\cdot N{:}N\cdot NH\cdot C_6H_5$, may be described as a typical compound of this class; it is conveniently prepared by passing nitrous fumes into an alcoholic solution of aniline, the diazobenzene nitrite, which is probably first produced, interacting with excess of aniline,

$$C_6H_5{\cdot}N{:}N{\cdot}NO_2 + C_6H_5{\cdot}NH_2 = C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5 + HNO_2.$$

Diazoamidobenzene crystallises in brilliant yellow needles, and is sparingly soluble in water, but readily in alcohol and ether; it does not form salts with acids.

Amidoazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$, is formed when diazoamidobenzene is warmed with a small quantity of aniline hydrochloride at 40°, intramolecular change taking place,

$$C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5 = C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2.$$

The course of this remarkable reaction, which is a general one, and shown by all diazoamido-compounds, may possibly be explained by assuming that the aniline hydrochloride first decomposes the diazoamidobenzene, yielding diazobenzene chloride and aniline thus:

$$C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5 + C_6H_5{\cdot}NH_2, HCl = C_6H_5{\cdot}N{:}NCl + 2C_6H_5{\cdot}NH_2.$$

The diazobenzene chloride then interacts with excess of aniline in such a way that the diazo-group displaces hydrogen of the nucleus from the *para*-position to the amido-group,

$$C_6H_5{\cdot}N{:}NCl + 2C_6H_5{\cdot}NH_2 = C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2 + C_6H_5{\cdot}NH_2, HCl.$$

The change is, therefore, theoretically continuous, the regenerated aniline hydrochloride being able to convert a further quantity of the diazoamidobenzene into the amidoazo-compound.

Amidoazobenzene may also be prepared by nitrating azobenzene (p. 378), and then reducing the *p*-nitroazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$, which is produced with ammonium sulphide, a series of reactions analogous to those which occur in the formation of aniline from benzene, and which prove the constitution of amidoazobenzene.

Amidoazobenzene crystallises from alcohol in brilliant orange-red plates, and melts at 125°; its salts are intensely coloured, the hydrochloride, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2, HCl$, for example, forms beautiful steel-blue needles, and used to come into the market under the name of 'aniline yellow' as a silk dye (p. 524).

Other amidoazo-compounds may be obtained *directly* by treating tertiary alkylanilines (p. 364) with diazo-salts: dimethylaniline, for example, interacts with diazobenzene chloride, yielding dimethylamidoazobenzene,

$$C_6H_5{\cdot}N{:}NCl + C_6H_5{\cdot}N(CH_3)_2 = C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2,\ HCl,$$

no intermediate diazoamido-compound being formed, because dimethylaniline does not contain an $NH<$ or NH_2- group.

In this case also the diazo-group, $C_6H_5{\cdot}N{:}N-$, takes up the *p*-position to the $N(CH_3)_2-$ group, as is shown by the fact that, on reduction, dimethylamidoazobenzene is converted into aniline and dimethyl-*p*-phenylenediamine, the latter being identical with the base which is produced by reducing *p*-nitrosodimethylaniline (p. 367).

Phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$, a compound of great practical importance, is easily prepared by the reduction of diazobenzene chloride,

$$C_6H_5{\cdot}N{:}NCl + 4H = C_6H_5{\cdot}NH{\cdot}NH_2,\ HCl.$$

Aniline (10 grams) is dissolved in concentrated hydrochloric acid (200 c.c.), and to the well-cooled solution sodium nitrite (7·5 grams) dissolved in water (50 c.c.) is added in small quantities at a time; the resulting solution of diazobenzene chloride is then mixed with stannous chloride (45 grams) dissolved in concentrated hydrochloric acid (45 grams). The precipitate of phenylhydrazine hydrochloride, which rapidly forms, is separated by filtration, dissolved in water, decomposed with potash, and the free base extracted with ether and purified by fractionation.

Phenylhydrazine crystallises in colourless prisms, melts at 23°, and boils with slight decomposition at 241°, so that it is best purified by distillation under reduced pressure. It is sparingly soluble in cold water, readily in alcohol and ether; it is a strong base, and forms well-characterised salts, such as the hydrochloride, $C_6H_5{\cdot}NH{\cdot}NH_2,\ HCl$, which crystallises in colourless needles, and is readily soluble in hot water; solutions of the free base and of its salts reduce Fehling's solution in the cold. The *constitution* of phenylhydrazine is established by the fact that, when heated with zinc-dust and hydrochloric acid, it is converted into aniline and ammonia.

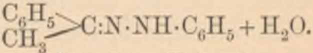
Phenylhydrazine interacts readily with aldehydes, ketones, and other substances containing a carbonyl-group, with elimination of water and formation of *phenylhydrazones* (hydrazones); as these compounds are usually sparingly soluble and often crystallise well, they may frequently be employed with advantage in the identification and isolation of aldehydes, ketones, &c. (part i. p. 133),

$$C_6H_5{\cdot}CHO + C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_5{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O$$

Benzaldehyde. Benzaldehyde Hydrazone.

$$C_6H_5{\cdot}CO{\cdot}CH_3 + C_6H_5{\cdot}NH{\cdot}NH_2 =$$

Acetophenone.



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>C{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O.$$

Acetophenone Hydrazone.

Most hydrazones are decomposed by strong mineral acids, with regeneration of the aldehyde or ketone, and formation of a salt of phenylhydrazine,

$$C_6H_5{\cdot}CH{:}N{\cdot}NH\ C_6H_5 + H_2O + HCl = C_6H_5{\cdot}CHO + C_6H_5{\cdot}NH{\cdot}NH_2,\ HCl.$$

The value of phenylhydrazine as a means of detecting and isolating the sugars has been explained (part i. p. 267).

In preparing hydrazones, the reacting substances may either be heated together without a solvent, or more frequently the substance is dissolved in water (or alcohol), and the solution of the requisite amount of phenylhydrazine in dilute acetic acid added. On warming, the hydrazone generally separates in a crystalline form, and may be readily purified by recrystallisation.

Osazones (part i. p. 268) are prepared by warming an aqueous solution of a sugar, with a large excess of phenylhydrazine dissolved in dilute acetic acid; after some time the osazone begins to be deposited in a crystalline form, the separation increasing as the liquid cools.

Azo-compounds.

It has already been shown that when nitro-compounds are treated with tin and hydrochloric acid, and other *acid* reducing agents, they are converted into amido-compounds, a similar change taking place when alcoholic ammonium sulphide is employed; when, however, nitro-compounds are treated with other *alkaline* reducing agents, such as sodium amalgam, stannous oxide and soda, or zinc-dust and soda, they yield *azo-compounds*, such as azobenzene, two molecules of the nitro-compound affording one molecule of the azo-compound,

$$2C_6H_5{\cdot}NO_2 + 4H = C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 2H_2O.$$

Azobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_5$, may be described as a typical example of this class of compounds. It is prepared by agitating nitrobenzene with the calculated quantity of stannous chloride, dissolved in soda, until the odour of nitrobenzene is imperceptible. The reddish precipitate is collected, washed with water, dried, and recrystallised from light petroleum.

Azobenzene crystallises in brilliant red plates, melts at 68°, and distils at 293°; it is readily soluble in ether and alcohol, but insoluble in water. Alkaline reducing agents, such as ammonium sulphide, zinc-dust and soda, &c., convert azobenzene into *hydrazobenzene*, a colourless, crystalline substance, which melts at 131°,

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 2H = C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5,$$

whereas a mixture of zinc-dust and acetic acid decomposes it, with formation of aniline,

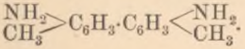
$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 4H = 2C_6H_5{\cdot}NH_2.$$

Other azo-compounds behave in a similar manner.

Hydrazobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$, is readily converted into azobenzene by mild oxidising agents such as mercuric oxide, and slowly even when air is passed through its alcoholic solution. When treated with strong acids, it undergoes a very remarkable intramolecular change, and is converted into *p*-diamidodiphenyl or *benzidine*, a strongly basic substance largely used in the preparation of azo-dyes (p. 526),

$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5 = \underset{\text{Benzidine.}}{NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2}.$$

Benzidine may be directly produced by reducing azobenzene with tin and strong hydrochloric acid; other azo-compounds, such as azo-toluene, $CH_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CH_3$, behave in a similar manner, and are readily converted into isomeric alkyl-derivatives of benzidine, such as *dimethylbenzidine* (tolidine),



$$\begin{matrix}NH_2\\CH_3\end{matrix}\!\!>C_6H_3{\cdot}C_6H_3<\!\!\begin{matrix}NH_2\\CH_3\end{matrix}.$$

CHAPTER XXV.

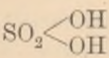
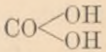
SULPHONIC ACIDS AND THEIR DERIVATIVES.

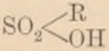
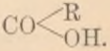
When benzene is heated with concentrated sulphuric acid, it gradually dissolves, and *benzenesulphonic acid* is formed by the substitution of the *sulphonic* group $-SO_3H$ or $-SO_2{\cdot}OH$ for an atom of hydrogen,

$$C_6H_6 + H_2SO_4 = C_6H_5{\cdot}SO_3H + H_2O.$$

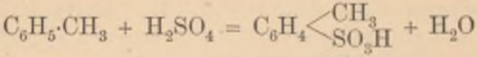
The homologues of benzene and aromatic compounds in general behave in a similar manner, and this property of readily yielding sulphonic derivatives by the displacement of hydrogen of the nucleus is one of the important characteristics of aromatic, as distinct from fatty, compounds.

The sulphonic acids are not analogous to the alkylsulphuric acids (part i. p. 182), which are ethereal salts, but rather to the carboxylic acids, since they may be regarded as derived from sulphuric acid, $SO_2(OH)_2$, just as the carboxylic acids are derived from carbonic acid, $CO(OH)_2$, namely, by the substitution of an aromatic radicle for one of the hydroxyl-groups.

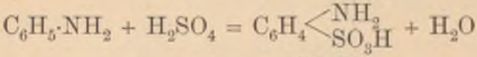
Sulphuric acid,  $SO_2<\begin{matrix}OH\\OH\end{matrix}$ Carbonic acid,  $CO<\begin{matrix}OH\\OH\end{matrix}$

Sulphonic acid,  $SO_2<\begin{matrix}R\\OH\end{matrix}$ Carboxylic acid,  $CO<\begin{matrix}R\\OH.\end{matrix}$

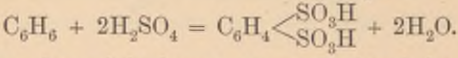
Preparation.—Sulphonic acids are prepared by treating an aromatic compound with sulphuric acid, or with anhydrosulphuric acid,



$$C_6H_5\cdot CH_3 + H_2SO_4 = C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H} + H_2O$$



$$C_6H_5\cdot NH_2 + H_2SO_4 = C_6H_4{<}\genfrac{}{}{0pt}{}{NH_2}{SO_3H} + H_2O$$



$$C_6H_6 + 2H_2SO_4 = C_6H_4{<}\genfrac{}{}{0pt}{}{SO_3H}{SO_3H} + 2H_2O.$$

The number of hydrogen atoms displaced by sulphonic groups depends (as in the case of nitro-groups) on the temperature, on the concentration of the acid, and on the nature of the substance undergoing *sulphonation*.

The substance to be sulphonated is mixed with, or dissolved in, excess of the acid, and, if necessary, the mixture or solution is then heated on a water- or sand-bath until the desired change is complete. After cooling, the product is carefully treated with water, and the acid isolated as described later (p. 382). In the case of substances which are insoluble in water or dilute sulphuric acid, the point at which the whole is converted into a monosulphonic acid is easily ascertained by taking out a small portion of the mixture and adding water; unless the whole is soluble, unchanged substance is still present.

Sometimes chlorosulphonic acid, $Cl\cdot SO_3H$, is employed in sulphonating substances, and, in such cases, chloroform or carbon bisulphide may be used as a solvent to moderate the action,

$$C_6H_6 + Cl\cdot SO_3H = C_6H_5\cdot SO_3H + HCl.$$

Properties.—Sulphonic acids are, as a rule, colourless, crystalline compounds, readily soluble in water, and often very hygroscopic; they have seldom a definite melting-point, and gradually decompose when heated, without volatilising, for which reason they cannot be distilled. They have a sour taste, a strongly acid reaction, turn blue litmus red, and show, in fact, all the properties of powerful acids, their basicity depending on the number of sulphonic groups which they contain. They decompose carbonates, and dissolve certain metals with evolution of hydrogen; their salts, as a rule, are readily soluble in water.

Although, generally speaking, the sulphonic acids are very stable, and are not decomposed by boiling aqueous alkalies or mineral acids, they undergo certain changes of great importance. When fused with potash they yield phenols (p. 387), and when strongly heated with potassium cyanide, or with potassium ferrocyanide, they are converted into cyanides (or nitriles, p. 421), which pass off in vapour, leaving a residue of potassium sulphite,

$$C_6H_5{\cdot}SO_3K + KCN = C_6H_5{\cdot}CN + K_2SO_3.$$

The sulphonic group may also be displaced by hydrogen. This may be done by strongly heating the acids alone, or with hydrochloric acid in sealed tubes, or by passing superheated steam into the acids, or into their solution in concentrated sulphuric acid.

Sulphonic acids yield numerous derivatives, which may generally be prepared by methods similar to those used in the case of the corresponding derivatives of carboxylic acids. When, for example, a sulphonic acid (or its alkali salt) is treated with phosphorus pentachloride, the hydroxyl-group is displaced by chlorine, and a *sulphonic chloride* is obtained,

$$C_6H_5{\cdot}SO_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}SO_2Cl + POCl_3 + HCl.$$

All sulphonic acids behave in this way, and their sulphonic chlorides are of great value, not only because they are often useful in isolating and identifying the ill-characterised acids, but also because, like the chlorides of the carboxylic acids, they interact readily with many other compounds.

The sulphonic chlorides are decomposed by water and by alkalies, giving the sulphonic acids or their salts; they interact with alcohols, yielding ethereal salts, such as *ethyl benzenesulphonate*,

$$C_6H_5{\cdot}SO_2Cl + C_2H_5{\cdot}OH = C_6H_5{\cdot}SO_2{\cdot}OC_2H_5 + HCl,$$

and when shaken with concentrated ammonia they are usually converted into well-defined crystalline *sulphonamides*, which also serve for the identification of the acids,

$$\underset{\text{Benzenesulphonic Chloride.}}{C_6H_5{\cdot}SO_2Cl} + NH_3 = \underset{\text{Benzenesulphonamide.}}{C_6H_5{\cdot}SO_2{\cdot}NH_2} + HCl.$$

The isolation of sulphonic acids is very often a matter of some difficulty, because, like the sugars, they are readily soluble in water and non-volatile, and cannot be extracted from their aqueous solutions by shaking with ether, &c., or separated from other substances by steam distillation. The first step usually consists in separating them from the excess of sulphuric acid employed in their preparation; this may be done in the following manner: The aqueous solution of the product of sulphonation (see above) is boiled with excess of barium (or calcium) carbonate, filtered from the precipitated barium (or calcium) sulphate, and the filtrate—which contains the barium (or calcium) salt of the sulphonic acid—treated with sulphuric acid drop by drop as long as a precipitate is produced; after again filtering, an aqueous solution of the sulphonic acid is obtained, and on evaporating to dryness, the acid remains as a syrup or in a crystalline form. If calcium carbonate has been used, the acid will contain a little calcium sulphate, which may be got rid of by adding a little alcohol, filtering, and again evaporating.

Lead carbonate is sometimes employed instead of barium or calcium carbonate; in such cases, the filtrate from the lead sulphate is treated with hydrogen sulphide, filtered from lead sulphide, and then evaporated. These methods are, of course, only applicable provided that the barium, calcium, or lead salt of the acid is soluble in water; in other cases the separation is much more troublesome.

When two or more sulphonic acids are present in the product, they are usually separated by fractional crystallisation of their salts, after first getting rid of the sulphuric acid as just described; the alkali salts are easily prepared from the barium, calcium, or lead salts by treating the solution of the latter with the alkali carbonate as long as a precipitate is produced, filtering from the insoluble carbonate, and then evaporating.

Sometimes a complete separation cannot be accomplished with the aid of any of the salts, or the salts and the acids themselves are so badly characterised that it is difficult to make sure of their purity; in such cases the sulphonic chlorides are prepared by treating the alkali salts with phosphorus pentachloride; these compounds are soluble in ether, chloroform, &c., and generally crystallise well, so that they are easily separated and obtained in a state of purity.

Benzenesulphonic acid, $C_6H_5{\cdot}SO_3H$, is prepared by gently boiling a mixture of equal volumes of benzene and concentrated sulphuric acid for twenty to thirty hours, using a reflux condenser; it is isolated with the aid of its barium or lead salt, both of which are soluble in water. It crystallises with 1½ mols. H_2O in colourless, hygroscopic plates, and dissolves freely in alcohol; when fused with potash, it yields phenol (p. 391). *Benzenesulphonic chloride*, $C_6H_5{\cdot}SO_2Cl$, is an oil, but the *sulphonamide*, $C_6H_5{\cdot}SO_2{\cdot}NH_2$, is crystalline, and melts at 149°.

Benzene-*m*-disulphonic acid, $C_6H_4(SO_3H)_2$, is also prepared by heating the hydrocarbon with concentrated sulphuric acid, but a larger proportion (two volumes) of the acid is employed, and the solution is heated more strongly (or anhydrosulphuric acid is used); it may be isolated by means of its barium salt, and thus obtained in crystals containing 2½ mols. H_2O, but it is very hygroscopic. When fused with potash, it yields resorcinol (p. 398).

Benzene-o-disulphonic acid and the corresponding *p*-compound are of little importance.

The three (*o.m.p.*) *toluenesulphonic acids*, $C_6H_4(CH_3){\cdot}SO_3H$, are crystalline, and their barium salts are soluble in water; only the *o*- and *p*-acids are formed when toluene is dissolved in anhydrosulphuric acid.

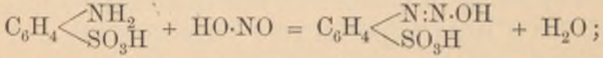
Sulphanilic acid, amidobenzene-*p*-sulphonic acid, or aniline-*p*-sulphonic acid, $C_6H_4(NH_2){\cdot}SO_3H$, is easily prepared by heating aniline sulphate at about 200° for some time.

Aniline is slowly added to a slight excess of the theoretical quantity of sulphuric acid contained in a porcelain dish, the mixture being constantly stirred as it becomes solid; the dish is then gently heated on a sand-bath, the contents being stirred, and care being taken to prevent charring. The process is at an end as soon as a small portion of the product, dissolved in water, gives no oily precipitate of aniline on adding excess of soda. After cooling, a little water is added, the sparingly soluble sulphonic acid separated by filtration, and purified by recrystallisation from boiling water, with addition of animal charcoal (see foot-note, p. 393).

Sulphanilic acid crystallises with 2 mols. H_2O, and is readily soluble in hot, but only sparingly in cold, water.

It forms salts with bases, but it does not combine with acids, the basic character of the amido-group being neutralised by the acid character of the sulphonic group; in this respect, therefore, it differs from glycine (part i. p. 292), which forms salts both with acids and bases.

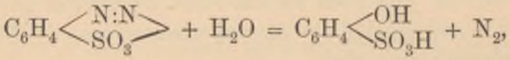
When sulphanilic acid is dissolved in dilute soda, the solution mixed with a slight excess of sodium nitrite, and poured into well-cooled, dilute sulphuric acid, *diazobenzenesulphonic acid* is formed,



$$C_6H_4{<}\begin{smallmatrix}NH_2\\SO_3H\end{smallmatrix} + HO{\cdot}NO = C_6H_4{<}\begin{smallmatrix}N{:}N{\cdot}OH\\SO_3H\end{smallmatrix} + H_2O;$$

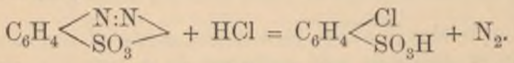
this compound, however, immediately loses water, and is converted into its anhydride,* $C_6H_4{<}\begin{smallmatrix}N{:}N\\SO_3\end{smallmatrix}{>}$, which separates from the solution in colourless crystals.

Diazobenzenesulphonic acid, or rather its anhydride, shows the characteristic properties of diazo-compounds in general; when boiled with water, it is converted into phenol-*p*-sulphonic acid (p. 395),



$$C_6H_4{<}\begin{smallmatrix}N{:}N\\SO_3\end{smallmatrix}{>} + H_2O = C_6H_4{<}\begin{smallmatrix}OH\\SO_3H\end{smallmatrix} + N_2,$$

whereas, when heated with concentrated hydrochloric or hydrobromic acid, it gives chlorobenzene- or bromobenzene-*p*-sulphonic acid,†



$$C_6H_4{<}\begin{smallmatrix}N{:}N\\SO_3\end{smallmatrix}{>} + HCl = C_6H_4{<}\begin{smallmatrix}Cl\\SO_3H\end{smallmatrix} + N_2.$$

Amidobenzene-o-sulphonic acid and the *m*-acid (*metanilic acid*) may be obtained by reducing the corresponding nitrobenzenesulphonic acids, $C_6H_4(NO_2){\cdot}SO_3H$, both of which are formed, together with the *p*-acid, on nitrating benzenesulphonic acid; they

---

* The existence of this anhydride (and of that of *amidobenzene-m-sulphonic acid*), is a very interesting fact, because, as a rule, anhydride formation takes place only between groups in the *o*-position to one another (compare p. 424).

† Many other diazo-compounds which, like diazobenzenesulphonic acid, contain some acid group, are decomposed by halogen acids in a similar manner.

resemble sulphanilic acid in properties, and are readily converted into the anhydrides of the corresponding diazobenzenesulphonic acids.

Many other sulphonic acids are described later.

CHAPTER XXVI.

PHENOLS.

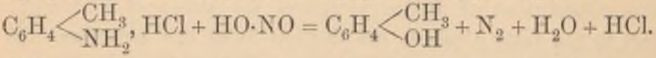
The hydroxy-compounds of the aromatic series, such as phenol or hydroxy-benzene, $C_6H_5{\cdot}OH$, the isomeric hydroxy-toluenes, $C_6H_4(CH_3){\cdot}OH$, and benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, are theoretically derived from the aromatic hydrocarbons by the substitution of hydroxyl-groups for atoms of hydrogen, just as the fatty alcohols are derived from the paraffins. It will be seen, however, from the examples just given that whereas, in benzene, hydrogen atoms of the nucleus must necessarily be displaced, in the case of toluene and all the higher homologues this is not so, since the hydroxyl-groups may displace hydrogen either of the nucleus or of the side-chain. Now the hydroxy-derivatives of benzene, and all those aromatic hydroxy-compounds, formed by the substitution of hydroxyl-groups for hydrogen atoms of the *nucleus*, differ in many respects not only from the fatty alcohols, but also from those aromatic compounds which contain the hydroxyl-group in the side-chain; it is convenient, therefore, to make some distinction between the two kinds of aromatic hydroxy-compounds, and for this reason they are classed in two groups, (*a*) the **phenols**, and (*b*) the **aromatic alcohols** (p. 402).

The **phenols**, then, are hydroxy-compounds in which the hydroxyl-groups are united directly with carbon of the nucleus; they may be subdivided into monohydric, dihydric, trihydric phenols, &c., according to the number of hydroxyl-groups which they contain. Phenol, or carbolic acid, $C_6H_5{\cdot}OH$, for example, is a monohydric phenol, as are also the three isomeric cresols or hydroxytoluenes, $C_6H_4(CH_3){\cdot}OH$; the three isomeric dihydroxybenzenes, $C_6H_4(OH)_2$, on the other hand, are dihydric phenols, whereas phloroglucinol, $C_6H_3(OH)_3$, is an example of a trihydric compound.

Many of the phenols are easily obtainable, well-known compounds; carbolic acid, for instance, is prepared from coal-tar in large quantities; carvacrol and thymol occur in various plants, and catechol, pyrogallol, &c., may be obtained by the dry distillation of certain vegetable products.

Preparation.—Phenols may be prepared by treating salts of amido-compounds with nitrous acid in aqueous solution, and then heating until nitrogen ceases to be evolved,

$$C_6H_5{\cdot}NH_2,HCl + HO{\cdot}NO = C_6H_5{\cdot}OH + N_2 + H_2O + HCl$$



$$C_6H_4{<}^{CH_3}_{NH_2}, HCl + HO{\cdot}NO = C_6H_4{<}^{CH_3}_{OH} + N_2 + H_2O + HCl.$$

It is possible, therefore, to prepare phenols, not only from the amido-compounds themselves, but also indirectly from the corresponding nitro-derivatives and from the hydrocarbons, since these substances may be converted into amido-compounds,

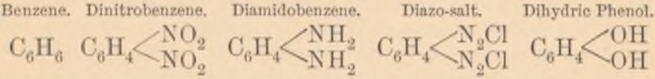
Benzene.	Nitrobenzene.	Amidobenzene.	Phenol.
C_6H_6	$C_6H_5{\cdot}NO_2$	$C_6H_5{\cdot}NH_2$	$C_6H_5{\cdot}OH.$

The conversion of an amido-compound into a phenol really takes place in two stages, as already explained (p. 370); at ordinary temperatures the salt of the amido-compound is transformed into a salt of a diazo-compound, but on heating its aqueous solution, the latter decomposes, yielding a phenol,

$$C_6H_5{\cdot}NH_2, HCl + HCl + KNO_2 = C_6H_5{\cdot}N{:}NCl + KCl + 2H_2O$$
$$C_6H_5{\cdot}N{:}NCl + H_2O = C_6H_5{\cdot}OH + HCl + N_2.$$

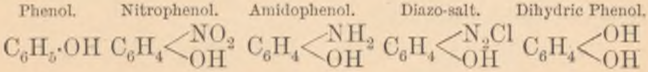
The amido-compound, aniline, for example, is dissolved in moderately dilute hydrochloric acid (2 mols.), or sulphuric acid (1 mol.), the solution is cooled in ice or water, and an aqueous solution of sodium nitrite (1 mol.) is slowly added, stirring constantly. The mixture is then gradually heated to boiling on a reflux condenser, until the evolution of nitrogen (which at first causes brisk effervescence) is at an end, and the diazo-salt is completely decomposed; the phenol is afterwards separated from the tarry matter, which is almost invariably produced, either by distillation in steam, by crystallisation from hot water, or by extraction with ether; in the last case the ethereal solution is usually shaken with soda, which dissolves out the phenol, leaving most of the impurities in the ether.

Dihydric phenols may sometimes be prepared from the corresponding di-substitution products of the hydrocarbon, as indicated by the following series of changes:



$$C_6H_6 \quad C_6H_4<^{NO_2}_{NO_2} \quad C_6H_4<^{NH_2}_{NH_2} \quad C_6H_4<^{N_2Cl}_{N_2Cl} \quad C_6H_4<^{OH}_{OH}$$

They may also be obtained from the monohydric compounds in the following manner:

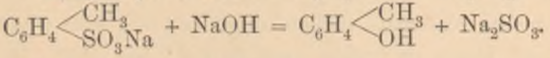


$$C_6H_5{\cdot}OH \quad C_6H_4<^{NO_2}_{OH} \quad C_6H_4<^{NH_2}_{OH} \quad C_6H_4<^{N_2Cl}_{OH} \quad C_6H_4<^{OH}_{OH}$$

These two methods, however, are limited in their application, because *o*- and *m*-diamido-compounds cannot always be converted into the corresponding diazo-salts, but more often yield products of quite a different nature; *o*- and *p*-amido-hydroxy-compounds also show an abnormal behaviour with nitrous acid, the former not being acted on at all, the latter only with difficulty. For these reasons dihydric phenols are usually most conveniently prepared by the methods given later.

Another important general method of preparing phenols consists in fusing sulphonic acids or their salts with potash or soda; in this case, also, their preparation from the hydrocarbons is often easily accomplished, since the latter are usually converted into sulphonic acids without difficulty,

$$C_6H_5{\cdot}SO_3K + KOH = C_6H_5{\cdot}OH^* + K_2SO_3$$



$$C_6H_4<^{CH_3}_{SO_3Na} + NaOH = C_6H_4<^{CH_3}_{OH} + Na_2SO_3.$$

The sulphonic acid or its alkali salt is placed in an iron, or, better,

---

* In all cases the phenols are present in the product as alkali salts.

nickel or silver dish,* together with excess of solid potash (or soda), and a little water, and the dish is heated over a free flame, the mixture being constantly stirred with a nickel or silver spatula, or with a thermometer, the bulb of which is encased in a glass tube, or covered with silver by electro-deposition; after the potash and the salt have dissolved, the temperature is slowly raised, during which process the mixture usually undergoes a variety of changes in colour, by which an experienced operator can tell when the decomposition of the sulphonic acid is complete; as a rule, a temperature considerably above 200° is required, so that simply boiling the sulphonic acid with concentrated potash does not bring about the desired change. When the operation is finished, the fused mass is allowed to cool, dissolved in water, the solution acidified with dilute sulphuric acid, and the liberated phenol extracted with ether, or isolated in some other manner.

Dihydric phenols may often be obtained in a similar manner from the disulphonic acids,

$$C_6H_4(SO_3K)_2 + 2KOH = C_6H_4(OH)_2 + 2K_2SO_3.$$

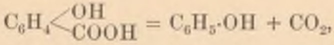
Owing to the high temperature at which these reactions must be carried out, secondary changes very often occur. When the sulphonic acid contains halogen atoms, the latter are usually displaced by hydroxyl-groups, especially if other acid radicles, such as $-NO_2$, or $-SO_3H$, are also present; when, for example, chlorobenzenesulphonic acid, $C_6H_4Cl{\cdot}SO_3H$, is fused with potash, a dihydric phenol, $C_6H_4(OH)_2$, is produced, the halogen as well as the sulphonic group being eliminated. For this reason also, compounds such as *o*- and *p*-chloronitrobenzene may be converted into the corresponding nitrophenols (p. 392), even by boiling them with concentrated potash, the presence of the nitro-group facilitating the displacement of the halogen atom; *m*-chloronitrobenzene, on the other hand, is not acted on under these conditions. Sometimes also the process is not one of direct substitution only —that is to say, the hydroxyl-groups in the product are not united with the same carbon atoms as those with which the displaced atoms or groups were united; the three (*o.m.p.*)

---

* Caustic alkalies readily attack platinum and porcelain at high temperatures, but have little action on nickel and none on silver.

bromobenzenesulphonic acids, for example, all yield one and the same dihydric phenol—namely, the *m*-compound, resorcinol, $C_6H_4(OH)_2$, because the *o*- and *p*-dihydric compounds, which are first produced from the corresponding bromosulphonic acids, are converted into the more stable *m*-derivative by intramolecular change.

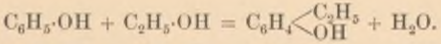
There are several other less important methods by which phenols may be obtained, as, for example, by distilling hydroxy-acids, such as salicylic acid, with lime,



$$C_6H_4{<}\begin{matrix}OH\\COOH\end{matrix} = C_6H_5{\cdot}OH + CO_2,$$

a reaction which is similar to that which occurs in preparing the hydrocarbons from the acids.

Also by heating other phenols with fatty alcohols in presence of zinc chloride, when the alkyl-group displaces hydrogen of the nucleus, just as in the production of toluidine, &c., from aniline (p. 357),



$$C_6H_5{\cdot}OH + C_2H_5{\cdot}OH = C_6H_4{<}\begin{matrix}C_2H_5\\OH\end{matrix} + H_2O.$$

Properties.—Most phenols are colourless, crystalline substances, readily soluble in alcohol and ether; their solubility in water usually increases with the number of hydroxyl-groups in the molecules, phenol and cresol, for example, being sparingly soluble, whereas the three dihydric phenols and the trihydric compounds are readily soluble. Conversely, their volatility diminishes, so that although phenol and cresol distil without decomposition, and are readily volatile in steam, the trihydric phenols usually undergo decomposition, and volatilise very slowly in steam. Alcoholic and aqueous solutions of phenols (and of their carboxylic acids) give a violet, blue, or green colouration with ferric salts, the particular colouration depending, in the case of the di- and poly-hydric compounds, on the relative positions of the hydroxyl-groups.

o-Dihydroxy-compounds, for example, give with ferric chloride a *green* colouration, which first becomes violet and then bright-red on addition of sodium bicarbonate; *m*-dihydroxy-compounds give a deep *violet* colouration;

p-dihydroxy-compounds give a green colouration, which immediately changes to yellow owing to the formation of a quinone (p. 413).

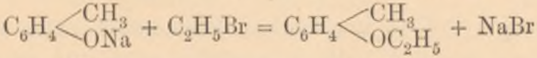
All phenols give Liebermann's reaction; when dissolved in concentrated sulphuric acid and treated with a nitroso-compound or a nitrite, they yield coloured solutions, which, after diluting and adding excess of alkali, assume an intense blue or green colour. This reaction, therefore, affords a convenient test for phenols as well as for nitroso-compounds (part i. p. 204).

Although phenols resemble the fatty alcohols and the alcohols of the aromatic series in some respects, they have, on the whole, very little in common with these substances. The reason of this is, that the character of the hydroxyl-group (like that of the amido-group, p. 359) is greatly modified by its union with carbon of the benzene nucleus, just as that of the hydroxyl-group in water is altered by combination with acid-forming atoms or radicles such as Cl–, NO_2–, &c., as, for example, in HOCl and $HO \cdot NO_2$; in other words, the phenolic hydroxyl-group has a much more pronounced acid character than that in alcohols, a fact which shows that the radicles *phenyl*, C_6H_5–, *phenylene*, $C_6H_4<$, &c., are acid-forming radicles.

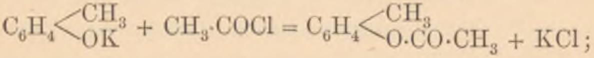
The acid character of the hydroxyl-group in phenols is shown in their behaviour with caustic alkalies, in which they dissolve freely, forming metallic derivatives or salts, such as *sodium phenate*, $C_6H_5 \cdot ONa$, *potassium cresate*, $C_6H_4(CH_3) \cdot OK$; these compounds, unlike the alkali derivatives of the alcohols, are stable in presence of water, but are decomposed by carbon dioxide and by all other acids, with regeneration of the phenols. For this reason phenols are insoluble in alkali carbonates unless they contain other acid-forming groups or atoms, as, for example, in nitrophenol, $C_6H_4(NO_2) \cdot OH$, and picric acid, $C_6H_2(NO_2)_3 \cdot OH$, when their acid character is often enhanced to such an extent that they decompose alkali carbonates.

The metallic derivatives of the phenols, like those of the alcohols, interact with alkyl halogen compounds and with acid chlorides, yielding substances analogous to the ethers and ethereal salts respectively,

$$C_6H_5{\cdot}OK + CH_3I = C_6H_5{\cdot}O{\cdot}CH_3 + KI$$

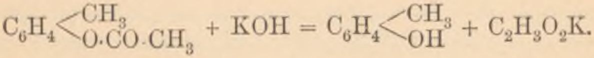


$$C_6H_4{<}\begin{matrix}CH_3\\ONa\end{matrix} + C_2H_5Br = C_6H_4{<}\begin{matrix}CH_3\\OC_2H_5\end{matrix} + NaBr$$



$$C_6H_4{<}\begin{matrix}CH_3\\OK\end{matrix} + CH_3{\cdot}COCl = C_6H_4{<}\begin{matrix}CH_3\\O{\cdot}CO{\cdot}CH_3\end{matrix} + KCl;$$

the former, like the ethers, are not decomposed by boiling alkalies, but the latter readily undergo hydrolysis, just as do the ethereal salts,



$$C_6H_4{<}\begin{matrix}CH_3\\O{\cdot}CO{\cdot}CH_3\end{matrix} + KOH = C_6H_4{<}\begin{matrix}CH_3\\OH\end{matrix} + C_2H_3O_2K.$$

Towards pentachloride and pentabromide of phosphorus, and towards acetic anhydride and acetyl chloride, phenols behave in the same way as the alcohols, as shown by the following equations:

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$
$$C_6H_5{\cdot}OH + (CH_3{\cdot}CO)_2O = C_6H_5{\cdot}O{\cdot}CO{\cdot}CH_3 + C_2H_4O_2.$$

Heating with halogen acids, however, does not change the phenols to any appreciable extent, because, being less basic in character than the alcohols, they do not so readily form salts with mineral acids.

The constitution of a phenol being quite different from that of a primary or secondary alcohol, the fact that they do not yield aldehydes or ketones on oxidation was only to be expected; they are, however, somewhat similar in constitution to the *tertiary* alcohols, and like the latter, they often undergo complex changes on oxidation.

Monohydric Phenols.

Phenol, *carbolic acid*, or hydroxybenzene, $C_6H_5{\cdot}OH$, occurs in very small quantities in human urine and also in that of cows; it may be obtained from benzene, nitrobenzene, aniline, diazobenzene chloride, benzenesulphonic acid, and salicylic acid (p. 437) by the methods already given, but the whole of the phenol of commerce is prepared from coal-tar (compare p. 297), in which it was discovered by Runge in 1834.

Phenol crystallises in colourless, deliquescent prisms, which melt at 42° and turn pink on exposure to air and light; it boils at 183°, and is volatile in steam. It has a very characteristic smell, is highly poisonous, and has a strong caustic action on the skin, quickly causing blisters. It dissolves freely in most organic liquids, but is only sparingly soluble (1 part in about 15) in cold water; its aqueous solution gives a violet colouration with ferric chloride, and a pale-yellow precipitate of *tribromophenol*, $C_6H_2Br_3{\cdot}OH$, with bromine water; both these reactions may serve for the detection of phenol. Owing to its poisonous and antiseptic properties, phenol is extensively used as a disinfectant; it is also employed in large quantities for the manufacture of picric acid. *Potassium phenate*, $C_6H_5{\cdot}OK$, is obtained when phenol is dissolved in potash and the solution evaporated; it is a crystalline substance, readily soluble in water, and is decomposed by carbon dioxide with separation of phenol.

Phenyl methyl ether, or *anisole*, $C_6H_5{\cdot}O{\cdot}CH_3$, may be prepared by heating potassium phenate with methyl iodide; it is a colourless liquid, boiling at 155°, and is similar to the ethers of the fatty series in chemical properties, although it also shows the usual behaviour of aromatic compounds, and readily yields nitro-derivatives, &c. When warmed with concentrated hydriodic acid, it yields phenol and methyl iodide,

$$C_6H_5{\cdot}O{\cdot}CH_3 + HI = C_6H_5{\cdot}OH + CH_3I.$$

Phenyl ethyl ether, or *phenetole*, $C_6H_5{\cdot}O{\cdot}C_2H_5$, can be obtained in a similar manner; it boils at 172°.

Nitrophenols, $C_6H_4(NO_2){\cdot}OH$, are formed very readily on treating phenol even with dilute nitric acid, the presence of the hydroxyl-group not only facilitating the introduction of the nitro-group, but also determining the position taken up by the latter. When phenol is gradually added to nitric acid of sp. gr. 1·11 (6 parts), the mixture being kept cold and frequently shaken, it is converted into a mixture of *o*- and *p*-nitrophenol, which separates as a dark-brown oil or resinous mass; this product is allowed to settle, washed with water by decantation, and then submitted to distillation in steam, whereupon the *ortho-nitrophenol* passes over as a yellow oil, which crystallises on cooling; the oily residue in the flask is mixed with a little more water, the mixture heated to boiling, and the hot solution filtered from tarry matter, the *para-nitrophenol* which separates on cooling being purified by recrystallisation from boiling water with addition of animal charcoal.* *Meta-nitrophenol* is prepared by reducing meta-dinitrobenzene to meta-nitraniline (p. 363), and treating a solution of the latter in excess of dilute sulphuric acid with nitrous acid; the solution of the diazo-salt is then slowly heated to boiling, and the meta-nitrophenol thus produced purified by recrystallisation from water.

The melting-points of the three compounds are:

Ortho-nitrophenol,	Meta-nitrophenol,	Para-nitrophenol,
45°.	96°.	114°.

The *o*- and the *m*-compounds are yellow, but the *p*-derivative is colourless; only the *o*-compound is volatile in steam. The three compounds are all sparingly soluble in cold water, but dissolve freely in alkalies and also in alkali carbonates, forming

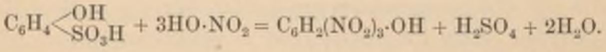
---

* Animal charcoal is prepared by strongly heating blood or bones out of contact with air; it is frequently used in the purification of organic compounds, as it has the property of absorbing coloured impurities from solutions. For this purpose the dark-coloured, impure substance is dissolved in water, ether, alcohol, benzene, or some other solvent, a small quantity of animal charcoal added, and the mixture heated for some time with reflux condenser (part i. p. 186); on subsequently filtering, a colourless or a much lighter coloured solution is usually obtained. Before use, the charcoal should be repeatedly extracted with boiling hydrochloric acid, washed well, dried, and heated strongly in a porcelain crucible closed with a lid.

dark-yellow or red salts which are not decomposed by carbon dioxide; they have, therefore, a more marked acid character than phenol itself, the presence of the nitro-group having an effect comparable to that of the nitro-group in nitric acid, $HO{\cdot}NO_2$.

Picric acid, or trinitrophenol, $C_6H_2(NO_2)_3{\cdot}OH$, is formed when substances such as wool, silk, leather, and resins are heated with concentrated nitric acid, very complex reactions taking place; it may be obtained by heating phenol, or the *o*- and *p*-nitrophenols, with nitric acid, but the product is not very easily purified from resinous substances which are formed at the same time. For this reason picric acid is best prepared by dissolving phenol (1 part) in an equal weight of concentrated sulphuric acid, and adding this solution to nitric acid of sp. gr. 1·4 (3 parts) in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water-bath for about two hours. On cooling, the product solidifies to a mass of crystals, which are collected, washed, and recrystallised from hot water.

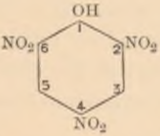
When phenol is dissolved in sulphuric acid, it is converted into a mixture of *o*- and *p*-phenolsulphonic acids, $C_6H_4(OH){\cdot}SO_3H$ (see below); on subsequent treatment with nitric acid, the sulphonic group, as well as two atoms of hydrogen, are displaced by nitro-groups,



$$C_6H_4{<}^{OH}_{SO_3H} + 3HO{\cdot}NO_2 = C_6H_2(NO_2)_3{\cdot}OH + H_2SO_4 + 2H_2O.$$

Picric acid is a yellow crystalline compound, melting at 122·5°. It is only very sparingly soluble in cold, but moderately easily in hot, water, and its solutions dye silk and wool (not cotton, p. 502) a beautiful yellow colour; it is, in fact, one of the earliest known artificial organic dyes. It has very marked acid properties, and readily decomposes carbonates. The *potassium* derivative, $C_6H_2(NO_2)_3{\cdot}OK$, and the *sodium* derivative, $C_6H_2(NO_2)_3{\cdot}ONa$, are yellow crystalline compounds, the former being sparingly, the latter readily soluble in cold water. These compounds, and also the ammonium derivative, explode violently on percussion or when heated, and are employed in the preparation of explosives; picric acid itself burns quietly when ignited, but can be caused to explode violently with a detonator.

Picric acid may be produced by oxidising symmetrical trinitrobenzene, $C_6H_3(NO_2)_3$, with potassium ferricyanide, the presence of the nitro-groups facilitating the substitution of hydroxyl for hydrogen; as, moreover, it is quite immaterial which of the three hydrogen atoms is displaced, since they all occupy a similar position relatively to the rest of the molecule, the constitution of picric acid must be represented by the formula

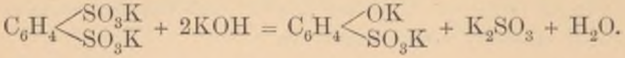


or, for the sake of convenience, the relative positions of the several groups may be indicated in this way $[\overset{1}{OH} : \overset{2}{NO_2} : \overset{4}{NO_2} : \overset{6}{NO_2}]$; it would, of course, be just the same if the groups were numbered $[\overset{1}{NO_2} : \overset{2}{OH} : \overset{3}{NO_2} : \overset{5}{NO_2}]$ or $[\overset{1}{NO_2} : \overset{3}{NO_2} : \overset{4}{OH} : \overset{5}{NO_2}]$, since the relative positions are the same in the three cases, and it is of no consequence at which carbon atom the numbering commences.

Picric acid has the curious property of forming crystalline compounds with benzene, naphthalene, anthracene, and many other hydrocarbons, so that it is sometimes used in detecting and also in purifying small quantities of the substances in question; the compound which it forms with benzene, for example, crystallises in yellow needles, is decomposed by water, and has the composition $C_6H_2(NO_2)_3{\cdot}OH,\ C_6H_6$.

Phenol-o-sulphonic acid, $C_6H_4(OH){\cdot}SO_3H$, is formed, together with a comparatively small quantity of the *p*-acid, when a solution of phenol in concentrated sulphuric acid is kept for some time at ordinary temperatures; if, however, the solution be heated at 100–110°, the *o*-acid, which is the primary product, is gradually converted into *phenol-p-sulphonic acid*.

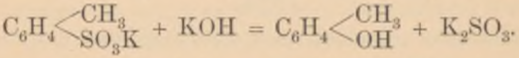
Phenol-m-sulphonic acid is prepared by carefully heating benzene-*m*-disulphonic acid with potash at 170–180°; under these conditions only one of the sulphonic groups is displaced,



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{SO_3K}\\ \mathrm{SO_3K}\end{matrix} + \mathrm{2KOH} = \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{OK}\\ \mathrm{SO_3K}\end{matrix} + \mathrm{K_2SO_3} + \mathrm{H_2O}.$$

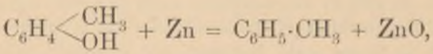
The *o*-acid is interesting on account of the fact that it is converted into the *p*-acid when boiled with water, and also because it is used as an antiseptic under the name *aseptol.*

The three (*o.m.p.*) **cresols** or hydroxytoluenes, $C_6H_4(CH_3){\cdot}OH$, the next homologues of phenol, occur in coal-tar, but cannot be conveniently isolated from this source owing to the difficulty of separating them from one another; they are prepared from the corresponding toluidines or amidotoluenes, $C_6H_4(CH_3){\cdot}NH_2$, by means of the diazo-reaction, or by fusing the corresponding toluenesulphonic acids with potash,



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CH_3}\\ \mathrm{SO_3K}\end{matrix} + \mathrm{KOH} = \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CH_3}\\ \mathrm{OH}\end{matrix} + \mathrm{K_2SO_3}.$$

They resemble phenol in most ordinary properties, as, for example, in being sparingly soluble in water, and in forming potassium and sodium derivatives, which are decomposed by carbon dioxide; they also yield alkyl-derivatives, &c., by the displacement of the hydrogen of the hydroxyl-group. On distillation with zinc-dust they are all converted into toluene,



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CH_3}\\ \mathrm{OH}\end{matrix} + \mathrm{Zn} = \mathrm{C_6H_5{\cdot}CH_3} + \mathrm{ZnO},$$

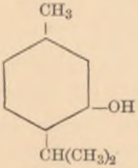
and they all give a bluish colouration with ferric chloride.

One very curious fact regarding the three cresols is that they are not oxidised by chromic acid, although toluene, as already stated, is slowly converted into benzoic acid; the presence of the hydroxyl-group, therefore, protects the methyl-group from the attack of acid oxidising agents, and this is true also in the case of other phenols of similar constitution. If, however, the hydrogen of the hydroxyl-group be displaced by an alkyl, or by an acid group such as acetyl, then the protection is withdrawn, and the methyl-group is converted into the carboxyl-group in the usual manner; the *methylcresols*, $C_6H_4(OCH_3)\cdot CH_3$, for example, are oxidised by chromic acid, yielding the corresponding methoxybenzoic acids, $C_6H_4(OCH_3)\cdot COOH$.

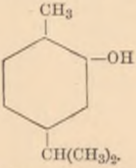
The melting and boiling points of the three cresols are given below:

	Ortho-cresol.	Meta-cresol.	Para-cresol.
M.p.	31°	5°	36°
B.p.	188°	201°	198°

Of the higher monohydric phenols, **thymol** and **carvacrol** may be mentioned; these two compounds are isomeric monohydroxy-derivatives of cymene, $C_6H_4(CH_3)\cdot C_3H_7$ (p. 339), and their constitutions are respectively represented by the formulæ

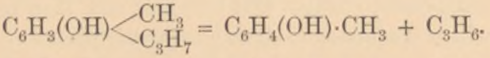


Thymol.



Carvacrol.

Thymol occurs in oil of thyme, together with cymene; it crystallises in large plates, melts at 51·5°, and has a characteristic smell like that of thyme. It is only very sparingly soluble in water, and does not give a colouration with ferric chloride; when heated with phosphoric anhydride, it yields propylene and *m*-cresol,



$$C_6H_3(OH){<}\begin{matrix}CH_3\\C_3H_7\end{matrix} = C_6H_4(OH)\cdot CH_3 + C_3H_6.$$

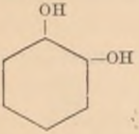
Carvacrol occurs in the oil of *Origanum hirtum*, and is easily prepared by heating camphor with iodine,

$$C_{10}H_{16}O + I_2 = C_{10}H_{14}O + 2HI;$$

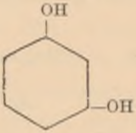
it is an oil boiling at 237°, and its alcoholic solution gives a green colouration with ferric chloride. When heated with phosphoric anhydride, it is decomposed into propylene and *o*-cresol.

Dihydric Phenols.

The isomeric dihydric phenols—catechol, resorcinol, and hydroquinone—are well-known compounds of considerable importance, and are respectively represented by the formulæ



Catechol,
or
Ortho-dihydroxybenzene.



Resorcinol,
or
Meta-dihydroxybenzene.

Hydroquinone,
or
Para-dihydroxybenzene.

Catechol, or pyrocatechin, $C_6H_4(OH)_2$, occurs in *catechu*, a substance obtained in India from *Acacia catechu* and other trees, and was first obtained by the dry distillation of this vegetable product; it may be obtained by fusing phenol-*o*-sulphonic acid, $C_6H_4(OH){\cdot}SO_3H$, with potash, but is most conveniently prepared by heating *guaiacol* or *methylcatechol* (a colourless liquid, boiling at 200°, obtained from the tar of beechwood), with concentrated hydriodic acid,

$$C_6H_4{<}\begin{matrix}OCH_3\\OH\end{matrix} + HI = C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} + CH_3I.$$

It is a colourless, crystalline substance, melting at 104°, and is readily soluble in water; its aqueous solution gives, with ferric chloride, a *green* colouration, which, on the addition of sodium bicarbonate, changes first to violet and then to red, a reaction which is common to all *ortho*-dihydric phenols (p. 389). Guaiacol shows a similar behaviour with ferric chloride, but when the hydrogen atoms of both the hydroxyl-groups are displaced, as, for example, in *dimethylcatechol* or *veratrol*, $C_6H_4(OCH_3)_2$, there is no colouration.

Resorcinol, $C_6H_4(OH)_2$, is prepared on a large scale by fusing benzene-*m*-disulphonic acid with potash,

$$C_6H_4{<}\begin{matrix}SO_3K\\SO_3K\end{matrix} + 2KOH = C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} + 2K_2SO_3,$$

but it is also obtained when the para-disulphonic acid, and many other ortho- and para-derivatives of benzene are treated in the same way, owing to intramolecular change taking place (compare p. 388). It is a crystalline substance, melting at 110°, and dissolves freely in water, alcohol, and ether; its aqueous solution gives a dark-violet colouration, with ferric chloride and a crystalline precipitate of *tribromoresorcinol*, $C_6HBr_3(OH)_2$, with bromine water. When resorcinol is strongly heated for a few minutes with phthalic anhydride (p. 426), or with the anhydride of some other dicarboxylic acid (succinic anhydride, for example), and the yellowish-red mass then dissolved in dilute soda, a yellowish-brown solution, which shows a beautiful green fluorescence, is obtained; this phenomenon is due to the formation of a *fluoresceïn* (p. 520). Other *m*-dihydric phenols give this *fluoresceïn reaction*, which, therefore, affords a convenient and very delicate test for such compounds; the fluoresceïn reaction may also be employed as a test for anhydrides of *dicarboxylic acids*.

Resorcinol is used in large quantities in preparing fluoresceïn, eosin, and azo-dyes.

Hydroquinone, or quinol, $C_6H_4(OH)_2$, is formed, together with glucose, when the glucoside, *arbutin*—a substance which occurs in the leaves of the bear-berry—is boiled with water,

$$C_{12}H_{16}O_7 + H_2O = C_6H_4(OH)_2 + C_6H_{12}O_6.$$

It is usually prepared by reducing quinone (p. 413) with sulphurous acid in aqueous solution, and then extracting with ether,

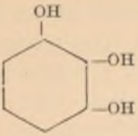
$$C_6H_4O_2 + H_2SO_3 + H_2O = C_6H_4(OH)_2 + H_2SO_4.$$

It melts at 169°, is readily soluble in water, and when treated with ferric chloride or other mild oxidising agents, it is converted into quinone,

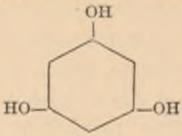
$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Trihydric Phenols.

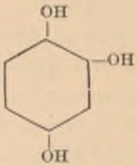
The three trihydric phenols, $C_6H_3(OH)_3$, which should exist in accordance with theory, are all known, and are respectively represented by the following formulæ:



Pyrogallol,
1:2:3-Trihydroxybenzene.



Phloroglucinol,
1:3:5-Trihydroxybenzene.



Hydroxyhydroquinone
1:2:4-Trihydroxybenzene.

Pyrogallol, $C_6H_3(OH)_3$, sometimes called pyrogallic acid, is prepared by heating gallic acid (p. 439) alone or with glycerol, at about 210°, until the evolution of carbon dioxide ceases,

$$C_6H_2(OH)_3 \cdot COOH = C_6H_3(OH)_3 + CO_2.$$

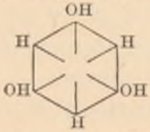
It is a colourless, crystalline substance, melting at 115°, and is readily soluble in water, but more sparingly in alcohol and ether (the effect of hydroxyl-groups); its aqueous solution gives, with ferric chloride, a red, and with ferrous sulphate containing a trace of ferric chloride, a deep, dark-blue colouration. It dissolves freely in alkalies, giving solutions which rapidly absorb oxygen and turn black on exposure to the air, a fact which is made use of in gas analysis for the estimation of oxygen. Pyrogallol has powerful reducing properties, and precipitates gold, silver, and mercury from solutions of their salts, being itself oxidised to oxalic and acetic acids; many other phenols, such as catechol, resorcinol, and hydroquinone, show a similar behaviour, especially in alkaline solution, but the monohydric-compounds are much less readily oxidised, and consequently do not exhibit reducing properties. Pyrogallol and hydroquinone are used in photography as developers.

Like glycerol and other trihydric-compounds, pyrogallol forms mono-, di-, and tri-alkyl-derivatives, such as $C_6H_3(OH)_2 \cdot OC_2H_5$, $C_6H_3(OH)(OC_2H_5)_2$, and $C_6H_3(OC_2H_5)_3$; the *dimethyl*-derivative, $C_6H_3(OCH_3)_2 \cdot OH$, occurs in beechwood tar.

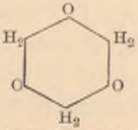
Phloroglucinol, or symmetrical trihydroxybenzene, $C_6H_3(OH)_3$, is produced when phenol, resorcinol, and many resinous substances, such as gamboge, dragon's-blood, &c., are fused with potash.

It is best prepared by fusing resorcinol (1 part) with soda (6 parts) for about twenty-five minutes, or until the vigorous evolution of hydrogen has ceased; the chocolate-coloured melt is dissolved in water, acidified with sulphuric acid, extracted with ether, the ethereal extract evaporated, and the residue recrystallised from water.

It crystallises in colourless prisms, melts at about 218°, and is very soluble in water; the solution, which has a sweet taste, gives, with ferric chloride, a bluish-violet colouration, and when mixed with potash, it rapidly turns brown in contact with air owing to absorption of oxygen. When digested with acetyl chloride, phloroglucinol yields a *triacetate*, $C_6H_3(C_2H_3O_2)_3$ melting at 106°, and in many other reactions it shows properties in harmony with the formula



On the other hand, when treated with hydroxylamine, it gives a *trioxime*, $C_6H_6(N\cdot OH)_3$, and in this and other respects it behaves as though it were a triketone of the constitution



Possibly, therefore, phloroglucinol is capable of existing in two forms, which are convertible, the one into the other, by intramolecular change (part i. p. 195).

Hydroxyhydroquinone, or trihydroxybenzene, (1:2:4), is formed when hydroquinone is fused with potash. It melts at 140°, and is very soluble in water, but its aqueous solution is coloured greenish-brown by ferric chloride, but on the addition of sodium carbonate the colour changes to blue and then to red (p. 389).

CHAPTER XXVII.

AROMATIC ALCOHOLS, ALDEHYDES, KETONES, AND QUINONES.

Alcohols.

The aromatic alcohols are derived from the hydrocarbons by substituting hydroxy-groups for hydrogen atoms of the *side-chain;* benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, for example, is derived from toluene, tolyl alcohol, $C_6H_4(CH_3){\cdot}CH_2{\cdot}OH$, from xylene, and so on. The compounds of this kind have not been very fully investigated, but from what is known of their properties, it is clear that they are very closely related to the alcohols of the fatty series, although, of course, they show at the same time the general behaviour of aromatic substances.

They may be prepared by methods exactly analogous to those employed in the case of the fatty alcohols—namely, by heating the corresponding halogen derivatives with water, weak alkalies, or silver hydroxide,

$$C_6H_5{\cdot}CH_2Cl + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + HCl,$$

and by reducing the corresponding aldehydes and ketones,

$$C_6H_5{\cdot}CH_2{\cdot}CHO + 2H = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$
$$C_6H_5{\cdot}CO{\cdot}CH_3 + 2H = C_6H_5{\cdot}CH(OH){\cdot}CH_3.$$

Those compounds which, like benzyl alcohol, contain the carbinol group, $-CH_2{\cdot}OH$, directly united with the benzene nucleus, may also be prepared by treating the corresponding aldehydes with potash (compare p. 408),

$$2C_6H_5{\cdot}CHO + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}COOH.$$

The aromatic alcohols are usually colourless liquids or solids, sparingly soluble in water; their behaviour with alkali metals, phosphorus pentachloride, and acids, is similar to that of the fatty compounds, as will be seen from a consideration of the properties of benzyl alcohol, one of the few well-known aromatic alcohols.

Benzyl alcohol, phenylcarbinol, or hydroxytoluene, $C_6H_5{\cdot}CH_2{\cdot}OH$, an isomeride of the three cresols (p. 396), occurs in storax (a resin obtained from the tree *Styrax officinalis*), and also in balsam of Peru and balsam of Tolu, either in the free state or as ethereal salts in combination with cinnamic and benzoic acids.

It may be obtained by reducing benzaldehyde (p. 405) with sodium amalgam,

$$C_6H_5{\cdot}CHO + 2H = C_6H_5{\cdot}CH_2{\cdot}OH,$$

and by boiling benzyl chloride with a solution of sodium carbonate,

$$C_6H_5{\cdot}CH_2Cl + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + HCl;$$

but it is most conveniently prepared by treating benzaldehyde with cold potash,

$$2C_6H_5{\cdot}CHO + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}COOH.$$

The aldehyde (10 parts) is shaken with a solution of potash (9 parts) in water (10 parts) until the whole forms an emulsion, which is then allowed to stand for twenty-four hours; after adding water to dissolve the potassium benzoate, the solution is extracted with ether, the ethereal extract evaporated, and the benzyl alcohol purified by distillation.

Benzyl alcohol is a colourless liquid, boiling at 206°; it is only sparingly soluble in water, but miscible with alcohol, ether, &c., in all proportions. It dissolves sodium and potassium with evolution of hydrogen, yielding metallic derivatives which are decomposed by water, and, when treated with phosphorus pentachloride, it is converted into benzyl chloride,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl.$$

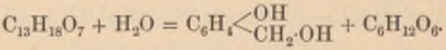
When heated with concentrated acids, or treated with anhydrides or acid chlorides, it gives ethereal salts; with hydrobromic acid, for example, it yields *benzyl bromide*, $C_6H_5{\cdot}CH_2Br$ (b.p. 199°), and with acetyl chloride or acetic anhydride it gives *benzyl acetate*, $C_6H_5{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$ (b.p.

206°). On oxidation with dilute nitric acid, it is first converted into benzaldehyde and then into benzoic acid,

$$C_6H_5\cdot CH_2\cdot OH + O = C_6H_5\cdot CHO + H_2O$$
$$C_6H_5\cdot CH_2\cdot OH + 2O = C_6H_5\cdot COOH + H_2O.$$

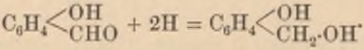
All these changes are strictly analogous to those undergone by the fatty alcohols.

Saligenin, $C_6H_4(OH)\cdot CH_2\cdot OH$, also known as *o*-hydroxybenzyl alcohol, or salicyl alcohol, is an example of a substance which is both a phenol and an alcohol. It is produced by the action of dilute acids or ferments on *salicin* (a glucoside existing in the bark of the willow-tree), which breaks up into saligenin and dextrose,



$$C_{13}H_{18}O_7 + H_2O = C_6H_4\left<\begin{matrix}OH\\ CH_2\cdot OH\end{matrix}\right. + C_6H_{12}O_6.$$

Synthetically, it may be prepared by reducing salicylaldehyde (p. 409) with sodium amalgam,

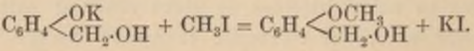


$$C_6H_4\left<\begin{matrix}OH\\ CHO\end{matrix}\right. + 2H = C_6H_4\left<\begin{matrix}OH\\ CH_2\cdot OH\end{matrix}\right..$$

Saligenin is a crystalline substance which melts at 82°, and is readily soluble in water, the solution acquiring a deep blue colouration on the addition of ferric chloride. Owing to its phenolic nature, it forms alkali salts, which, when heated with alkyl halogen compounds, give the corresponding ethers (the *methyl ether*, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$, is a colourless oil, boiling at 247°); on the other hand, it shows the properties of an alcohol, and yields salicylaldehyde and salicylic acid on oxidation.

The *m*- and *p-hydroxybenzyl alcohols* may be prepared by the reduction of the *m*- and *p*-hydroxybenzaldehydes (p. 410); they are colourless, crystalline substances, which melt at 67° and 110° respectively.

Anisyl alcohol, or *p*-methoxybenzyl alcohol, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$, is obtained by treating anisaldehyde, $C_6H_4(OCH_3)\cdot CHO$ (p. 410), with sodium amalgam or with alcoholic potash. Synthetically, it has been prepared by heating a mixture of *p*-hydroxybenzyl alcohol, potash, and methyl iodide in alcoholic solution at 100°,



$$C_6H_4\left<\begin{matrix}OK\\ CH_2\cdot OH\end{matrix}\right. + CH_3I = C_6H_4\left<\begin{matrix}OCH_3\\ CH_2\cdot OH\end{matrix}\right. + KI.$$

It is a crystalline solid, which melts at 25° and boils at 258°; on oxidation, it yields anisaldehyde and anisic acid, $C_6H_4(OCH_3)\cdot COOH$.

Aldehydes.

The relation between the aromatic aldehydes and the aromatic alcohols is the same as that which exists between the corresponding classes of fatty compounds—that is to say, the aldehydes are derived from the primary alcohols by taking away two atoms of hydrogen from the $-CH_2{\cdot}OH$ group; benzaldehyde, $C_6H_5{\cdot}CHO$, for example, corresponds with benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, salicylaldehyde, $C_6H_4(OH){\cdot}CHO$, with salicyl alcohol, $C_6H_4(OH){\cdot}CH_2{\cdot}OH$, phenylacetaldehyde, $C_6H_5{\cdot}CH_2{\cdot}CHO$, with phenylethyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and so on.

Now those compounds which contain an aldehyde-group directly united with carbon of the nucleus have been much more thoroughly investigated, and are of far greater importance, than those in which the aldehyde-group is combined with a carbon atom of the side-chain, as in phenylacetaldehyde (see above), cinnamic aldehyde, $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$, &c.; whereas, moreover, the latter resemble the fatty aldehydes very closely in general character, and do not therefore require any detailed description, the former differ from the fatty compounds in several important particulars, as will be seen from the following account of benzaldehyde and salicylaldehyde, two of the best-known aromatic compounds which contain the aldehyde group directly united with the benzene nucleus.

Benzaldehyde, $C_6H_5{\cdot}CHO$, sometimes called 'oil of bitter almonds,' was formerly obtained from the glucoside (compare foot-note, p. 488), amygdalin, which occurs in bitter almonds, and which, in contact with water, gradually undergoes decomposition into benzaldehyde, hydrocyanic acid, and dextrose (compare part i. p. 279).

Benzaldehyde may be obtained by oxidising benzyl alcohol with nitric acid, and by distilling a mixture of calcium benzoate and calcium formate,

$$(C_6H_5{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca = 2C_6H_5{\cdot}CHO + 2CaCO_3,$$

reactions analogous to those employed in the fatty series.

It is prepared both in the laboratory and on the large scale, either by heating benzal chloride (p. 349) with moderately dilute sulphuric acid, or calcium hydroxide, under pressure, or by boiling benzyl chloride with an aqueous solution of lead nitrate or copper nitrate. In the first method, the benzal chloride is probably first converted into the corresponding dihydroxy-derivative of toluene,

$$C_6H_5{\cdot}CHCl_2 + 2H_2O = C_6H_5{\cdot}CH(OH)_2 + 2HCl;$$

but as this compound contains two hydroxyl-groups united with one and the same carbon atom, it is very unstable (part i. p. 259), and subsequently undergoes decomposition into benzaldehyde and water. In the second method, the benzyl chloride is probably transformed into benzyl alcohol, which is then oxidised to the aldehyde by the metallic nitrate, with evolution of oxides of nitrogen and formation of copper or lead chloride, as indicated by the equation

$$2C_6H_5{\cdot}CH_2{\cdot}OH + Cu(NO_3)_2 + 2HCl = 2C_6H_5{\cdot}CHO + CuCl_2 + 2HNO_2 + 2H_2O.$$

Benzyl chloride (5 parts), water (25 parts), and copper nitrate (4 parts) are placed in a flask connected with a reflux condenser, and the mixture is boiled for six to eight hours, a stream of carbon dioxide being passed into the liquid all the time, in order to expel the oxides of nitrogen, which would otherwise oxidise the benzaldehyde to benzoic acid; the process is at an end when the oil contains only traces of chlorine, which is ascertained by washing a small portion with water, and boiling it with silver nitrate and nitric acid. The benzaldehyde is then extracted with ether, the ethereal extract shaken with a concentrated solution of sodium bisulphite, and the crystals of the bisulphite compound, $C_6H_5{\cdot}CHO, NaHSO_3$, separated by filtration and washed with ether; the benzaldehyde is then regenerated by decomposing the crystals with dilute sulphuric acid, extracted with ether, and distilled.

Benzaldehyde is a colourless, highly refractive liquid of sp. gr. 1·05 at 15°; it boils at 179°, and is volatile in steam. It has a pleasant smell like that of bitter almonds, and is only sparingly soluble in water, but miscible with alcohol, ether, &c., in all proportions. It is extensively used for flavouring purposes, and is employed on the large scale in the manufacture of various dyes.

Benzaldehyde, and aromatic aldehydes in general, *resemble* the fatty aldehydes in the following respects: They readily undergo oxidation on exposure to the air, yielding the corresponding acids,

$$C_6H_5\cdot CHO + O = C_6H_5\cdot COOH,$$

and consequently they reduce ammoniacal solutions of silver hydroxide. On reduction, they are converted into the corresponding alcohols,

$$C_6H_5\cdot CHO + 2H = C_6H_5\cdot CH_2\cdot OH.$$

When treated with phosphorus pentachloride, they give dihalogen derivatives such as benzal chloride, $C_6H_5\cdot CHCl_2$, two atoms of chlorine being substituted for one atom of oxygen. They interact with hydroxylamine, yielding aldoximes, and with phenylhydrazine, giving hydrazones,

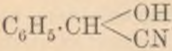
$$C_6H_5\cdot CHO + NH_2\cdot OH = H_2O + C_6H_5\cdot CH{:}N\cdot OH$$

Benzaldoxime.

$$C_6H_5\cdot CHO + NH_2\cdot NH\cdot C_6H_5 = H_2O + C_6H_5\cdot CH{:}N_2H\cdot C_6H_5.$$

Benzylidenehydrazone.

They combine directly with sodium bisulphite, forming crystalline compounds, and with hydrocyanic acid they yield hydroxycyanides such as *benzylidenehydroxycyanide*,*



$C_6H_5\cdot CH{<}\begin{matrix}OH\\ CN\end{matrix}$. They readily undergo condensation with many other fatty and aromatic compounds; when, for example, a mixture of benzaldehyde and acetone is treated with a few drops of soda at ordinary temperatures, condensation occurs, and *benzylideneacetone*, $C_6H_5\cdot CH{:}CH\cdot CO\cdot CH_3$ (m.p. 42°), is formed.

Benzaldehyde, and other aromatic aldehydes which contain the –CHO group directly united with the benzene nucleus, *differ* from the fatty aldehydes in the following respects:

---

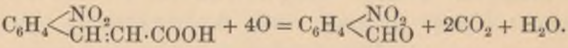
* The name *benzylidene* is given to the group of atoms, $C_6H_5\cdot CH=$, which is analogous to ethylidene, $CH_3\cdot CH=$ (part i. p. 139).

They do not reduce Fehling's solution, and they do not undergo polymerisation; they do not form additive compounds with ammonia, but yield complex products such as *hydrobenzamide*, $(C_6H_5\cdot CH)_3N_2$, which is obtained by treating benzaldehyde with ammonia. When shaken with concentrated potash (or soda), they yield a mixture of the corresponding alcohol and acid (compare p. 403),

$$2C_6H_5\cdot CHO + KOH = C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot COOK.$$

Nitrobenzaldehydes, $C_6H_4(NO_2)\cdot CHO$.—When treated with a mixture of nitric and sulphuric acids, benzaldehyde yields *m*-nitrobenzaldehyde (m.p. 58°) as principal product, small quantities of *o*-nitrobenzaldehyde (m.p. 46°) being formed at the same time.

p-Nitrobenzaldehyde (m.p. 107°), and also the *o*-compound, are most conveniently prepared by the oxidation of the corresponding nitrocinnamic acids (p. 432) with potassium permanganate,

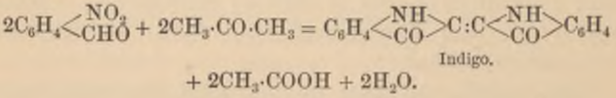


$$C_6H_4<\begin{matrix}NO_2\\CH{:}CH\cdot COOH\end{matrix} + 4O = C_6H_4<\begin{matrix}NO_2\\CHO\end{matrix} + 2CO_2 + H_2O.$$

During the operation the mixture is shaken with benzene in order to extract the aldehyde as fast as it is formed, and thus remove it from the further action of the oxidising agent. The benzene solution is then evaporated, and the aldehyde purified by recrystallisation.

The nitrobenzaldehydes are colourless, crystalline substances, which show much the same behaviour as benzaldehyde itself; when reduced with ferrous sulphate and ammonia they are converted into the corresponding *amidobenzaldehydes*, $C_6H_4(NH_2)\cdot CHO$.

o-Nitrobenzaldehyde is a particularly interesting substance, as, when its solution in acetone is mixed with a few drops of dilute soda, a precipitate of *indigo* gradually forms (Baeyer). This important synthesis of this vegetable dye may be represented by the equation

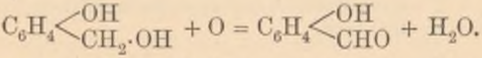


$$2C_6H_4<\begin{matrix}NO_2\\CHO\end{matrix} + 2CH_3\cdot CO\cdot CH_3 = \underset{\text{Indigo.}}{C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C{:}C<\begin{matrix}NH\\CO\end{matrix}>C_6H_4}$$
$$+ 2CH_3\cdot COOH + 2H_2O.$$

Hydroxy-aldehydes.

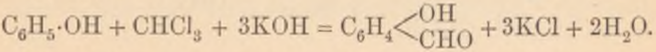
The hydroxy-derivatives of the aldehydes, such as the hydroxybenzaldehydes, $C_6H_4(OH)\cdot CHO$, which contain the hydroxyl-group united with the nucleus, combine the properties of phenols and aldehydes.

They may be obtained by the oxidation of the corresponding hydroxy-alcohols; saligenin (p. 404), or *o*-hydroxybenzyl alcohol, for example, yields salicylaldehyde or *o*-hydroxybenzaldehyde,



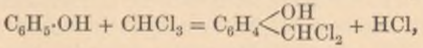
$$C_6H_4{<}\begin{matrix}OH\\CH_2\cdot OH\end{matrix} + O = C_6H_4{<}\begin{matrix}OH\\CHO\end{matrix} + H_2O.$$

As, however, such alcohols are not easily obtained, and indeed in many cases have only been produced by the reduction of the hydroxy-aldehydes, the latter are usually prepared by heating the phenols with chloroform in alkaline solution (Reimer's reaction),



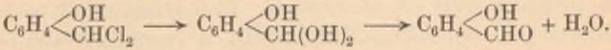
$$C_6H_5\cdot OH + CHCl_3 + 3KOH = C_6H_4{<}\begin{matrix}OH\\CHO\end{matrix} + 3KCl + 2H_2O.$$

The actual changes which occur in carrying out Reimer's reaction are not clearly understood; but it may be assumed that, in the first place, the phenol interacts with the chloroform in the presence of the alkali, yielding an intermediate product containing halogen,



$$C_6H_5\cdot OH + CHCl_3 = C_6H_4{<}\begin{matrix}OH\\CHCl_2\end{matrix} + HCl,$$

which by the further action of the alkali is converted into a hydroxybenzaldehyde, just as benzalchloride, $C_6H_5\cdot CHCl_2$, is transformed into benzaldehyde (compare p. 406),



$$C_6H_4{<}\begin{matrix}OH\\CHCl_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}OH\\CH(OH)_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}OH\\CHO\end{matrix} + H_2O.$$

As a rule, the primary product is the *o*-hydroxyaldehyde, small quantities of the corresponding *p*-compound being produced at the same time.

Salicylaldehyde, $C_6H_4(OH)\cdot CHO$ (*o*-hydroxybenzaldehyde), may be obtained by oxidising saligenin with chromic acid (see above), but it is usually prepared from phenol by Reimer's reaction.

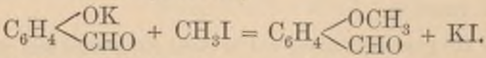
Phenol (20 grams) is dissolved in soda (60 grams) and water (120 grams), the solution heated to 60° in a flask provided with a reflux condenser, and chloroform (30 grams) added in small quantities at a time from a dropping funnel. After slowly heating to boiling, the unchanged chloroform is distilled off, the alkaline liquid acidified and distilled in steam, when a mixture of phenol and salicylaldehyde passes over. (The residue in the flask contains *p*-hydroxybenzaldehyde, which may be extracted from the filtered liquid with ether, and purified by recrystallisation.) The oily mixture is extracted from the distillate with ether, and the extract shaken with dilute sodium bisulphite, which dissolves the aldehyde in the form of its bisulphite compound. The aqueous liquid is then separated, acidified, and the regenerated salicylaldehyde extracted with ether and purified by distillation.

Salicylaldehyde is a colourless oil which boils at 196°, and possesses a penetrating, aromatic odour; it is moderately soluble in water, its solution giving a deep violet colouration on the addition of ferric chloride. When reduced with sodium amalgam, it yields saligenin, $C_6H_4(OH){\cdot}CH_2{\cdot}OH$ (p. 404), whereas oxidising agents convert it into salicylic acid, $C_6H_4(OH){\cdot}COOH$.

p-Hydroxybenzaldehyde is crystalline, and melts at 116°; it dissolves readily in hot water, and gives, with ferric chloride, a violet colouration.

m-Hydroxybenzaldehyde is obtained from *m*-nitrobenzaldehyde by conversion into *m*-amidobenzaldehyde, and subsequent displacement of the amido-group by hydroxyl, by means of the diazo-reaction (p. 372). It crystallises from water in colourless needles, and melts at 104°.

Anisaldehyde, $C_6H_4(OCH_3){\cdot}CHO$ (*p*-methoxybenzaldehyde), is prepared from oil of aniseed. This ethereal oil contains *anethole*, $C_6H_4(OCH_3){\cdot}CH{:}CH{\cdot}CH_3$, a crystalline substance which melts at 21° and distils at 232°, and which on oxidation with potassium bichromate and sulphuric acid is converted into anisaldehyde, the propenyl group $-CH{:}CH{\cdot}CH_3$ being oxidised to the aldehyde group. Synthetically, it may be prepared by digesting *p*-hydroxybenzaldehyde with alcoholic potash and methyl iodide,



$$C_6H_4{<}\begin{matrix}OK\\CHO\end{matrix} + CH_3I = C_6H_4{<}\begin{matrix}OCH_3\\CHO\end{matrix} + KI.$$

Anisaldehyde is a colourless oil which boils at 248°, and possesses a penetrating, aromatic odour; on reduction with sodium amalgam, it yields anisyl alcohol, $C_6H_4(OCH_3){\cdot}CH_2{\cdot}OH$

(p. 404); oxidising agents convert it into anisic acid, $C_6H_4(OCH_3){\cdot}COOH$ (p. 439).

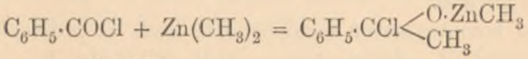
Ketones.

The ketones of the aromatic, like those of the fatty series, have the general formula $R-CO-R'$, where R and R′ represent different or identical radicles, one of which must, of course, be aromatic.

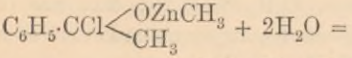
Acetophenone, phenylmethyl ketone, or acetylbenzene, $C_6H_5{\cdot}CO{\cdot}CH_3$, may be described as a typical aromatic ketone. It is formed on distilling a mixture of calcium benzoate and calcium acetate, a reaction which is exactly analogous to that which is made use of in obtaining mixed ketones of the fatty series,

$$(C_6H_5{\cdot}COO)_2Ca + (CH_3{\cdot}COO)_2Ca = 2C_6H_5{\cdot}CO{\cdot}CH_3 + 2CaCO_3.$$

It may also be obtained by treating benzoyl chloride (p. 420) with zinc methyl, just as diethyl ketone may be produced from propionyl chloride and zinc ethyl (part i. p. 136),



$$C_6H_5{\cdot}COCl + Zn(CH_3)_2 = C_6H_5{\cdot}CCl{<}\begin{matrix}O{\cdot}ZnCH_3\\ CH_3\end{matrix}$$



$$C_6H_5{\cdot}CCl{<}\begin{matrix}OZnCH_3\\ CH_3\end{matrix} + 2H_2O =$$

$$C_6H_5{\cdot}CO{\cdot}CH_3 + CH_4 + \vdots Zn(OH)_2 + HCl \vdots$$

It is, however, most conveniently prepared by treating benzene with acetyl chloride in presence of aluminium chloride,

$$C_6H_6 + CH_3{\cdot}COCl = C_6H_5{\cdot}CO{\cdot}CH_3 + HCl.$$

This method is of general use, as by employing other acid chlorides and other hydrocarbons, many other ketones may be prepared; it is comparable to Friedel and Craft's method of preparing hydrocarbons (p. 329).

Acetophenone is a crystalline substance, melting at 20·5°, and boiling at 202°; it is used as a hypnotic in medicine, under the name of *hypnone.* Its chemical behaviour is so similar to that of the fatty ketones, that most of its reactions, or at any rate those which are determined by the carbonyl-group, might be foretold from a consideration of those of acetone; on reduction with sodium amalgam, acetophenone is converted into phenylmethyl carbinol, $C_6H_5{\cdot}CH(OH){\cdot}CH_3$, just as acetone is transformed into isopropyl alcohol; like acetone, and other fatty ketones, it interacts readily with hydroxylamine and with phenylhydrazine, giving the *oxime*, $C_6H_5{\cdot}C(NOH){\cdot}CH_3$, and the *hydrazone*, $C_6H_5{\cdot}C(N_2HC_6H_5){\cdot}CH_3$, respectively. On oxidation, it is resolved into benzoic acid and carbon dioxide, just as acetone is oxidised to acetic acid and carbon dioxide,

$$C_6H_5{\cdot}CO{\cdot}CH_3 + 4O = C_6H_5{\cdot}COOH + CO_2 + H_2O.$$

Acetophenone shows also the general behaviour of aromatic compounds, inasmuch as it may be converted into nitro-, amido-, and halogen-derivatives by displacement of hydrogen of the nucleus.

The homologues of acetophenone, such as *propiophenone*, $C_6H_5{\cdot}CO{\cdot}C_2H_5$, *butyrophenone*, $C_6H_5{\cdot}CO{\cdot}C_3H_7$, &c., are of little importance, but benzophenone, an aromatic ketone of a different series, may be briefly described.

Benzophenone, diphenyl ketone, or benzoylbenzene, $C_6H_5{\cdot}CO{\cdot}C_6H_5$, may be obtained by distilling calcium benzoate, and by treating benzene with benzoyl chloride in presence of aluminium chloride; it is most conveniently prepared by adding aluminium chloride to a solution of carbonyl chloride in benzene,

$$2C_6H_6 + COCl_2 = C_6H_5{\cdot}CO{\cdot}C_6H_5 + 2HCl.$$

It is a crystalline substance, melting at 48–49°, and is very similar to acetophenone in most respects; when distilled over zinc-dust, it is converted into *diphenylmethane*, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$ (p. 340).

Quinones.

When an aqueous solution of hydroquinone is oxidised with excess of ferric chloride, a dark-brown solution is obtained which has a very penetrating odour, and from which, on standing, yellowish-brown crystals are deposited,

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

The substance formed in this way is named *quinone*, or benzoquinone, and is the simplest member of a very interesting class of compounds.

Quinone, or benzoquinone, $C_6H_4O_2$, is usually prepared by oxidising aniline with potassium bichromate and sulphuric acid.

Aniline (1 part) is dissolved in water (25 parts) and sulphuric acid (8 parts), and finely-powdered potassium bichromate (3·5 parts) gradually added, the whole being well cooled during the operation; the product, which is very dark coloured, owing to the presence of aniline black, is extracted with ether, the ether evaporated, and the crude quinone purified by recrystallisation from light petroleum or by sublimation.

Quinone crystallises in golden-yellow prisms, melts at 116°, sublimes very readily, and is volatile in steam; it has a peculiar, irritating, and very characteristic smell, and is only sparingly soluble in water, but dissolves freely in alcohol and ether. It is readily reduced by sulphurous acid, zinc and hydrochloric acid, &c., being converted into hydroquinone,

$$C_6H_4O_2 + 2H = C_6H_4(OH)_2.$$

In some respects quinone behaves as if it contained two carbonyl-groups, each having properties similar to those of the carbonyl-groups in compounds such as acetone, acetophenone, &c.; when treated with hydroxylamine hydrochloride, for example, quinone yields a *monoxime*, $C_6H_4\genfrac{}{}{0pt}{}{<O}{<N\cdot OH}$ (identical with nitrosophenol, p. 367), and also a *dioxime*, $C_6H_4\genfrac{}{}{0pt}{}{<N\cdot OH}{<N\cdot OH}$. The two carbonyl-groups, moreover, are in the *para*-position to one another, as is shown by the fact that, when quinone-dioxime is reduced with tin and hydrochloric acid, it yields *p*-phenylenediamine.

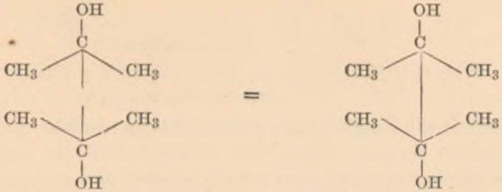
In other respects, however, quinone undergoes changes which are quite different from those observed in the case of ordinary ketones; on reduction, for instance, each $>CO$ group is transformed into $\geq C\cdot OH$, and not into $>CH\cdot OH$, as might have been expected from analogy; again, on treatment with phosphorus pentachloride, each oxygen atom is displaced by one atom of chlorine, *p*-dichlorobenzene, $C_6H_4\genfrac{}{}{0pt}{}{<Cl}{<Cl}$, being formed, and not a tetrachloro-derivative, $C_6H_4\genfrac{}{}{0pt}{}{<Cl_2}{<Cl_2}$, as might have been expected.

This curious behaviour, and the close connection between quinone and hydroquinone, is well explained by assuming that quinone has the constitution represented by the formula I., and that when it is reduced to hydroquinone (formula II.), the two $\overset{CO}{\wedge}$ groups are converted into two $\overset{C\cdot OH}{\wedge}$ groups,

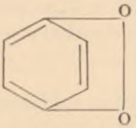

I. Quinone.

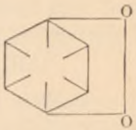

II. Hydroquinone.

Such a change would indeed be similar to the formation of pinacone from acetone, as in the latter case the acetone $CH_3\overset{CO}{\wedge}CH_3$ is probably first reduced to $CH_3\overset{\overset{OH}{|}}{\overset{C}{\wedge}}CH_3$, two molecules of which immediately combine to form pinacone (compare part i. p. 138):



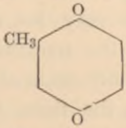
Three other constitutional formulæ may be put forward, as possibly representing the constitution of quinone—namely:





The first of these is practically identical with that given above, but the second and third are different and not so probable, because, although they explain in a simple way many of the reactions of quinone, they do not so readily account for the formation of a dioxime.

Benzoquinone and many other para-quinones (that is to say, quinones in which the two carbonyl-groups are in the para-position to one another*) may be produced by the oxidation, with chromic acid or ferric chloride, of many hydroxy- and amido-compounds, which contain the substituting groups in the para-position; quinone, for example, is formed on oxidising *p*-amidophenol, $C_6H_4(OH)\cdot NH_2$, and *p*-phenylenediamine, $C_6H_4(NH_2)_2$, whereas *o*-toluidine, *p*-toluylenediamine, $C_6H_4(NH_2)_2\cdot CH_3$, $[NH_2:NH_2:CH_3 = 1:4:6]$, &c., yield *toluquinone.*



---

* Other quinones, of a somewhat different class to benzoquinone, are described later (pp. 456, 470).

When, however, bleaching-powder is used as the oxidising agent, *quinone chlorimides* and *quinone dichlorodiimides* are formed in the place of quinone,

$$NH_2{\cdot}C_6H_4{\cdot}OH + 4Cl = \underset{\text{Quinone Chlorimide.}}{NCl{:}C_6H_4{:}O} + 3HCl$$

$$NH_2{\cdot}C_6H_4{\cdot}NH_2 + 6Cl = \underset{\text{Quinone Dichlorodiimide.}}{NCl{:}C_6H_4{:}NCl} + 4HCl.$$

The quinone chlorimides and dichlorodiimides resemble quinone in many respects; they are crystalline, readily volatile in steam, and are respectively converted into *p*-amidophenol and *p*-phenylenediamine or their derivatives on reduction.

Chloranil, or tetrachloroquinone, $O{:}C_6Cl_4{:}O$, is produced when chlorine acts on quinone, but it is usually prepared by treating phenol with hydrochloric acid and potassium chlorate, oxidation and chlorination taking place simultaneously,

$$C_6H_5{\cdot}OH + 10Cl + O = O{:}C_6Cl_4{:}O + 6HCl.$$

It crystallises in yellow plates, sublimes without melting, and is sparingly soluble in alcohol, and insoluble in water.

It is readily reduced to tetrachlorohydroquinone, $OH{\cdot}C_6Cl_4{\cdot}OH$, and is therefore a powerful oxidising agent, for which reason it is much employed in colour chemistry, when the use of inorganic oxidising agents is undesirable.

CHAPTER XXVIII.

CARBOXYLIC ACIDS.

The carboxylic acids of the aromatic series are derived from the aromatic hydrocarbons, just as those of the fatty series are derived from the paraffins—namely, by the substitution of one or more carboxyl-groups for a corresponding number of hydrogen atoms. In this, as in other cases, however, one of two classes of compounds may be obtained according as substitution takes place in the nucleus or in the side-chain; benzene yields, of course, only acids of the first class, such as benzoic acid, $C_6H_5{\cdot}COOH$, the three (*o.m.p.*) phthalic acids, $C_6H_4(COOH)_2$, the three tricarboxylic acids, $C_6H_3(COOH)_3$, &c., but toluene and all the higher homologues may give rise to derivatives of both kinds—as, for example, the three toluic acids, $C_6H_4(CH_3)\cdot COOH$, and phenylacetic acid, $C_6H_5\cdot CH_2\cdot COOH$.

Although there are no very important differences in the properties of these two classes of acids, it is more convenient to describe them separately, taking first those compounds in which the carboxyl-groups are directly united with carbon of the nucleus.

Preparation.—Such acids may be obtained by oxidising the alcohols or aldehydes,

$$C_6H_5\cdot CH_2\cdot OH + 2O = C_6H_5\cdot COOH + H_2O$$
$$C_6H_5\cdot CHO + O = C_6H_5\cdot COOH,$$

and by hydrolysing the nitriles (p. 421) with alkalies or mineral acids,

$$C_6H_5\cdot CN + 2H_2O = C_6H_5\cdot COOH + NH_3$$
$$C_6H_5\cdot CH_2\cdot CN + 2H_2O = C_6H_5\cdot CH_2\cdot COOH + NH_3,$$

reactions which are exactly similar to those employed in the case of the fatty acids (part i. p. 165).

Perhaps, however, the most important method, and one which has no counterpart in the fatty series, consists in oxidising the homologues of benzene with dilute nitric acid or chromic acid,

$$C_6H_5\cdot CH_3 + 3O = C_6H_5\cdot COOH + H_2O$$
$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + H_2O.$$

In this way only those acids which contain the *carboxyl-group united with the nucleus* can be obtained, because the side-chain is always oxidised to $-COOH$, no matter how many $-CH_2-$ groups it may contain; in other words, all homologues of benzene which contain only one side-chain yield benzoic acid, whereas those containing two give one of the phthalic acids. In the latter case, however, one of the side-chains is oxidised before the other is attacked, so that by stopping the process at the right time, an alkyl-derivative of benzoic acid is obtained,

$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3)\cdot COOH + H_2O$$
$$C_6H_4(CH_3)\cdot COOH + 3O = C_6H_4(COOH)_2 + H_2O.$$

Oxidation is frequently carried out by boiling the hydrocarbon (1 vol.) with nitric acid (1 vol.) diluted with water (2–4 vols.) until brown fumes are no longer formed. The mixture is then made slightly alkaline with soda, and any unchanged hydrocarbon and traces of nitro-hydrocarbon separated with a funnel or extracted with ether; the alkaline solution is then acidified and the acid separated by filtration or extracted with ether, and purified by recrystallisation.

Most hydrocarbons are only very slowly attacked by dilute nitric or chromic acid; in such cases it is advantageous to first substitute chlorine or some other group for hydrogen of the side-chain, as in this way oxidation is facilitated. Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, for example, is much more readily oxidised than toluene, whereas benzyl acetate, $C_6H_5{\cdot}CH_2{\cdot}OC_2H_3O$ (p. 349), and benzyl ethyl ether, $C_6H_5{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, are even more readily attacked.

Properties.—The aromatic acids are crystalline, and distil without decomposition; they are sparingly soluble in cold water, but much more readily in hot water, alcohol, and ether. As regards all those properties which are determined by the carboxyl-group, the aromatic acids are closely analogous to the fatty compounds, and give corresponding derivatives, as the following examples show:

Benzoic acid,	$C_6H_5{\cdot}COOH$	Benzoyl chloride,	$C_6H_5{\cdot}COCl$.
Sodium benzoate,	$C_6H_5{\cdot}COONa$	Benzamide,	$C_6H_5{\cdot}CO{\cdot}NH_2$.
Ethyl benzoate,	$C_6H_5{\cdot}COOC_2H_5$	Benzoic anhydride,	$(C_6H_5{\cdot}CO)_2O$.

When distilled with lime, they are decomposed with loss of carbon dioxide and formation of the corresponding hydrocarbons, just as acetic acid under similar circumstances yields marsh-gas,

$$C_6H_5{\cdot}COOH = C_6H_6 + CO_2$$
$$C_6H_4(CH_3){\cdot}COOH = C_6H_5{\cdot}CH_3 + CO_2.$$

Benzoic acid, $C_6H_5{\cdot}COOH$, occurs in the free state in many resins, especially in gum benzoïn and Peru balsam; also in the urine of cows and horses, as hippuric acid or benzoylglycine, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$, to the extent of about two per cent.

It is generally prepared either by the sublimation of gum benzoïn in iron pots, the crude sublimate being purified by recrystallisation from water, or by treating hippuric acid with hydrochloric acid (part i. p. 292),

$$\begin{aligned} &C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH + HCl + H_2O = \\ &\qquad C_6H_5\cdot COOH + \underset{\text{Glycine Hydrochloride.}}{NH_2\cdot CH_2\cdot COOH, HCl.} \end{aligned}$$

The urine of horses, cows, or other herbivorous animals is evaporated to one-third of its volume, filtered, and acidified with hydrochloric acid; the crystals of hippuric acid which are deposited on standing, are collected and boiled for a short time with four parts of concentrated hydrochloric acid, the benzoic acid which separates on cooling being purified by recrystallisation; the mother-liquors contain glycine hydrochloride.

Benzoic acid is manufactured by oxidising benzyl chloride (p. 348) with 60 per cent. nitric acid,

$$C_6H_5\cdot CH_2Cl + 2O = C_6H_5\cdot COOH + HCl.$$

It may also be prepared by oxidising toluene, or by any other of the general methods.

Benzoic acid separates from water in glistening crystals, melts at 120°, and boils at 250°, but it sublimes very readily even at 100°, and is volatile in steam; it dissolves in 400 parts of water at 15°, but is readily soluble in hot water, alcohol, and ether. Its vapour has a characteristic odour, and an irritating action on the throat, causing violent coughing. Most of the metallic salts of benzoic acid are soluble in water and crystallise well; *calcium benzoate*, $(C_6H_5\cdot COO)_2Ca + 3H_2O$, for example, prepared by neutralising benzoic acid with milk of lime, crystallises in needles, and is very soluble in water.

The ethereal salts are prepared in precisely the same way as those of the fatty acids (part i. p. 187); *ethyl benzoate*, for example, $C_6H_5\cdot COOC_2H_5$, is obtained by saturating an alcoholic solution of benzoic acid with hydrogen chloride, and after some time pouring the solution into water, the precipitated oil being purified by fractional distillation. It boils at 211°, has a pleasant aromatic odour, and is readily hydrolysed by boiling alcoholic potash.

Benzoyl chloride, $C_6H_5 \cdot COCl$, is obtained by treating benzoic acid with phosphorus pentachloride. It is a colourless oil, possessing a very irritating odour, and boils at 200°; it is gradually decomposed by water, yielding benzoic acid and hydrochloric acid.

Benzoic anhydride, $(C_6H_5 \cdot CO)_2O$, is produced when benzoyl chloride is treated with sodium benzoate, just as acetic anhydride is formed by the interaction of acetyl chloride and sodium acetate (part i. p. 160); it is a crystalline substance, melting at 42°, and closely resembles acetic anhydride in ordinary chemical properties.

Benzoyl chloride and benzoic anhydride may be used for the detection of hydroxy-compounds, as they interact with all such substances (although not so readily as the corresponding derivatives of acetic acid, part i. p. 159), yielding benzoyl-derivatives, the monovalent *benzoyl*-group, $C_6H_5 \cdot CO-$, taking the place of the hydrogen of the hydroxyl-group,

$$C_6H_5 \cdot OH + C_6H_5 \cdot COCl = \underset{\text{Phenyl Benzoate.}}{C_6H_5 \cdot O \cdot CO \cdot C_6H_5} + HCl$$

$$C_2H_5 \cdot OH + (C_6H_5 \cdot CO)_2O = \underset{\text{Ethyl Benzoate.}}{C_2H_5 \cdot O \cdot CO \cdot C_6H_5} + C_6H_5 \cdot COOH.$$

Benzoyl-derivatives may be prepared by heating the hydroxy-compound with benzoyl chloride or with benzoic anhydride. A more convenient method, however, and one which gives a purer product, is that of Baumann and Schotten: it consists in adding benzoyl chloride and 10 per cent. potash alternately, in small quantities at a time, to the hydroxy-compound, which is either dissolved or suspended in water, the mixture being well shaken and kept cool during the operation. Potash alone is then added until the disagreeable smell of benzoyl chloride is no longer noticed, and the product finally separated by filtration or by extraction with ether. This method is also used in preparing benzoyl-derivatives of amido-compounds; aniline, for example, yields benzoyl-aniline,

$$C_6H_5 \cdot NH_2 + C_6H_5 \cdot COCl = C_6H_5 \cdot NH \cdot CO \cdot C_6H_5 + HCl.$$

In the above method the alkali serves to neutralise the hydrochloric acid as fast as it is formed, the interaction taking place much more readily in the neutral or slightly alkaline solution.

Benzamide, $C_6H_5{\cdot}CO{\cdot}NH_2$, may be taken as an example of an aromatic amide; it may be obtained by reactions similar to those employed in the case of acetamide (part i. p 162), as, for example, by treating ethyl benzoate with ammonia,

$$C_6H_5{\cdot}COOC_2H_5 + NH_3 = C_6H_5{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH;$$

but it is most conveniently prepared by triturating benzoyl chloride with dry ammonium carbonate in a mortar, and purifying the product by recrystallisation from water,

$$2C_6H_5{\cdot}COCl + (NH_4)_2CO_3 = 2C_6H_5{\cdot}CO{\cdot}NH_2 + CO_2 + H_2O + 2HCl.$$

It is a colourless, crystalline substance, melts at 130°, and is sparingly soluble in cold, but readily soluble in hot, water; like other amides, it is decomposed by boiling alkalies, yielding ammonia and an alkali salt,

$$C_6H_5{\cdot}CO{\cdot}NH_2 + KOH = C_6H_5{\cdot}COOK + NH_3.$$

Benzonitrile, or phenyl cyanide, $C_6H_5{\cdot}CN$, may be obtained by treating benzamide with dehydrating agents, a method similar to that employed in the preparation of fatty nitriles,

$$C_6H_5{\cdot}CO{\cdot}NH_2 = C_6H_5{\cdot}CN + H_2O.$$

Although it cannot be prepared by treating chloro- or bromobenzene with potassium cyanide (the halogen atom being so firmly held that no interaction occurs), it may be obtained by fusing benzenesulphonic acid with potassium cyanide (or with potassium ferrocyanide, which yields the cyanide), just as fatty nitriles may be prepared by heating the alkylsulphuric acids with potassium cyanide,

$$C_6H_5{\cdot}SO_3K + KCN = C_6H_5{\cdot}CN + K_2SO_3$$
$$C_2H_5{\cdot}SO_4K + KCN = C_2H_5{\cdot}CN + K_2SO_4.$$

It is, however, most conveniently prepared from aniline by Sandmeyer's reaction—namely, by treating a solution of diazobenzene chloride with potassium cyanide and copper sulphate (p. 372),

$$C_6H_5{\cdot}N_2Cl + KCN = C_6H_5{\cdot}CN + KCl + N_2.$$

Benzonitrile is a colourless oil, boiling at 191°, and smells like nitrobenzene. It undergoes changes exactly similar to those which are characteristic of fatty nitriles, being converted into the corresponding acid on hydrolysis with alkalies or mineral acids,

$$C_6H_5{\cdot}CN + 2H_2O = C_6H_5{\cdot}COOH + NH_3,$$

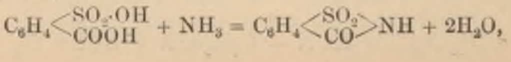
and into a primary amine on reduction,

$$C_6H_5{\cdot}CN + 4H = \underset{\text{Benzylamine.}}{C_6H_5{\cdot}CH_2{\cdot}NH_2}.$$

Other aromatic nitriles, such as the three tolunitriles, $C_6H_4(CH_3){\cdot}CN$, are known, also compounds such as phenylacetonitrile (benzyl cyanide, p. 429), $C_6H_5{\cdot}CH_2{\cdot}CN$, which contain the cyanogen group in the side-chain.

Substitution Products of Benzoic Acid.—Benzoic acid is attacked by halogens (although not so readily as the hydrocarbons), the product consisting of the *meta*-derivative (p. 351); when, for example, benzoic acid is heated with bromine and water at 125°, *m*-bromobenzoic acid, $C_6H_4Br{\cdot}COOH$ (m.p. 155°), is formed. The *o*- and *p*-bromobenzoic acids are obtained by oxidising the corresponding bromotoluenes with nitric acid; the former melts at 148°, the latter at 251°. Nitric acid, in the presence of sulphuric acid, acts readily on benzoic acid, *m*-nitrobenzoic acid, $C_6H_4(NO_2){\cdot}COOH$ (m.p. 142°), being the principal product; *o*-nitrobenzoic acid (m.p. 147°) and *p*-nitrobenzoic acid (m.p. 240°) are obtained by the oxidation of *o*- and *p*-nitrotoluene respectively (p. 355); when these acids are reduced with tin and hydrochloric acid, they yield the corresponding amidobenzoic acids, $C_6H_4(NH_2){\cdot}COOH$, which, like glycine (part i. p. 292), form salts both with acids and bases.

When heated with sulphuric acid, benzoic acid is converted into *m*-sulphobenzoic acid, $C_6H_4(SO_3H){\cdot}COOH$, small quantities of the *p*-acid also being produced. The *o*-acid is obtained by oxidising toluene-*o*-sulphonic acid; when treated with ammonia it yields an imide (p. 426),



$$C_6H_4{<}\begin{matrix}SO_2{\cdot}OH\\COOH\end{matrix} + NH_3 = C_6H_4{<}\begin{matrix}SO_2\\CO\end{matrix}{>}NH + 2H_2O,$$

which is remarkable for possessing an exceedingly sweet taste, and which comes into the market under the name of *saccharin.*

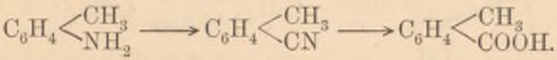
The sulphobenzoic acids are very soluble in water; when fused with potash they yield hydroxy-acids (p. 433), just as benzenesulphonic acid gives phenol,

$$C_6H_4(SO_3K)\cdot COOK + 2KOH = C_6H_4(OK)\cdot COOK + K_2SO_3 + H_2O.$$

The three (*o.m.p.*) **toluic acids,** $C_6H_4(CH_3)\cdot COOH$, may be produced by oxidising the corresponding xylenes with dilute nitric acid,

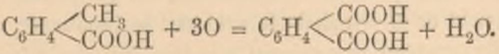
$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3)\cdot COOH + H_2O,$$

but the *o*- and *p*-acids are best prepared by converting the corresponding toluidines into the nitriles by Sandmeyer's reaction (p. 372), and then hydrolysing with acids or alkalies,



$$C_6H_4\Big<{CH_3 \atop NH_2} \longrightarrow C_6H_4\Big<{CH_3 \atop CN} \longrightarrow C_6H_4\Big<{CH_3 \atop COOH}.$$

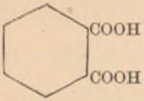
As *m*-toluidine cannot easily be obtained, and as *m*-xylene is only very slowly oxidised by dilute nitric acid, in order to prepare *m*-toluic acid, *m*-xylyl bromide, $C_6H_4(CH_3)\cdot CH_2Br$ (b.p. 215°), is first prepared by adding bromine (1 mol.) to boiling *m*-xylene (1 mol.); this product is then heated with sodium ethoxide, in alcoholic solution, to convert it into *m-xylyl ethyl ether*, $C_6H_4(CH_3)\cdot CH_2\cdot O\cdot C_2H_5$ (b.p. 204°), a substance which is readily oxidised by potassium bichromate and sulphuric acid (p. 418), yielding *m-toluic acid.* The three *o*-, *m*-, *p*-toluic acids melt at 103°, 110°, and 180° respectively, and resemble benzoic acid very closely, but since they contain a methyl-group, they have also properties which are not shown by benzoic acid; on oxidation, for example, they are converted into the corresponding phthalic acids, just as toluene is transformed into benzoic acid,



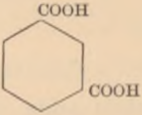
$$C_6H_4\Big<{CH_3 \atop COOH} + 3O = C_6H_4\Big<{COOH \atop COOH} + H_2O.$$

Dibasic Acids.

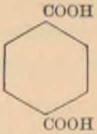
The most important dicarboxylic acids are the three (*o.m.p.*) phthalic acids, or benzenedicarboxylic acids, which are represented by the formulæ,



Phthalic Acid.



Isophthalic Acid.



Terephthalic Acid.

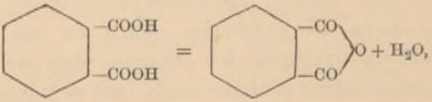
These compounds may be prepared by the oxidation of the corresponding dimethylbenzenes with dilute nitric acid, or more conveniently by treating the toluic acids with potassium permanganate in alkaline solution,

$$C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix} + 6O = C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix} + 2H_2O$$

$$C_6H_4{<}\begin{matrix}CH_3\\COOH\end{matrix} + 3O = C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix} + H_2O.$$

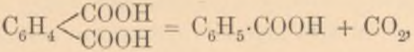
They are colourless, crystalline substances, and have all the ordinary properties of carboxylic acids. They yield neutral and acid metallic salts, ethereal salts, acid chlorides, amides, &c., which are similarly constituted to, and formed by the same reactions as, those of other dicarboxylic acids (part i. pp. 234–238).

Phthalic acid, like succinic acid (part i. pp. 234–236), yields an anhydride when strongly heated,



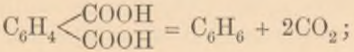
but it is very important to notice that no anhydride of iso phthalic acid or of terephthalic acid can be produced; it may, in fact, be accepted as a general rule that anhydride formation takes place only when the two carboxyl-groups in the benzene nucleus are in the *o*-position, never when they occupy the *m*- or *p*-position.

When cautiously heated with lime (1 mol.) the phthalic acids yield benzoic acid,



$$C_6H_4<^{COOH}_{COOH} = C_6H_5{\cdot}COOH + CO_2,$$

but if excess of lime be employed, and the distillation conducted at a high temperature, both carboxyl-groups are displaced by hydrogen, and benzene is formed,



$$C_6H_4<^{COOH}_{COOH} = C_6H_6 + 2CO_2\,;$$

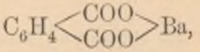
this behaviour clearly shows that these acids are all dicarboxy-derivatives of benzene.

When a trace of phthalic acid is heated with resorcinol and a drop of sulphuric acid, fluoresceïn (p. 520) is produced, and the reddish-brown product, when dissolved in dilute soda and poured into a quantity of water, yields a magnificently fluorescent solution. This reaction is shown by all the *o*-dicarboxylic acids of the benzene series, but not by the *m*- and *p*-dicarboxylic acids.

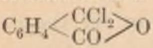
Phthalic acid, $C_6H_4(COOH)_2$ (benzene-*o*-dicarboxylic acid), may be obtained by oxidising *o*-xylene or *o*-toluic acid, but it is usually manufactured by the oxidation of naphthalene (p. 442) with chromic acid; for laboratory purposes naphthalene tetrachloride, $C_{10}H_8Cl_4$ (p. 450), is oxidised with nitric acid.

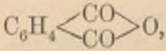
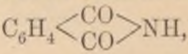
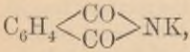
Concentrated nitric acid (sp. gr. 1·45, 10 parts) is gradually added to naphthalene tetrachloride (1 part), and the mixture heated until a clear solution is produced. This is then evaporated to dryness, and the residue distilled, the phthalic anhydride (see below), which passes over, being reconverted into phthalic acid by dissolving it in dilute soda; the acid is then precipitated by adding a mineral acid, and the crystalline precipitate purified by recrystallisation from water.

Phthalic acid crystallises in colourless prisms, and melts at 184°, with formation of the anhydride, so that, if the melted substance be allowed to solidify, and the melting-point again determined, it will be found to be about 128°, the melting-point of phthalic anhydride.

Phthalic acid is readily soluble in hot water, alcohol, and ether, and gives with metallic hydroxides well-characterised salts; the *barium* salt,  $C_6H_4\left<\begin{matrix}COO\\COO\end{matrix}\right>Ba$, obtained as a white precipitate by adding barium chloride to a neutral solution of the ammonium salt, is very sparingly soluble in water.

Ethyl phthalate, $C_6H_4(COOC_2H_5)_2$, is readily prepared by saturating an alcoholic solution of phthalic acid (or its anhydride) with hydrogen chloride. It is a colourless liquid, boiling at 295°.

Phthalyl chloride, $C_6H_4(COCl)_2$, is prepared by heating phthalic anhydride (1 mol.) with phosphorus pentachloride (1 mol.). It is a colourless oil, which boils at 275°, and is slowly decomposed by water, with regeneration of phthalic acid. In many of its reactions it behaves as if it had the constitution represented by the formula  $C_6H_4\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O$ (compare succinyl chloride, part i. p. 237).

Phthalic anhydride,  $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O$, is formed when phthalic acid is distilled. It sublimes readily in long needles, melts at 128°, boils at 284°, and is only very gradually decomposed by water, but dissolves readily in alkalies, yielding salts of phthalic acid. When heated in a stream of ammonia it is converted into *phthalimide*,  $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NH$, a substance which melts at 229°, and yields a potassium derivative,  $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NK$, on treatment with alcoholic potash. There is thus a great similarity between phthalimide and succinimide (part i. p. 237).

Isophthalic acid, $C_6H_4(COOH)_2$ (benzene-*m*-dicarboxylic acid), is produced by oxidising *m*-xylene or *m*-xylyl diethyl ether, $C_6H_4(CH_2{\cdot}OC_2H_5)_2$ (compare p. 418), with nitric acid or chromic acid; or from *m*-toluic acid (p. 423) by oxidation with potassium permanganate in alkaline solution.

It crystallises in needles, melts above 300°, and when strongly heated, sublimes unchanged; it is very sparingly soluble in water. *Methyl isophthalate*, $C_6H_4(COOCH_3)_2$, melts at 65°.

Terephthalic acid, $C_6H_4(COOH)_2$ (benzene-*p*-dicarboxylic acid), is formed by the oxidation of *p*-xylene, *p*-toluic acid, and of all di-alkyl substitution-derivatives of benzene, which, like cymene, $CH_3{\cdot}C_6H_4{\cdot}CH(CH_3)_2$, contain the alkyl-groups in the *p*-position. It is best prepared by oxidising *p*-toluic acid (p. 423) in alkaline solution with potassium permanganate.

Terephthalic acid is almost insoluble in water, and, when heated, sublimes without melting; the *methyl* salt, $C_6H_4(COOCH_3)_2$, melts at 140°.

Acids, such as isophthalic acid and terephthalic acid, which have no definite melting-point, or which melt above 300°, are best identified by conversion into their methyl salts, which generally crystallise well, and melt at a comparatively low temperature.

For this purpose a centigram of the acid is warmed in a test tube with about three times its weight of phosphorus pentachloride, and the clear solution, which now contains the chloride of the acid, poured into excess of methyl alcohol. As soon as the vigorous reaction has subsided, the liquid is diluted with water, the crude methyl salt collected, recrystallised, and its melting-point determined.

Phenylacetic Acid, Phenylpropionic Acid, and their Derivatives.

Many cases have already been met with in which aromatic compounds have been found to have certain properties similar to those of members of the fatty series, and it has been pointed out that this is due to the presence in the former of groups of atoms (side-chains) which may be considered as fatty radicles; benzyl chloride, for example, has some properties in common with methyl chloride, benzyl alcohol with methyl alcohol, benzylamine with methylamine, and so on, simply because similar groups or radicles in a similar state of combination confer, as a rule, similar properties on the compounds in which they occur. Inasmuch, however, as nearly all fatty compounds may theoretically be converted into aromatic compounds of the same type by the substitution of a phenyl group for hydrogen, it follows that any series of fatty compounds may have its counterpart in the aromatic group. This is well illustrated in the case of the carboxylic acids, because, corresponding with the fatty acids, there is a series of aromatic acids which may be regarded as derived from them in the manner just mentioned:

Formic acid, $H{\cdot}COOH$,
Benzoic acid, $C_6H_5{\cdot}COOH$ (phenylformic acid).
Acetic acid, $CH_3{\cdot}COOH$,
Phenylacetic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$.
Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.
Butyric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$,
Phenylbutyric acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

With the exception of benzoic acid all the above aromatic acids are derived from the aromatic hydrocarbons by the substitution of carboxyl for hydrogen of the *side-chain*. They have not only the characteristic properties of aromatic compounds in general, but also those of fatty acids, and, like the latter, they may be converted into unsaturated compounds by loss of two or more atoms of hydrogen, giving rise to new series, as the following example will show:

Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
Acrylic acid, $CH_2{:}CH{\cdot}COOH$,
Phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$.
Propiolic acid, $CH{\vdots}C{\cdot}COOH$,
Phenylpropiolic acid, $C_6H_5{\cdot}C{\vdots}C{\cdot}COOH$.

Preparation.—Aromatic acids, containing the carboxyl-group in the side-chain, may be prepared by *carefully* oxidising the corresponding alcohols and aldehydes, and by hydrolysing the nitriles with alkalies or mineral acids,

$$C_6H_5{\cdot}CH_2{\cdot}CN + 2H_2O = C_6H_5{\cdot}CH_2{\cdot}COOH + NH_3,$$

but these methods are limited in application, owing to the difficulty of obtaining the requisite substances.

The most important general methods are: (*a*) By the reduction of the corresponding unsaturated acids, compounds which are prepared without much difficulty (p. 430),

$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH + 2H = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH\,;$$

and (*b*) by treating the sodium compound of ethyl malonate or of ethyl acetoacetate with the halogen derivatives of the aromatic hydrocarbons. As, in the latter case, the procedure is exactly similar to that employed in preparing fatty acids (part i. pp. 189, 194, and 198), one example only need be given—namely, the synthesis of phenylpropionic acid.

The sodium compound of ethyl malonate is heated with benzyl chloride, and the ethyl benzylmalonate which is thus produced,

$$C_6H_5{\cdot}CH_2Cl + CHNa(COOC_2H_5)_2 = \underset{\text{Ethyl Benzylmalonate.}}{C_6H_5{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2} + NaCl,$$

is hydrolysed with alcoholic potash. The benzylmalonic acid is then isolated, and heated at 200°, when it is converted into phenylpropionic acid, with loss of carbon dioxide,

$$C_6H_5{\cdot}CH_2{\cdot}CH(COOH)_2 = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2.$$

It should be remembered that only those halogen derivatives in which the halogen is in the *side-chain* can be employed in such syntheses, because when the halogen is united with the nucleus, as in monochlorotoluene, $C_6H_4Cl{\cdot}CH_3$, for example, no action takes place (compare p. 346).

The properties of two of the most typical acids of this class are described below.

Phenylacetic acid, or α-toluic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$, is prepared by boiling a solution of benzyl chloride (1 mol.) and potassium cyanide (1 mol.) in dilute alcohol for about three hours; the benzyl cyanide which is thus formed is purified by fractional distillation, and the fraction 220–235° (benzyl cyanide boils at 232°) is hydrolysed by boiling with dilute sulphuric acid, the product being purified by recrystallisation from water,

$$C_6H_5{\cdot}CH_2Cl \longrightarrow C_6H_5{\cdot}CH_2{\cdot}CN \longrightarrow C_6H_5{\cdot}CH_2{\cdot}COOH.$$

Phenylacetic acid melts at 76·5°, boils at 262°, and crystallises from boiling water in glistening plates; it has an agreeable, characteristic smell, and forms salts and derivatives just as do benzoic and acetic acids.

When oxidised with chromic acid it yields benzoic acid, a change very different to that undergone by the isomeric toluic acids (p. 423),

$$C_6H_5{\cdot}CH_2{\cdot}COOH + 3O = C_6H_5{\cdot}COOH + CO_2 + H_2O.$$

Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ (hydrocinnamic acid), is most conveniently prepared by reducing cinnamic acid (see below) with sodium amalgam,

$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH + 2H = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

Synthetically, it may be obtained from the product of the action of benzyl chloride on the sodium compound of ethyl malonate (p. 429). It crystallises from water in needles, melts at 47°, and distils at 280° without decomposition.

Cinnamic acid, or phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$, is closely related to phenylpropionic acid, and is one of the best-known *unsaturated* acids of the aromatic series. It occurs in large quantities in storax (*Styrax officinalis*), and may be easily obtained from this resin by warming it with soda; the filtered aqueous solution of sodium cinnamate is then acidified with hydrochloric acid, and the precipitated cinnamic acid purified by recrystallisation from boiling water.

Cinnamic acid is usually prepared synthetically by heating benzaldehyde with acetic anhydride and anhydrous sodium acetate, a process of condensation which is most simply expressed by the equation,

$$C_6H_5{\cdot}CHO + CH_3{\cdot}COOH = C_6H_5{\cdot}CH{:}CH{\cdot}COOH + H_2O.$$

A mixture of benzaldehyde (3 parts), acetic anhydride (10 parts), and anhydrous sodium acetate (3 parts) is heated to boiling in a flask placed in an oil-bath. After about eight hours the mixture is poured into water, and distilled in steam to separate the unchanged benzaldehyde; the residue is then treated with caustic soda, the hot alkaline solution filtered from oily and tarry impurities, and acidified with hydrochloric acid, the precipitated cinnamic acid being purified by recrystallisation from boiling water.

This method (Perkin's reaction) is a general one for the preparation of unsaturated aromatic acids, as by employing the anhydrides and sodium salts of other fatty acids, homologues of cinnamic acid are obtained. When, for example, benzaldehyde is treated with sodium propionate and propionic anhydride, *phenylmethylacrylic acid* (*α-methylcinnamic acid*), $C_6H_5{\cdot}CH{:}C(CH_3){\cdot}COOH$, is formed; *phenylisocrotonic acid*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, is not obtained by this reaction, because condensation always takes place between the aldehyde oxygen atom and the hydrogen atoms of that $-CH_2-$ group, which is directly united with the carboxyl-radicle.

Phenylisocrotonic acid may, however, be prepared by heating benzaldehyde with a mixture of sodium succinate and succinic anhydride,

$$C_6H_5{\cdot}CHO + COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH = C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH + CO_2 + H_2O.$$

It is a colourless, crystalline substance, which melts at 86°, and boils at 302°; at its boiling-point it is gradually converted into α-naphthol and water (p. 453).

Cinnamic acid crystallises from water in needles, and melts at 133°. Its chemical behaviour is in many respects similar to that of acrylic acid and other unsaturated fatty acids; it combines directly with bromine, for example, yielding *phenyl αβ-dibromopropionic acid*, $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$, and with hydrobromic acid, giving *phenyl-β-bromopropionic acid*, $C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}COOH$; on reduction with sodium amalgam it is converted into phenylpropionic acid (p. 430), just as acrylic acid is transformed into propionic acid.

When distilled with lime, cinnamic acid is decomposed into carbon dioxide, and *phenylethylene* or *styrolene*,* just as benzoic acid yields benzene,

$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH = C_6H_5{\cdot}CH{:}CH_2 + CO_2.$$

Concentrated nitric acid converts cinnamic acid into a mixture of about equal quantities of *o*- and *p-nitrocinnamic acids*, $C_6H_4(NO_2){\cdot}CH{:}CH{\cdot}COOH$, which may be separated by conversion into their ethyl salts, $C_6H_4(NO_2){\cdot}CH{:}CH{\cdot}COOC_2H_5$ (by means of alcohol and hydrogen chloride), and recrystallising these from alcohol, the sparingly soluble ethyl salt of the *p*-acid being readily separated from the readily soluble ethyl *o*-nitrocinnamate. From the pure ethyl salts the acids are then regenerated by hydrolysing with dilute sulphuric acid. They resemble cinnamic acid closely in properties, and combine directly with bromine, yielding the corresponding nitrophenyldibromopropionic acids, $C_6H_4(NO_2){\cdot}CHBr{\cdot}CHBr{\cdot}COOH$.

Phenylpropiolic acid, $C_6H_5{\cdot}C{\vdots}C{\cdot}COOH$, is obtained by treating phenyldibromopropionic acid, or, better, its ethyl salt, with alcoholic potash,

$$C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH = C_6H_5{\cdot}C{\vdots}C{\cdot}COOH + 2HBr,$$

a method which is exactly similar to that employed in preparing acetylene by the action of alcoholic potash on ethylene dibromide. It melts at 137°, and at higher temperatures, or when heated with water at 120°, it decomposes into carbon dioxide and *phenylacetylene*, a colourless liquid, which boils at 140°, and is closely related to acetylene in chemical properties,

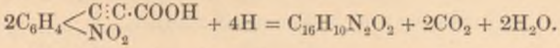
$$C_6H_5{\cdot}C{\vdots}C{\cdot}COOH = C_6H_5{\cdot}C{\vdots}CH + CO_2.$$

o-Nitrophenylpropiolic acid, $C_6H_4(NO_2){\cdot}C{\vdots}C{\cdot}COOH$, may be similarly prepared from *o*-nitrophenyldibromopropionic acid; it is a substance of great interest, as when treated with reducing agents,

---

* *Styrolene*, $C_6H_5{\cdot}CH{:}CH_2$, may be taken as a typical example of an aromatic hydrocarbon containing an unsaturated side-chain. It is a colourless liquid which boils at 145°, and in chemical properties shows the closest resemblance to ethylene, of which it is the phenyl substitution product. With bromine, for example, it yields a dibromadditive product, $C_6H_5{\cdot}CHBr{\cdot}CH_2Br$ (dibromethylbenzene), and when heated with hydriodic acid, it is reduced to ethylbenzene, $C_6H_5{\cdot}CH_2{\cdot}CH_3$.

such as hydrogen sulphide, or grape-sugar and potash, it is converted into indigo blue (Baeyer),



$$2C_6H_4\left\langle\begin{matrix}C{:}C\cdot COOH\\ NO_2\end{matrix}\right. + 4H = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O.$$

This method of preparation, however, is not of technical value, owing to the high price of phenylpropiolic acid.

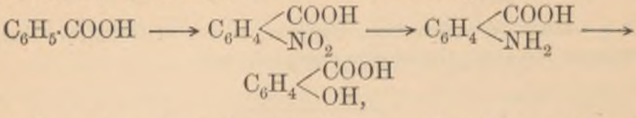
CHAPTER XXIX.

HYDROXYCARBOXYLIC ACIDS.

The hydroxy-acids of the aromatic series are derived from benzoic acid and its homologues, by the substitution of hydroxyl-groups for hydrogen atoms, just as glycollic acid, for example, is derived from acetic acid (part i. p. 225); like the simple hydroxy-derivatives of the hydrocarbons, they may be divided into two classes, according as the hydroxyl-group is united with carbon of the nucleus or of the side-chain. In the first case the hydroxyl-group has the same character as in phenols, and consequently hydroxy-acids, of this class, as, for example, the three (*o.m.p.*) hydroxybenzoic acids, $C_6H_4(OH)\cdot COOH$, are both phenols and carboxylic acids; in the second case, however, the hydroxyl-group has the same character as in alcohols, so that the compounds of this class, such as mandelic acid, $C_6H_5\cdot CH(OH)\cdot COOH$, have properties closely resembling those of the fatty hydroxy-acids; in other words, the differences between the two classes of aromatic hydroxy-acids are practically the same as those between phenols and alcohols.

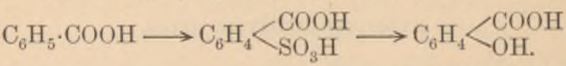
As those acids, which contain the hydroxyl-group united with carbon of the nucleus, form by far the more important class, the following statements refer to them only, except where stated to the contrary.

Preparation.—The hydroxy-acids may be prepared from the simple carboxylic acids, by reactions exactly similar to those employed in the preparation of phenols from hydrocarbons; that is to say, the acids are converted into nitro-compounds, then into amido-compounds, and the latter are treated with nitrous acid in the usual manner,



$$C_6H_5\cdot COOH \longrightarrow C_6H_4{<}\begin{matrix}COOH\\NO_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}COOH\\NH_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}COOH\\OH,\end{matrix}$$

or, the acids are heated with sulphuric acid, and the sulphonic acids obtained in this way are fused with potash,

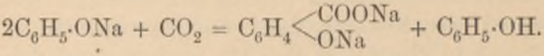


$$C_6H_5\cdot COOH \longrightarrow C_6H_4{<}\begin{matrix}COOH\\SO_3H\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}COOH\\OH.\end{matrix}$$

It must be borne in mind, however, that as the carboxyl-group of the acid determines the position taken up by the nitro- and sulphonic-groups (p. 352), only the *meta*-hydroxy-compounds are conveniently prepared in this way directly from the carboxylic acids.

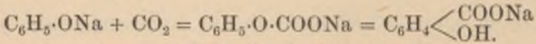
The *ortho*-hydroxy-acids, and in some cases the meta- and para-compounds, are most conveniently prepared from the phenols by one of the following methods:

The dry sodium compound of the phenol is heated at about 200° in a stream of carbon dioxide,



$$2C_6H_5\cdot ONa + CO_2 = C_6H_4{<}\begin{matrix}COONa\\ONa\end{matrix} + C_6H_5\cdot OH.$$

Under these conditions half the phenol distils over and is recovered; but if the sodium compound be first saturated with carbon dioxide under pressure, it is converted into an aromatic derivative of carbonic acid, which, when heated at about 130° under pressure, is completely transformed into a salt of the hydroxy-acid by molecular change,

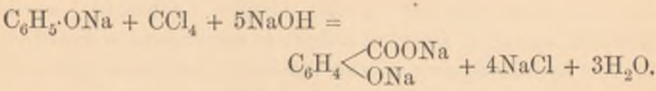


$$C_6H_5\cdot ONa + CO_2 = C_6H_5\cdot O\cdot COONa = C_6H_4{<}\begin{matrix}COONa\\OH.\end{matrix}$$

Sodium Phenylcarbonate.

Many dihydric and trihydric phenols may be converted into the corresponding hydroxy-acids, simply by heating them with ammonium carbonate or potassium bicarbonate; when resorcinol, for example, is treated in this way, it yields a mixture of isomeric *resorcylic acids*, $C_6H_3(OH)_2\cdot COOH$.

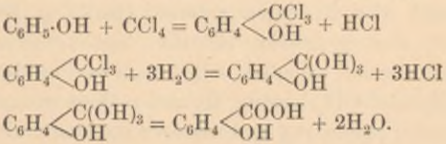
The second general method of preparing hydroxy-acids from phenols consists in boiling a strongly alkaline solution of the phenol with carbon tetrachloride; the principal product is the *ortho*-acid, but varying proportions of the *para*-acid are also formed,



$$C_6H_5{\cdot}ONa + CCl_4 + 5NaOH = C_6H_4{<}\begin{matrix}COONa\\ONa\end{matrix} + 4NaCl + 3H_2O.$$

After the substances have been heated together for some hours, the unchanged carbon tetrachloride is distilled off, the residue acidified, and the solution extracted with ether; the crude acid, obtained on evaporating the ethereal solution, is then separated from unchanged phenol by dissolving it in sodium carbonate, re-precipitated with a mineral acid, and purified by recrystallisation.

The above method is clearly analogous to Reimer's reaction (p. 409), and the changes which occur during the process may be assumed to be indicated by the following equations, in which water is represented instead of soda for the sake of simplicity:

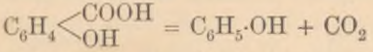


$$C_6H_5{\cdot}OH + CCl_4 = C_6H_4{<}\begin{matrix}CCl_3\\OH\end{matrix} + HCl$$

$$C_6H_4{<}\begin{matrix}CCl_3\\OH\end{matrix} + 3H_2O = C_6H_4{<}\begin{matrix}C(OH)_3\\OH\end{matrix} + 3HCl$$

$$C_6H_4{<}\begin{matrix}C(OH)_3\\OH\end{matrix} = C_6H_4{<}\begin{matrix}COOH\\OH\end{matrix} + 2H_2O.$$

Properties.—The hydroxy-acids are colourless, crystalline substances, more readily soluble in water and less volatile than the acids from which they are derived; many of them undergo decomposition on distillation, carbon dioxide being evolved; when heated with lime they are completely decomposed, with formation of phenols,



$$C_6H_4{<}\begin{matrix}COOH\\OH\end{matrix} = C_6H_5{\cdot}OH + CO_2$$

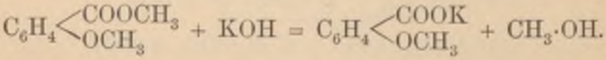
$$C_6H_3(OH)_2{\cdot}COOH = C_6H_4(OH)_2 + CO_2.$$

The *o*-acids, as, for example, salicylic acid, give, in neutral solution, a violet colouration with ferric chloride, whereas the *m*- and *p*-hydroxy-acids, such as the *m*- and *p*-hydroxybenzoic acids, give no colouration.

The chemical properties of the hydroxy-acids will be readily understood, when it is remembered that they are both phenols and carboxylic acids. As carboxylic acids they form salts by the displacement of the hydrogen atom of the carboxyl-group, such salts being obtained on treating with *carbonates* or with the calculated quantity of the metallic hydroxide; when, however, excess of *alkali hydroxide* is employed, the hydrogen of the hydroxyl-group is also displaced, just as in phenols. It is clear, therefore, that hydroxy-acids form both mono- and di-metallic salts, salicylic acid, for example, yielding the two sodium salts, $C_6H_4(OH)\cdot COONa$ and $C_6H_4(ONa)\cdot COONa$.

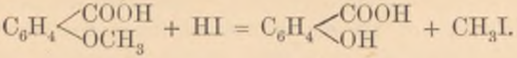
The di-metallic salts are decomposed by carbon dioxide, with formation of mono-metallic salts, just as the phenates are resolved into the phenols; the metal in combination with the carboxyl-group, however, cannot be displaced in this way.

The ethereal salts of the hydroxy-acids are prepared in the usual manner—namely, by saturating a solution of the acid in the alcohol with hydrogen chloride (part i. p. 187); by this treatment the hydrogen of the carboxyl-group only is displaced, normal ethereal salts, such as *methyl salicylate*, $C_6H_4(OH)\cdot COOCH_3$, being formed; these compounds have still phenolic properties, and dissolve in caustic alkalies, forming metallic derivatives, such as *methyl potassiosalicylate*, $C_6H_4(OK)\cdot COOCH_3$, which, when heated with alkyl halogen compounds, yield alkyl-derivatives, such as *methyl methylsalicylate*, $C_6H_4(OCH_3)\cdot COOCH_3$. On hydrolysing di-alkyl compounds of this kind with alcoholic potash, only the alkyl of the carboxyl-group is removed, methyl methylsalicylate, for example, yielding the potassium salt of *methylsalicylic acid*,



$$C_6H_4{<}\begin{array}{l}COOCH_3\\OCH_3\end{array} + KOH = C_6H_4{<}\begin{array}{l}COOK\\OCH_3\end{array} + CH_3\cdot OH.$$

The other alkyl-group is not eliminated even on boiling with alkalies, a behaviour which corresponds with that of the alkyl-group in derivatives of phenols, such as anisole, $C_6H_5\cdot OCH_3$ (p. 392); just, however, as anisole is decomposed into phenol and methyl iodide when heated with hydriodic acid, so methylsalicylic acid under similar conditions yields the hydroxy-acid,



$$C_6H_4{<}\begin{matrix}COOH\\OCH_3\end{matrix} + HI = C_6H_4{<}\begin{matrix}COOH\\OH\end{matrix} + CH_3I.$$

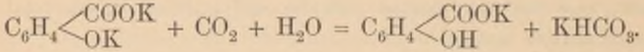
Salicylic acid, or *o*-hydroxybenzoic acid, $C_6H_4(OH){\cdot}COOH$, occurs in the blossom of *Spiræa ulmaria,* and is also found in considerable quantities, as methyl salicylate, in oil of wintergreen (*Gaultheria procumbens*). It used to be prepared, especially for pharmaceutical purposes, by hydrolysing this oil with potash; after boiling off the methyl alcohol (part i. p. 88), the solution is acidified with dilute sulphuric acid, and the precipitated salicylic acid purified by recrystallisation from water.

Salicylic acid may be obtained by oxidising salicylaldehyde (p. 409) or salicylic alcohol (saligenin, p. 404) with chromic acid, by treating *o*-amidobenzoic acid (anthranilic acid) with nitrous acid, and also by boiling phenol with soda and carbon tetrachloride.

It is now prepared on the large scale by treating sodium phenate with carbon dioxide under pressure, and then heating the *sodium phenylcarbonate,* $C_6H_5{\cdot}O{\cdot}COONa$, which is thus formed, at 120–140° under pressure, when it undergoes intramolecular change into sodium salicylate (p. 434).

Salicylic acid is sparingly soluble in cold (1 in 400 parts at 15°), but readily in hot, water, from which it crystallises in needles, melting at 156°; its neutral solutions give with ferric chloride an intense violet colouration. When rapidly heated it sublimes, and only slight decomposition occurs; but when distilled slowly, a large proportion decomposes into phenol and carbon dioxide, this change being complete if the acid be distilled with lime. All these properties serve for the detection of salicylic acid.

Salicylic acid is a powerful antiseptic, and, as it has no smell, it is frequently used as a disinfectant instead of phenol; it is also extensively employed in medicine and as a food preservative. The mono-metallic salts of salicylic acid, as, for example, *potassium salicylate*, $C_6H_4(OH)\cdot COOK$, and *calcium salicylate*, $\{C_6H_4(OH)\cdot COO\}_2Ca$, are prepared by neutralising a hot aqueous solution of the acid with metallic *carbonates*; they are, as a rule, soluble in water. The di-metallic salts, such as $C_6H_4(OK)\cdot COOK$ and $C_6H_4{<}\begin{smallmatrix}O\text{—}\\ COO\end{smallmatrix}{>}Ba$, are obtained in a similar manner, employing excess of the metallic *hydroxides*; with the exception of the salts of the alkali metals, these di-metallic compounds are insoluble; they are all decomposed by carbon dioxide, with formation of the mono-metallic salts,



$$C_6H_4{<}\begin{matrix}COOK\\OK\end{matrix} + CO_2 + H_2O = C_6H_4{<}\begin{matrix}COOK\\OH\end{matrix} + KHCO_3.$$

Methyl salicylate, $C_6H_4(OH)\cdot COOCH_3$, prepared in the manner described (p. 436), or by distilling a mixture of salicylic acid, methyl alcohol, and sulphuric acid (part i. p. 188), is an agreeably-smelling oil, boiling at 224°; *ethyl salicylate*, $C_6H_4(OH)\cdot COOC_2H_5$, boils at 223°.

Methyl methylsalicylate, $C_6H_4(OCH_3)\cdot COOCH_3$, is formed when methyl salicylate is heated with methyl iodide and alcoholic potash (1 mol.); it is an oil boiling at 228°.

Methylsalicylic acid, $C_6H_4(OCH_3)\cdot COOH$, is obtained when its methyl salt is hydrolysed with potash; it is a crystalline substance, melting at 98·5°, and when heated with hydriodic acid it is decomposed, giving salicylic acid and methyl iodide; the other halogen acids have a similar action.

m-Hydroxybenzoic acid is prepared by fusing *m*-sulphobenzoic acid with potash, and also by the action of nitrous acid on *m*-amidobenzoic acid (p. 422). It melts at 200°, gives no colouration with ferric chloride, and when distilled with lime it is decomposed into phenol and carbon dioxide.

p-Hydroxybenzoic acid is formed, together with salicylic acid, by the action of carbon tetrachloride and soda on phenol; it may also be obtained from *p*-sulphobenzoic acid by fusion with potash, or by the action of nitrous acid on *p*-amidobenzoic acid.

It is prepared by heating potassium phenate in a stream of carbon dioxide at 220° as long as phenol distils over; if, however, the temperature be kept below 150°, potassium salicylate is formed; the residue is dissolved in water, the acid precipitated from the filtered solution by adding hydrochloric acid, and purified by recrystallisation from water. *p*-Hydroxybenzoic acid melts at 210°, and is completely decomposed on distillation into phenol and carbon dioxide; its aqueous solution gives no colouration with ferric chloride.

Anisic acid, *p*-methoxybenzoic acid, $C_6H_4(OCH_3)\cdot COOH$, is obtained by oxidising *anethole*, $C_6H_4(OCH_3)\cdot CH{:}CH\cdot CH_3$ (the principal constituent of oil of aniseed) with chromic acid, when the group $-CH{:}CH\cdot CH_3$ is converted into $-COOH$ (p. 410); it may also be prepared from *p*-hydroxybenzoic acid by a series of reactions analogous to those employed in the formation of methylsalicylic acid from salicylic acid (see above). Anisic acid melts at 185°, and when distilled with lime it is decomposed, with formation of anisole (p. 392); when heated with fuming hydriodic acid, it yields *p*-hydroxybenzoic acid and methyl iodide.

There are six *dihydroxybenzoic acids*, $C_6H_3(OH)_2\cdot COOH$, two of which are derived from catechol, three from resorcinol, and one from hydroquinone; the most important of these is **protocatechuic acid,** [OH:OH:COOH = 1:2:4], one of the two isomeric catecholcarboxylic acids. This compound is formed on fusing many resins, such as catechu and gum benzoïn, and also certain alkaloids, with potash, and it may be prepared synthetically by heating catechol with water and ammonium carbonate at 140°.

It crystallises from water, in which it is very soluble, in needles, melts at 199°, and when strongly heated it is decomposed into catechol and carbon dioxide; its aqueous solution gives with ferric chloride a green solution, which becomes violet and then red on the addition of sodium bicarbonate.

Gallic acid, or pyrogallolcarboxylic acid,

$$C_6H_2(OH)_3\cdot COOH\ [OH{:}OH{:}OH{:}COOH = 1{:}2{:}3{:}5],$$

is a trihydroxybenzoic acid; it occurs in gall-nuts, tea, and many other vegetable products, and is best prepared by boiling *tannin* (see below) with dilute acids. It crystallises in needles, and melts at 220°, being at the same time resolved into pyrogallol (p. 400) and carbon dioxide; it is readily soluble in water, and its aqueous solution gives with ferric chloride a bluish-black precipitate. Gallic acid is a strong reducing agent, and precipitates gold, silver, and platinum from solutions of their salts.

Tannin, digallic acid, or tannic acid, $C_{14}H_{10}O_9$, occurs in large quantities in gall-nuts, and in all kinds of bark, from which it may be extracted with boiling water. It is an almost colourless, amorphous substance, and is readily soluble in water; its solution possesses a very astringent taste, and gives with ferric chloride an intense dark-blue solution, for which reason tannin is largely used in the manufacture of inks.

When boiled with dilute sulphuric acid, tannin is completely converted into gallic acid, a fact which shows that it is the anhydride of this acid,

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Tannin is used largely in dyeing as a mordant, owing to its property of forming insoluble coloured compounds with many dyes. It is also extensively employed in 'tanning;' when animal skin or membrane is placed in a solution of tannin, or in contact with moist bark containing tannin, it absorbs and combines with the tannin, and is converted into a much tougher material; such tanned skins constitute leather.

Mandelic acid, $C_6H_5{\cdot}CH(OH){\cdot}COOH$ (phenylglycollic acid), is an example of an aromatic hydroxy-acid containing the hydroxyl-group in the *side-chain.* It may be obtained by boiling amygdalin (which yields benzaldehyde, hydrogen cyanide, and glucose, p. 405) with hydrochloric acid, but it is usually prepared by treating benzaldehyde with hydrocyanic acid and hydrolysing the resulting hydroxycyanide, a method analogous to that employed in the synthesis of lactic acid from aldehyde (part i. p. 139),

$$C_6H_5{\cdot}CHO + HCN = C_6H_5{\cdot}CH(OH){\cdot}CN$$
$$C_6H_5{\cdot}CH(OH){\cdot}CN + 2H_2O = C_6H_5{\cdot}CH(OH){\cdot}COOH + NH_3.$$

Mandelic acid melts at 133°, is moderately soluble in water, and shows in many respects the greatest resemblance to lactic acid (methylglycollic acid); when heated with hydriodic acid, for example, it is reduced to phenylacetic acid (p. 429), just as lactic acid is reduced to propionic acid (part i. p. 227),

$$C_6H_5{\cdot}CH(OH){\cdot}COOH + 2HI = C_6H_5{\cdot}CH_2{\cdot}COOH + I_2 + H_2O.$$

The character of the hydroxyl-group in mandelic acid is, in fact, quite similar to that of the hydroxyl-group in the fatty hydroxy-acids and in the alcohols, so that there are many points of difference between mandelic acid and acids, such as salicylic acid, which contain the hydroxyl-group united with carbon of the nucleus; when, for example, *ethyl mandelate*, $C_6H_5{\cdot}CH(OH){\cdot}COOC_2H_5$, is treated with caustic alkalies, it does not yield an alkali derivative, although the hydrogen of the hydroxyl-group is displaced on treating with sodium or potassium.

Mandelic acid, like lactic acid, contains an asymmetric carbon atom (p. 533), and can, therefore, exist in three optically different forms. The synthetical acid is optically inactive—that is to say, it is a mixture of the dextro- and levo-rotatory acids, but the acid prepared from amygdalin is levo-rotatory. The dextro-rotatory acid may be obtained by growing the organism *Penicillium glaucum* in a solution of the inactive acid under suitable conditions, when the levo-rotatory acid is destroyed, the dextro-rotatory acid remaining (p. 544).

CHAPTER XXX.

NAPHTHALENE AND ITS DERIVATIVES.

All the aromatic hydrocarbons hitherto described, with the exception of diphenyl, diphenylmethane, and triphenylmethane (p. 340), contain only one closed-chain of six carbon atoms, and are very closely and directly related to benzene; most of them may be prepared from benzene by comparatively simple reactions, and reconverted into this hydrocarbon, perhaps even more readily, so that they may all be classed as simple benzene derivatives. The exceptions just mentioned are also, strictly speaking, derivatives of benzene, although at the same time they may be regarded as hydrocarbons of quite another class, since diphenyl and diphenylmethane contain two, and triphenylmethane three, closed-chains of six carbon atoms. There are, in fact, numerous classes or types of aromatic hydrocarbons, and, just as benzene is the first member of a homologous series and the parent substance of a vast number of derivatives, so also these other hydrocarbons form the starting-points of new homologous series and of derivatives of a different type.

The hydrocarbons naphthalene and anthracene, which are now to be described, are perhaps second only to benzene in importance; each forms the starting-point of a great number of compounds, many of which are extensively employed in the manufacture of dyes.

Naphthalene, $C_{10}H_8$, occurs in coal-tar in larger quantities than any other hydrocarbon, and is easily isolated from this source in a pure condition; the crystals of crude naphthalene, which are deposited on cooling from the fraction of coal-tar passing over between 170 and 230° (p. 297), are first pressed to get rid of liquid impurities, and then warmed with a small quantity of concentrated sulphuric acid, which converts most of the foreign substances into non-volatile sulphonic acids;

the naphthalene is then distilled in steam, or sublimed, and is thus obtained almost chemically pure.

Naphthalene crystallises in large, lustrous plates, melts at 80°, and boils at 218°. It has a highly characteristic smell, and is extraordinarily volatile, considering its high molecular weight, so much so, in fact, that only part of the naphthalene in crude coal-gas is deposited in the condensers (p. 295), the rest being carried forward into the purifiers, and even into the gas-mains, in which it is deposited in crystals in cold weather, principally at the bends of the pipes, frequently causing stoppages. It is insoluble in water, but dissolves freely in hot alcohol and ether, from either of which it may be crystallised. Like many other aromatic hydrocarbons, it combines with picric acid, when the two substances are dissolved together in alcohol, forming *naphthalene picrate*, a yellow crystalline compound of the composition,

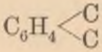
$$C_{10}H_8,C_6H_2(NO_2)_3{\cdot}OH,$$

which melts at 149°.

As the vapour of naphthalene burns with a highly luminous flame, the hydrocarbon is used to some extent for carburetting coal-gas—that is to say, for increasing its illuminating power; for this purpose the gas is passed through a vessel which contains coarsely-powdered naphthalene, gently heated by the gas flame, so that the hydrocarbon volatilises and burns with the gas. The principal use of naphthalene, however, is for the manufacture of a number of derivatives which are employed in the colour industry.

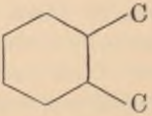
Constitution.—Naphthalene has the characteristic properties of an aromatic compound—that is to say, its behaviour under various conditions is similar to that of benzene and its derivatives, and different from that of fatty compounds; when treated with nitric acid, for example, it yields a nitro-derivative, and with sulphuric acid it gives sulphonic acids. This similarity between benzene and naphthalene at once suggests a resemblance in constitution, a view which is confirmed by the fact that naphthalene, like benzene, is a very stable substance, and is resolved into simpler substances only with difficulty. When, however, naphthalene is boiled with dilute nitric or chromic acid, it is slowly oxidised, yielding carbon dioxide and (*ortho*)-phthalic acid, $C_6H_4(COOH)_2$.

Now the formation of phthalic acid in this way is a fact of very great importance, since it is a proof that naphthalene contains the group,



$$C_6H_4{<}\begin{array}{l}C\\C\end{array}$$

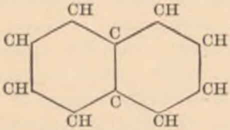
or



that is to say, that it contains a benzene nucleus to which two carbon atoms are united in the ortho-position to one another. Nevertheless, further evidence is required in order to arrive at the constitution of the hydrocarbon, since there are still two carbon and four hydrogen atoms to be accounted for, and there are many different ways in which these might be united with the $C_6H_4{<}\begin{array}{l}C\\C\end{array}$ group.

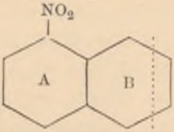
Clearly, therefore, it is important to ascertain the structure of that part of the naphthalene molecule which has been oxidised to carbon dioxide and water—to obtain, if possible, some simple decomposition product in which these carbon and hydrogen atoms are retained in their original state of combination.

Now this can be done in the following way: When nitronaphthalene, $C_{10}H_7 \cdot NO_2$, a simple mono-substitution product of the hydrocarbon, is boiled with dilute nitric acid, it yields nitrophthalic acid, $C_6H_3(NO_2)(COOH)_2$; therefore, again, naphthalene contains a benzene nucleus, and the nitro-group in nitronaphthalene is combined with this nucleus. If, however, the *same* nitronaphthalene be reduced to amidonaphthalene, $C_{10}H_7 \cdot NH_2$, and the latter oxidised, phthalic acid (and not amidophthalic acid) is obtained; this fact can only be explained by assuming either that the benzene nucleus, which is known to be united with the amido-group, has been destroyed, or that the amido-group has been displaced by hydrogen during oxidation. Since, however, the latter alternative is contrary to all experience, the former must be accepted, and it is clear that the benzene nucleus which is contained in the oxidation product of amidonaphthalene is not the same as that present in the oxidation product of nitronaphthalene; in other words, different parts of the naphthalene molecule have been oxidised to carbon dioxide and water in the two cases, and yet in both the group $C_6H_4{<}^{C}_{C}$ remains. The constitution of naphthalene must therefore be expressed by the formula

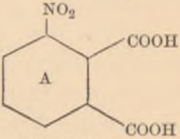


This will be evident if the above changes be expressed with the aid of this formula. When nitronaphthalene is oxidised, the nucleus B (see below), which does not contain the nitro-group, is destroyed, as indicated by the dotted lines, the product being nitrophthalic acid; when, on the other hand, amidonaphthalene is oxidised, the nucleus A, combined with the amido-group, is attacked and destroyed in preference to the other, and phthalic acid is formed,

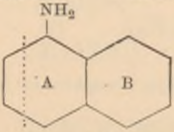

Naphthalene.



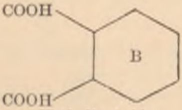
Nitronaphthalene.



Nitrophthalic Acid.



Amidonaphthalene.

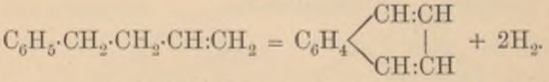


Phthalic Acid.

The constitution of naphthalene was first established in this way by Graebe in 1880, although the above formula had been suggested by Erlenmeyer as early as 1866; that the hydrocarbon is composed of two benzene nuclei partially superposed or *condensed* together in the *o*-position, as shown above, has since been confirmed by syntheses of its derivatives, but even more conclusively by the study of the isomerism of its substitution products.

The difficulty of determining and of expressing the actual state or disposition of the fourth affinity of each of the carbon atoms in naphthalene is just as great as in the case of benzene. If the carbon atoms be represented as united by alternate double linkings, as in the formula on the left-hand side (see below), there is the objection that they do not show, as indicated, the behaviour of carbon atoms in fatty unsaturated compounds, as explained more fully in the case of benzene. For this reason the formula on the right-hand side (see below) has been suggested as perhaps preferable, the lines drawn towards the centres of the nuclei having the same significance as in the centric formula for benzene (p. 307). The simple, double-hexagon formula given above is usually employed for the sake of convenience.

Naphthalene may be obtained synthetically by passing the vapour of phenylbutylene, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$* (or of phenylbutylene dibromide, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$), over red-hot lime, the change being a process of destructive distillation, accompanied by loss of hydrogen, similar to, but much simpler than that which occurs in the formation of other aromatic from fatty hydrocarbons (p. 300),



$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 = C_6H_4\left<\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\right. + 2H_2.$$

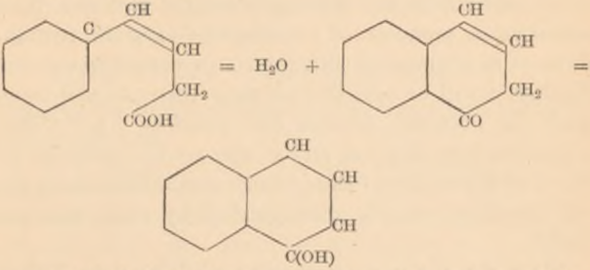
---

* *Phenylbutylene* is obtained by treating a mixture of benzyl chloride and allyl iodide with sodium,

$$C_6H_5{\cdot}CH_2Cl + CH_2I{\cdot}CH{:}CH_2 + 2Na = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + NaCl + NaI.$$

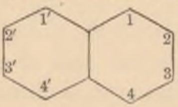
It is a liquid, boiling at 178°, and, like butylene (part i. p. 79), it combines directly with one molecule of bromine, yielding the dibromide.

A most important synthesis of naphthalene was accomplished by Fittig, who showed that α-naphthol (α-hydroxynaphthalene) is formed on boiling phenylisocrotonic acid (p. 431) with water. This change probably takes place in two stages, the first product being a keto-derivative of naphthalene, which passes into α-naphthol by intramolecular change (compare part i. p. 195),

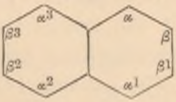


The α-naphthol thus obtained is converted into naphthalene on distillation with zinc-dust, just as phenol is transformed into benzene (p. 331).

Isomerism of Naphthalene Derivatives.—As in the case of benzene, the study of the isomerism of the substitution products of naphthalene affords the most convincing evidence that the accepted constitutional formula is correct. In the first place, naphthalene differs from benzene in yielding two different series of mono-substitution products; there are, for example, two monochloronaphthalenes, two monohydroxynaphthalenes, two mononitronaphthalenes, &c. This fact is readily accounted for, as, on considering the constitutional formula of naphthalene, which may be conveniently written



or



numbered or lettered as shown (the symbols C and H being omitted for the sake of simplicity), it will be evident that the eight hydrogen atoms are not all similarly situated relatively to the rest of the molecule. If, for example, the hydrogen atom (1) were displaced by chlorine, hydroxyl, &c., the substitution product would be isomeric, but not identical with that produced by the displacement of the hydrogen atom (2). In the first case, the substituting atom or group would be united with a carbon atom which is itself directly united with a carbon atom common to both nuclei, whereas in the other case this would not be so. Clearly, then, the fact that the mono-substitution products of naphthalene exist in two isomeric forms is in accordance with the above constitutional formula. Further, it will be seen that not more than two such isomerides could be obtained, because the positions 1.4.1′.4′ (the four α-positions) are identical, and so also are the positions 2.3.2′.3′ (the four β-positions); the isomeric mono-substitution products are, therefore, usually distinguished by using the letters α and β.

When *two* hydrogen atoms in naphthalene are displaced by two identical groups or atoms, *ten* isomeric di-derivatives may be obtained. Denoting the positions of the substituents by the system of numbering shown above, these isomerides would be

1:2, 1:3, 1:4, 1:4′, 1:3′, 1:2′, 1:1′, 2:3, 2:3′, 2:2′,

all other possible positions being identical with one of these; 2:4′, for example, is the same as 1:3′, 2′:4 and 3:1′, and 1′:4 is identical with 1:4′. The constitution of such a di-derivative is usually expressed with the aid of numbers, as it is necessary to show whether the substituents are combined with the same, or with different, nuclei.

When the two atoms or groups are present in the same nucleus, their relative position is similar to the *o*-, *m*-, or *p*-position in benzene. The positions 1:2, 2:3, and 3:4 correspond with the ortho-, 1:3, and 2:4, with the meta-, and 1:4 with the para-position, and similarly in the case of the other nucleus. The position 1:1′ or 4:4′, however, is different from any of these, and is termed the *peri*-position; groups thus situated behave in much the same way as those in the *o*-position in the benzene and naphthalene nuclei.

Derivatives of Naphthalene.

The *homologues of naphthalene*—that is to say, its *alkyl substitution products*, are of comparatively little importance, but it may be mentioned that they may be prepared from the parent hydrocarbon by methods similar to those employed in the case of the corresponding benzene derivatives, as, for example, by treating naphthalene with alkyl halogen compounds and aluminium chloride,

$$C_{10}H_8 + C_2H_5I = C_{10}H_7{\cdot}C_2H_5 + HI,$$

and by treating the bromonaphthalenes with an alkyl halogen compound and sodium,

$$C_{10}H_7Br + CH_3Br + 2Na = C_{10}H_7{\cdot}CH_3 + 2NaBr.$$

α-Methylnaphthalene, $C_{10}H_7{\cdot}CH_3$, is a colourless liquid, boiling at 240–242°, but *β-methylnaphthalene* is a solid, melts at 32°, and boils at 242°; both these hydrocarbons occur in coal-tar.

The *halogen mono-substitution products* of naphthalene are also of little importance. They may be obtained by treating the hydrocarbon, at its boiling-point, with the halogens (chlorine and bromine), but only the α-derivatives are formed in this way. Both the α- and the β-compounds may be obtained by treating the corresponding naphthols (p. 452), or, better, the naphthalenesulphonic acids (p. 455) with pentachloride or pentabromide of phosphorus,

$$C_{10}H_7{\cdot}SO_2Cl + PCl_5 = C_{10}H_7Cl + POCl_3 + SOCl_2,$$

or by converting the naphthylamines (p. 452) into the corresponding diazo-compounds, and decomposing the latter with a halogen cuprous salt (p. 372),

$$C_{10}H_7{\cdot}NH_2 \longrightarrow C_{10}H_7{\cdot}N{:}NCl \longrightarrow C_{10}H_7Cl.$$

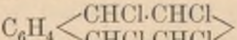
All these methods correspond with those described in the case of the halogen derivatives of benzene, and are carried out practically in a similar manner.

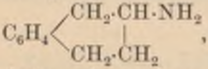
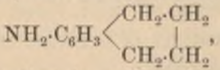
α-Chloronaphthalene, $C_{10}H_7Cl$, is a liquid, boiling at about

263°, but the *β-derivative* is a crystalline substance, melting at 56°, and boiling at 264°.

a-Bromonaphthalene, $C_{10}H_7Br$, is also a liquid, which boils at 280°, but the *β-derivative* is crystalline, and melts at 68°.

The chemical properties of these, and of other halogen derivatives of naphthalene, are similar to those of the halogen derivatives of benzene; the halogen atoms are very firmly combined, and are not displaced by hydroxyl-groups on boiling with alkàlies, &c.

Naphthalene tetrachloride, $C_{10}H_8Cl_4$, is an important halogen *additive product*, which is produced on passing chlorine into a vessel containing coarsely-powdered naphthalene at ordinary temperatures. It forms large colourless crystals, melts at 182°, and is converted into *dichloronaphthalene* $C_{10}H_6Cl_2$ (a substitution product), when heated with alcoholic potash; it is readily oxidised by nitric acid, yielding phthalic and oxalic acids, a fact which shows that all the chlorine atoms are present in one and the same nucleus; the constitution of the compound is therefore expressed by the formula  $C_6H_4\left<\begin{array}{l}CHCl\cdot CHCl\\CHCl\cdot CHCl\end{array}\right>$

The formation of this additive product shows that naphthalene, like benzene, is not really a saturated compound, although it usually behaves as such; other compounds, formed by the addition of four atoms of hydrogen to naphthalene or to a naphthalene derivative, are known, and experience has shown that when one of the nuclei is thus fully reduced, the atoms or groups of which it is composed acquire the character which they have in fatty compounds, whereas the unreduced nucleus retains the character of that in benzene. The amido-group in the *tetrahydro-β-naphthylamine* of the constitution  $C_6H_4\left<\begin{array}{l}CH_2\cdot CH\cdot NH_2\\ \quad\quad |\\CH_2\cdot CH_2\end{array}\right.$, for example, has the same character as that in fatty amines, whereas in the case of the isomeric *tetrahydro-β-naphthylamine*,  $NH_2\cdot C_6H_3\left<\begin{array}{l}CH_2\cdot CH_2\\ \quad\quad |\\CH_2\cdot CH_2\end{array}\right.$, the amido-group has the same properties as that in aniline, because it is combined with the unreduced nucleus.

Nitro-derivatives.—Naphthalene, like benzene, is readily acted on by concentrated nitric acid, yielding nitro-derivatives, one, two, or more atoms of hydrogen being displaced according to the concentration of the acid employed and the temperature at which the reaction is carried out; the presence of sulphuric acid facilitates nitration for reasons already mentioned. The chemical properties of the nitro-naphthalenes are in all respects similar to those of the nitro-benzenes.

α-**Nitronaphthalene,** $C_{10}H_7{\cdot}NO_2$, is best prepared in small quantities by dissolving naphthalene in acetic acid, adding concentrated nitric acid, and then heating on a water-bath for half an hour; the product is poured into water, and the nitronaphthalene purified by recrystallisation from alcohol. On the large scale it is prepared by treating naphthalene with nitric and sulphuric acids, the method being similar to that employed in the case of nitrobenzene. It crystallises in yellow prisms, melts at 61°, and boils at 304°; on oxidation with nitric acid, it yields nitrophthalic acid (p. 445).

β-**Nitronaphthalene** is not formed on nitrating naphthalene, but it may be prepared by dissolving β-nitro-α-naphthylamine (a compound obtained on treating α-naphthylamine with *dilute* nitric acid) in an alcoholic solution of hydrogen chloride, adding finely-divided sodium nitrite, and then heating the solution of the diazo-compound (compare p. 371),

$$C_{10}H_6(NO_2){\cdot}N{:}NCl + C_2H_5{\cdot}OH = C_{10}H_7{\cdot}NO_2 + N_2 + HCl + C_2H_4O.$$

It crystallises in yellow needles, melting at 79°.

The **amido-derivatives** of naphthalene are very similar in properties to the corresponding benzene derivatives, except that even the monamido-compounds are crystalline solids; they have a neutral reaction to litmus, and yet are distinctly basic in character, since they neutralise acids, forming salts, which, however, are decomposed by the hydroxides and carbonates of the alkalies. These amido-compounds, moreover, may be converted into diazo-compounds, amidoazo-compounds, &c., by reactions similar to those employed in the case of the amido-benzenes, and many of the substances obtained in this way, as well as the amido-compounds themselves, are extensively employed in the manufacture of dyes.

α-**Naphthylamine**, $C_{10}H_7{\cdot}NH_2$, may be obtained by heating α-naphthol with ammonio-zinc chloride, or ammonio-calcium chloride,*

$$C_{10}H_7{\cdot}OH + NH_3 = C_{10}H_7{\cdot}NH_2 + H_2O,$$

but it is best prepared by reducing α-nitronaphthalene with iron-filings and acetic acid,

$$C_{10}H_7{\cdot}NO_2 + 6H = C_{10}H_7{\cdot}NH_2 + 2H_2O.$$

It is a colourless, crystalline substance, melting at 50°, and boiling at 300°; it has a disagreeable smell, turns red on exposure to the air, and its salts give a blue precipitate with ferric chloride and other oxidising agents. On oxidation with a boiling solution of chromic acid, it is first converted into α-naphthaquinone (p. 455), and then into phthalic acid.

β-**Naphthylamine** is not prepared from β-nitronaphthalene (as this substance is itself only obtained with difficulty), but from β-naphthol, as described in the case of the α-compound. It crystallises in colourless plates, melts at 112°, and boils at 294°; it differs markedly from α-naphthylamine in having only a faint odour, and its salts give no colouration with ferric chloride. On oxidation with potassium permanganate, it yields phthalic acid.

The two **naphthols**, or monohydroxy-derivatives of naphthalene, correspond with the monohydric phenols, and

---

* Prepared by passing ammonia over anhydrous zinc or calcium chloride. These compounds decompose when heated, evolving ammonia, and are, therefore, conveniently employed in many reactions requiring the presence of ammonia at high temperatures; the zinc or calcium chloride resulting from their decomposition also favours the reaction in those cases in which water is formed, as both substances are powerful dehydrating agents. Ammonium acetate may be employed for a similar purpose, as it dissociates at comparatively low temperatures, but its action is less energetic.

are compounds of considerable importance, as they are extensively employed in the colour industry. They both occur in coal-tar, but only in small quantities, and are, therefore, prepared either by diazotising the corresponding naphthylamines,

$$C_{10}H_7{\cdot}NH_2 \longrightarrow C_{10}H_7{\cdot}N{:}NCl \longrightarrow C_{10}H_7{\cdot}OH,$$

or by fusing the corresponding sulphonic acids with potash (compare p. 387),

$$C_{10}H_7{\cdot}SO_3K + KOH = C_{10}H_7{\cdot}OH + K_2SO_3.$$

Their properties are, on the whole, very similar to those of the phenols, and, like the latter, they dissolve in alkalies, yielding metallic derivatives, which are decomposed by carbon dioxide; the hydrogen of the hydroxyl-group in the naphthols may also be displaced by an acetyl-group or by an alkyl-group, just as in phenols, and on treatment with pentachloride or pentabromide of phosphorus, a halogen atom is substituted for the hydroxyl-group. The naphthols further resemble the phenols in giving a colour reaction with ferric chloride.

In a few respects, however, there are certain differences between the chemical properties of the naphthols and phenols, inasmuch as the hydroxyl-groups in the former more readily undergo change; when, for example, a naphthol is heated with ammonio-zinc chloride at 250°, it is converted into the corresponding amido-compound (see above), whereas the conversion of phenol into aniline requires a temperature of 300–350°, other conditions remaining the same. Again, when a naphthol is heated with an alcohol and hydrogen chloride, it is converted into an alkyl-derivative, whereas alkyl-derivatives of phenols cannot, as a rule, be obtained in this way; in this respect, the naphthols form, as it were, a connecting-link between the phenols and the alcohols.

α-**Naphthol**, $C_{10}H_7{\cdot}OH$, is formed, as previously stated (p. 447), on boiling phenylisocrotonic acid with water, an important synthesis, which proves that the hydroxyl-group is in the *α*-position; it is prepared from *α*-naphthylamine or from naphthalene-*α*-sulphonic acid (see above). It is a colourless, crystalline substance, melting at 94°, and boiling at 280°; it has a faint smell, recalling that of phenol, and it dissolves freely in alcohol and ether, but is only sparingly soluble in hot water. Its aqueous solution gives with ferric chloride a violet, flocculent precipitate, consisting probably of an iron compound of *α-dinaphthol*, $OH \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$, an oxidation product of the naphthol.

α-Naphthol, like phenol, is very readily acted on by nitric acid, yielding a *dinitro*-derivative, $C_{10}H_5(NO_2)_2 \cdot OH$, which crystallises in yellow needles, and melts at 138°; this nitro-compound, like picric acid, has a much more strongly marked acid character than the hydroxy-compound from which it is derived, and decomposes carbonates, forming deep-yellow salts which dye silk a beautiful golden yellow; its sodium derivative, $C_{10}H_5(NO_2)_2 \cdot ONa + H_2O$, is known commercially as *Martius' yellow*, or *naphthalene yellow*. Another dye obtained from α-naphthol is *naphthol yellow* (p. 527), the potassium salt of dinitro-α-naphtholsulphonic acid, $C_{10}H_4(NO_2)_2(OK) \cdot SO_3K$; the acid itself is manufactured by nitrating α-naphtholtrisulphonic acid (prepared by heating α-naphthol with anhydrosulphuric acid), in which process two of the sulphonic groups are displaced by nitro-groups.

β-**Naphthol**, prepared by fusing naphthalene-β-sulphonic acid with potash (p. 453), melts at 122°, and boils at 285°; it is a colourless, crystalline compound, readily soluble in hot water, and like the α-derivative, it has a faint phenol-like smell. Its aqueous solution gives, with ferric chloride, a green colouration and a flocculent precipitate of β-dinaphthol, $OH \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$.

Sulphonic Acids.—Perhaps the most important derivatives of naphthalene, from a commercial point of view, are the various mono- and di-sulphonic acids, which are obtained from the hydrocarbon itself, from the naphthylamines, and from the naphthols, many of these compounds being used in large quantities in the manufacture of dyes. It would be impossible to give here even the names of the very numerous compounds of this class, but some indication of their properties may be afforded by the following statements:

Naphthalene is readily sulphonated, yielding two *monosulphonic acids*, $C_{10}H_7 \cdot SO_3H$, namely, the α- and β-compounds, both of which are formed when the hydrocarbon is heated with concentrated sulphuric acid at 80°; if, however, the operation be carried out at 160°, only the β-acid is obtained, because at this temperature the α-acid is converted into the β-acid by intramolecular change, just as phenol-*o*-sulphonic acid is transformed into the *p*-acid by heating. The two naphthalenesulphonic acids are crystalline hygroscopic substances, and show all the characteristic properties of acids of this class.

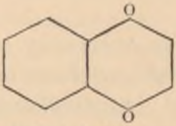
Di- and tri-sulphonic acids may be obtained by strongly heating naphthalene with sulphuric or anhydrosulphuric acid.

Fourteen isomeric *naphthylaminemonosulphonic acids*, $C_{10}H_6(NH_2) \cdot SO_3H$, may theoretically be obtained—namely, seven from α-naphthylamine, and seven from the β-base; as a matter of fact, nearly all these acids are known. One of the most important, perhaps, is 1:4-naphthylaminemonosulphonic acid, or *naphthionic acid*, which is the sole product of the action of sulphuric acid on α-naphthylamine; it is a crystalline compound, very sparingly soluble in cold water, and is used in the manufacture of Congo-red (p. 526), and other dyes.

The *naphtholmonosulphonic acids* correspond in number with the naphthylaminemonosulphonic acids, and are also extensively used in the colour industry.

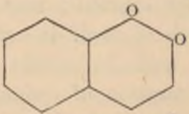
α-**Naphthaquinone**, $C_{10}H_6O_2$, is a derivative of naphthalene corresponding with (benzo)quinone, and, like the latter, it is formed on oxidising various mono- and di-substitution products of the hydrocarbon with sodium bichromate and sulphuric acid, but only those in which the substituting groups occupy the α-positions; α-naphthylamine, 1:4-amidonaphthol, and 1:4-diamidonaphthalene, for example, may be employed. As a rule, however, naphthalene itself is oxidised with a boiling solution of chromic acid in acetic acid (a method not applicable for the preparation of quinone from benzene), as the product is then easily obtained in a state of purity.

α-Naphthaquinone crystallises from alcohol in deep-yellow needles, melting at 125°; it resembles quinone in colour, in having a curious pungent smell, and in being very volatile, subliming readily even at 100°, and distilling rapidly in steam. Like quinone, moreover, it is readily reduced by sulphurous acid, yielding 1:4-dihydroxynaphthalene, $C_{10}H_6(OH)_2$, just as quinone yields hydroquinone (p. 399). This close similarity in properties clearly points to a similarity in constitution, so that α-naphthaquinone may be represented by the formula,



for reasons similar to those stated more fully in the case of quinone.

β-Naphthaquinone, $C_{10}H_6O_2$, isomeric with the α-compound, is formed when α-amido-β-naphthol is oxidised with potassium bichromate and dilute sulphuric acid, or with ferric chloride; it crystallises in red needles, decomposes at about 115° without melting, and on reduction with sulphurous acid, is converted into 1:2-dihydroxynaphthalene. It differs from α-naphthaquinone and from quinone in colour, in having no smell, and in being non-volatile, properties which, though apparently insignificant, are really of some importance, as showing the difference between *ortho*-quinones and *para*-quinones; the latter are generally deep-yellow, volatile compounds, having a pungent odour, whereas the former are red, non-volatile, and odourless. β-Naphthaquinone is an example of an ortho-quinone, and its constitution may be represented by the formula,

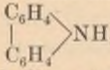
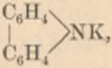


The above description of some of the more important naphthalene derivatives will be sufficient to show the close relationship which these compounds bear to the corresponding derivatives of benzene; although the former exist in a larger number of isomeric forms, they are, as a rule, prepared by the same methods as their analogues of the benzene series, and resemble them closely in chemical properties. It may, in fact, be stated as a general rule, that all general reactions and generic properties of benzene derivatives are met with again in studying naphthalene derivatives.

CHAPTER XXXI.

ANTHRACENE AND PHENANTHRENE.

Anthracene, $C_{14}H_{10}$, is a hydrocarbon of great commercial importance, as it is the starting-point in the manufacture of alizarin, the colouring matter employed in producing Turkey-red dye; it is prepared exclusively from coal-tar. The crude mixture of hydrocarbons and other substances known as '50 per cent. anthracene' (p. 298) is first distilled with one-third of its weight of potash from an iron retort; the distillate, which consists almost entirely of anthracene and phenanthrene, is then treated with carbon bisulphide, when the phenanthrene dissolves, leaving the anthracene, which is further purified by crystallisation from benzene.

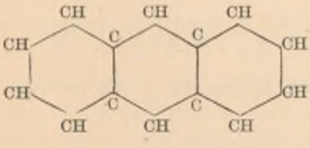
Crude anthracene contains considerable quantities of carbazole,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>NH$, a colourless, crystalline substance, melting at 238°, and boiling at 355°. On treatment with potash, this substance is converted into a potassium derivative,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>NK$, which remains in the retort, or is decomposed on subsequent distillation; many other impurities, which cannot readily be separated by crystallisation, are also got rid of in this way.

Anthracene crystallises from benzene in colourless, lustrous plates, which show a beautiful blue fluorescence; it melts at 213°, boils at about 360°, and dissolves freely in boiling benzene, but is only sparingly soluble in alcohol and ether. On mixing saturated alcoholic solutions of anthracene and picric acid, *anthracene picrate*, $C_{14}H_{10},C_6H_2(NO_2)_3{\cdot}OH$, is deposited in ruby-red needles, which melt at 138°; this compound is resolved into its components when treated with a large quantity of alcohol (distinction from phenanthrene picrate, p. 468).

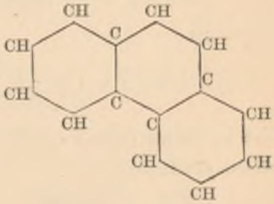
Constitution.—The behaviour of anthracene towards chlorine and bromine is, on the whole, similar to that of benzene and naphthalene—that is to say, it yields additive or substitution products according to the conditions employed; towards concentrated sulphuric acid, also, it behaves like other aromatic compounds, and is converted into sulphonic acids by substitution. When treated with nitric acid, however, instead of yielding a nitro-derivative, as was to be expected from the molecular formula of the hydrocarbon (which, from the relatively small proportion of hydrogen, clearly indicates the presence of one or more closed chains), it is oxidised to anthraquinone, $C_{14}H_8O_2$, two atoms of hydrogen being displaced by two atoms of oxygen; this change always takes place, even when dilute nitric acid, or some other oxidising agent, is employed, and as it is closely analogous to that which occurs in the conversion of naphthalene, $C_{10}H_8$, into α-naphthaquinone, $C_{10}H_6O_2$ (p. 455), it is an indication of the presence of a closed-chain, oxidation processes of this kind (namely, the substitution of oxygen for an *equal* number of hydrogen atoms) being unknown in the case of fatty (open-chain) substances. Another highly important fact, owing to its bearing on the constitution of anthracene, is this, that, although the hydrocarbon and most of its derivatives are resolved into simpler substances only with very great difficulty, when this does occur, one of the products is always some benzene derivative, usually phthalic acid.

Now, if the molecule of anthracene contained only one benzene nucleus, or even if, like naphthalene, it contained two condensed nuclei, there would still be certain carbon and hydrogen atoms to be accounted for, and this could only be done by assuming the presence of unsaturated side-chains; as, however, all experience has shown that such side-chains in benzene and in naphthalene are oxidised to carboxyl (compare p. 327) with the utmost facility, it is impossible to accept the assumption of their presence in anthracene, a compound which is always oxidised to the neutral substance anthraquinone, without loss of carbon. Arguments of this kind lead, therefore, to only one conclusion—namely, that the molecule of anthracene is composed only of combined or condensed nuclei; as, moreover, the hydrocarbon may be indirectly converted into phthalic acid, it must be assumed that two of these nuclei are condensed together in the *o*-position, as in naphthalene.

If, now, an attempt be made to deduce a constitutional formula for anthracene on this basis, and it be further assumed that all the closed-chains are composed of six carbon atoms, as in naphthalene, the following formulæ suggest themselves as the most probable,



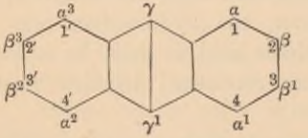
I.



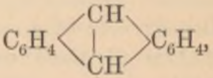
II.

although, of course, neither could be accepted as final without further evidence.

Experience has shown, however, that formula I. must be taken as representing the constitution of anthracene (formula II. expressing that of phenanthrene, p. 468), because it accounts satisfactorily for all known facts, amongst others, for a number of important syntheses of the hydrocarbon (see below), for the relation of anthracene to anthraquinone, and for the isomerism of the anthracene derivatives. It is, nevertheless, just as difficult to determine and to express the actual disposition of the fourth affinity of each carbon atom in anthracene, as in the cases of benzene and naphthalene; as, however, there are reasons for supposing that the state of combination of the two central CH groups (that is, those which form part of the central nucleus only) is different from that of all the others (inasmuch as they are generally attacked first), and that the two carbon atoms of these groups are directly united, the above formula (I.) is usually written



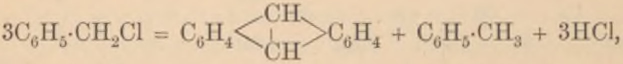
or



$$C_6H_4{<}\begin{array}{c}CH\\ |\\ CH\end{array}{>}C_6H_4,$$

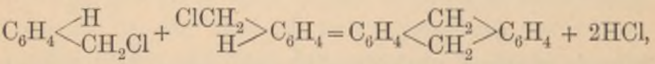
the disposition of the fourth affinities of the carbon atoms in the two $C_6H_4{<}$ groups being taken to be the same as in the centric formula for benzene.*

Anthracene may be obtained synthetically in various ways. It is produced when benzyl chloride is heated with aluminium chloride,



$$3C_6H_5{\cdot}CH_2Cl = C_6H_4{<}\begin{array}{c}CH\\ |\\ CH\end{array}{>}C_6H_4 + C_6H_5{\cdot}CH_3 + 3HCl,$$

the hydranthracene (p. 461) which is formed as an intermediate product,



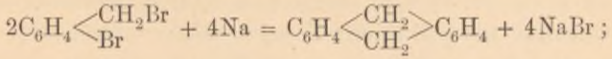
$$C_6H_4{<}\begin{array}{l}H\\ CH_2Cl\end{array} + \begin{array}{r}ClCH_2\\ H\end{array}{>}C_6H_4 = C_6H_4{<}\begin{array}{c}CH_2\\ CH_2\end{array}{>}C_6H_4 + 2HCl,$$

being converted into anthracene by loss of hydrogen, which reduces part of the benzyl chloride to toluene, as shown in the first equation. Anthracene is also formed, together with hydranthracene and phenanthrene (p. 469), when *ortho*-bromo-

---

* The letters or numbers serve to denote the constitution of the anthracene derivatives (p. 461).

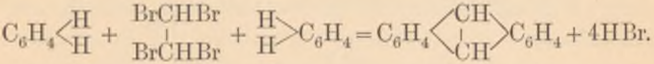
benzyl bromide (prepared by brominating *boiling* *o*-bromotoluene, $C_6H_4Br{\cdot}CH_3$) is treated with sodium,



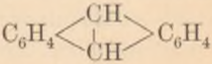
$$2C_6H_4<^{CH_2Br}_{Br} + 4Na = C_6H_4<^{CH_2}_{CH_2}>C_6H_4 + 4NaBr\,;$$

here, again, hydranthracene is the primary product, and from it anthracene is formed by loss of hydrogen.

Another interesting synthesis may be mentioned—namely, the formation of anthracene on treating a mixture of tetrabromethane and benzene with aluminum chloride,

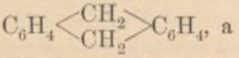


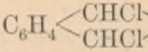
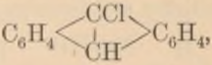
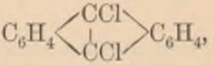
$$C_6H_4<^{H}_{H} + \begin{matrix}BrCHBr\\ |\\ BrCHBr\end{matrix} + {}^{H}_{H}>C_6H_4 = C_6H_4<\begin{matrix}CH\\ |\\ CH\end{matrix}>C_6H_4 + 4HBr.$$

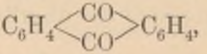
All these methods of formation are accounted for in a simple manner with the aid of the above constitutional formula, the last one especially indicating that the two central carbon atoms are directly united; the formula  $C_6H_4<\begin{matrix}CH\\ |\\ CH\end{matrix}>C_6H_4$ will, therefore, be employed in describing the anthracene derivatives.

Isomerism of Anthracene Derivatives.—Further evidence in support of the above constitutional formula is afforded by the study of the isomerism of the substitution products of anthracene, although, in most cases, all the isomerides theoretically possible have not yet been prepared.

When one atom of hydrogen is displaced, *three* isomerides may be obtained, since there are three hydrogen atoms (α,β,γ), all of which are differently situated relatively to the rest of the molecule; these mono-substitution products are usually distinguished by the letters α, β, γ, according to the position of the substituent (compare formula p. 460). When two atoms of hydrogen are displaced by similar atoms or groups, fifteen isomeric di-substitution products may be obtained.

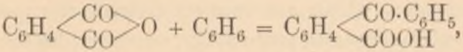
Hydranthracene,  $C_6H_4<^{CH_2}_{CH_2}>C_6H_4$, a substance of little importance, is formed on reducing anthracene with boiling concentrated hydriodic acid, or with sodium amalgam. It is a colourless, crystalline compound, melting at 106–108°, and when heated with sulphuric acid, it is converted into anthracene, the acid being reduced to sulphur dioxide.

Anthracene dichloride,  $C_6H_4\left\langle\begin{array}{c}CHCl\\CHCl\end{array}\right\rangle C_6H_4$, like hydranthracene, is an additive product of the hydrocarbon; it is obtained when chlorine is passed into a *cold* solution of anthracene in carbon bisulphide, whereas at 100° substitution takes place, *monochloranthracene,*  $C_6H_4\left\langle\begin{array}{c}CCl\\|\\CH\end{array}\right\rangle C_6H_4$, and *dichloranthracene,*  $C_6H_4\left\langle\begin{array}{c}CCl\\|\\CCl\end{array}\right\rangle C_6H_4$, being formed; these substitution products crystallise in yellow needles, melting at 103° and 209° respectively, and they are both converted into anthraquinone on oxidation, a fact which shows the positions of the chlorine atoms.

Anthraquinone,  $C_6H_4\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle C_6H_4$, is formed, as already mentioned, on oxidising anthracene with chromic or nitric acid. It is conveniently prepared by dissolving anthracene (1 part) in boiling glacial acetic acid, and gradually adding a concentrated solution of chromic acid (2 parts) in glacial acetic acid. As soon as oxidation is complete, the product is allowed to cool, and the anthraquinone, which separates in long needles, is collected and purified either by sublimation or by recrystallisation from acetic acid.

Anthraquinone is manufactured by oxidising finely-divided '50 per cent. anthracene,' suspended in water, with the calculated quantity of sodium bichromate and sulphuric acid. The crude anthraquinone is collected on a filter, washed, dried, and heated at 100° with 2–3 parts of concentrated sulphuric acid, by which means the impurities are converted into soluble sulphonic acids, whereas the anthraquinone is not acted on. The almost black product is now allowed to stand in a damp place, when the anthraquinone gradually separates in crystals as the sulphuric acid becomes dilute; water is then added, and the anthraquinone collected, washed, and dried and sublimed.

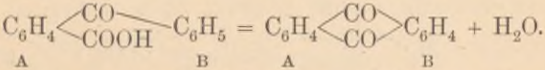
Anthraquinone may be produced synthetically by treating a solution of phthalic anhydride (p. 426) in benzene, with a strong dehydrating agent, such as aluminium chloride, the reaction taking place in two stages; *o*-benzoylbenzoic acid is first produced,



$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{O} + \mathrm{C_6H_6} = \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO\cdot C_6H_5}}{\mathrm{COOH}},$$

o-Benzoylbenzoic Acid.

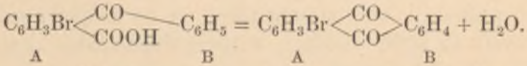
but by the further action of the aluminium chloride (or when treated with sulphuric acid), this substance is converted into anthraquinone with loss of 1 molecule of water,



$$\underset{\mathrm{A}}{\mathrm{C_6H_4}}<\genfrac{}{}{0pt}{}{\mathrm{CO}\text{—}}{\mathrm{COOH}}\underset{\mathrm{B}}{\mathrm{C_6H_5}} = \underset{\mathrm{A}}{\mathrm{C_6H_4}}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\underset{\mathrm{B}}{\mathrm{C_6H_4}} + \mathrm{H_2O}.$$

Anthraquinone contains, therefore, two $\mathrm{C_6H_4}<$ groups, united by two $\mathrm{CO}<$ groups.

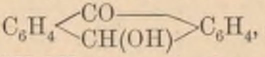
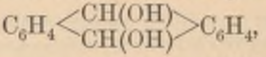
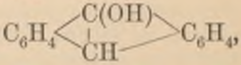
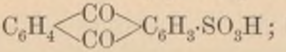
That the two $\mathrm{CO}<$ groups occupy the *o*-position in the one benzene ring (A) is known, because they do so in phthalic acid; that they occupy the *o*-position in the second benzene ring (B) has been proved, as follows: When bromophthalic anhydride is treated with benzene and aluminium chloride, bromobenzoylbenzoic acid is produced, and this, when treated with sulphuric acid, yields bromanthraquinone,



$$\underset{\mathrm{A}}{\mathrm{C_6H_3Br}}<\genfrac{}{}{0pt}{}{\mathrm{CO}\text{—}}{\mathrm{COOH}}\underset{\mathrm{B}}{\mathrm{C_6H_5}} = \underset{\mathrm{A}}{\mathrm{C_6H_3Br}}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\underset{\mathrm{B}}{\mathrm{C_6H_4}} + \mathrm{H_2O}.$$

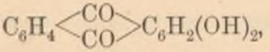
The formation of this substance from bromophthalic acid proves, as before, that the two $\mathrm{CO}<$ groups are united to the ring A in the *o*-position.

Now, when bromanthraquinone is heated with potash at 160°, it is converted into hydroxyanthraquinone, $\underset{\mathrm{A}}{\mathrm{C_6H_3(OH)}}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\underset{\mathrm{B}}{\mathrm{C_6H_4}}$, and this, on oxidation with nitric acid, yields phthalic acid, $\genfrac{}{}{0pt}{}{\mathrm{COOH}}{\mathrm{COOH}}>\mathrm{C_6H_4}$, the group A being destroyed; therefore the two $\mathrm{CO}<$ groups are attached to B, as well as to A, in the *o*-position, and therefore anthraquinone has the constitution represented above, a conclusion which affords strong support to the above views regarding the constitution of anthracene.

Anthraquinone crystallises from glacial acetic acid in pale-yellow needles, melts at 277°, and sublimes very readily at higher temperatures in long, sulphur-yellow prisms; it is exceedingly stable, and is only with difficulty attacked by oxidising agents, by sulphuric acid, or by nitric acid. In all those properties which are connected with the presence of the two carbonyl-groups, anthraquinone resembles the aromatic ketones much more closely than the quinones. It has no smell, is by no means readily volatile, and is not reduced when treated with sulphurous acid; unlike quinone, therefore, it is not an oxidising agent. When treated with more powerful reducing agents, however, it is converted into *oxanthranol*,  $C_6H_4<\begin{array}{c}CO\\CH(OH)\end{array}>C_6H_4$, one of the CO< groups becoming >CH·OH, just as in the reduction of ketones; on further reduction the other CO< group undergoes a similar change, but the product,  $C_6H_4<\begin{array}{c}CH(OH)\\CH(OH)\end{array}>C_6H_4$, loses one molecule of water, yielding *anthranol*,  $C_6H_4<\begin{array}{c}C(OH)\\|\\CH\end{array}>C_6H_4$, which is finally reduced to hydranthracene; when anthraquinone is distilled with zinc-dust, anthracene is produced. Anthraquinone is only slowly acted on by ordinary sulphuric acid even at 250°, yielding anthraquinone-β-monosulphonic acid,  $C_6H_4<\begin{array}{c}CO\\CO\end{array}>C_6H_3\cdot SO_3H$; but when heated with a large excess of anhydrosulphuric acid at 160–170°, it yields a mixture of disulphonic acids, $C_{14}H_6O_2(SO_3H)_2$.

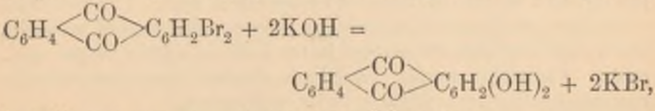
Sodium anthraquinone-monosulphonate, which is used in such large quantities in the manufacture of alizarin (see below), is prepared by heating anthraquinone with an equal weight of anhydrosulphuric acid (containing 50 per cent. of SO_3) in enamelled iron pots at 160°. The product is diluted with water, filtered from unchanged anthraquinone, and neutralised with soda; on cooling, sparingly soluble sodium anthraquinone-monosulphonate separates in glistening plates, and is collected in filter-presses. The more soluble sodium salts of the anthraquinone-disulphonic acids, which are always formed at the same time, remain in solution.

Test for Anthraquinone.—When a trace of finely-divided anthraquinone is mixed with dilute soda, a little zinc-dust added, and the mixture heated to boiling, an intense red colouration is produced, but on shaking in contact with air, the solution is decolourised; in this reaction oxanthranol is formed, and this substance dissolves in the alkali, forming a deep-red solution; on shaking with air, however, it is oxidised to anthraquinone, which separates as a white flocculent precipitate.

Alizarin,  $C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2$, or αβ-dihydroxyanthraquinone, occurs in madder (the root of *Rubia tinctorum*), a substance which has been used from the earliest times for dyeing purposes, and which owes its tinctorial properties to two substances, alizarin and purpurin (see below), both of which are present in the root in the form of glucosides. *Ruberythric acid*, the glucoside of alizarin, is decomposed when boiled with acids, or when the madder extract is allowed to undergo fermentation, with formation of alizarin and two molecules of dextrose,

$$\underset{\text{Ruberythric Acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2C_6H_{12}O_6.$$

A dye of such great importance as alizarin naturally attracted the attention of chemists, and many attempts were made to prepare it synthetically. This was first accomplished in 1868 by Graebe and Liebermann, who found that alizarin could be produced by fusing αβ-dibromanthraquinone* with potash,



$$C_6H_4<\substack{CO\\CO}>C_6H_2Br_2 + 2KOH =$$
$$C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2 + 2KBr,$$

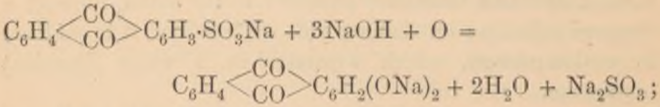
but the process was not a commercial success.

---

[*] Obtained by heating anthraquinone with bromine and a trace of iodine in a sealed tube at 160°.

At the present day, however, the madder root is no longer used, and the whole of the alizarin of commerce is made from (coal-tar) anthracene in the following manner:

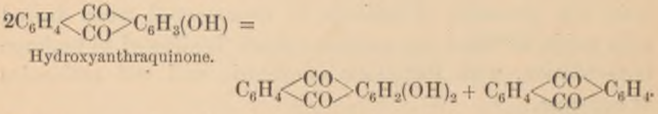
Anthracene is first oxidised to anthraquinone, and the latter is converted into anthraquinone-β-sulphonic acid by the method already described (p. 464); the sodium salt of this acid is then fused with soda and a little potassium chlorate, and is thus converted into the sodium derivative of alizarin,



$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3\cdot SO_3Na + 3NaOH + O = C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2(ONa)_2 + 2H_2O + Na_2SO_3;$$

from this sodium salt the colouring matter itself is obtained by adding acid.

When anthraquinonesulphonic acid is fused with soda, the $-SO_3H$ group is displaced by $-OH$ in the usual manner, but the *hydroxyanthraquinone* thus produced is very readily converted into alizarin by the further action of the soda, part of it being reduced to anthraquinone,



$$2C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3(OH) = C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2(OH)_2 + C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4.$$

Hydroxyanthraquinone.

This regeneration of anthraquinone, and consequent diminished yield of alizarin, is prevented by the addition of the oxidising agent ($KClO_3$); the operation is usually conducted as follows:

Sodium anthraquinonesulphonate (100 parts) is heated in a closed iron cylinder, fitted with a stirrer, with soda (300 parts) and potassium chlorate (14 parts), for two days at 180°. The dark-violet product, which consists of the sodium salt of alizarin, is dissolved in water, the solution filtered if necessary, and the alizarin precipitated by the addition of hydrochloric acid. The yellowish crystalline precipitate is collected in filter-presses, washed well with water, and sent into the market in the form of a 10 or 20 per cent. paste. From this product alizarin is obtained in a pure state by recrystallisation from toluene, or by sublimation.

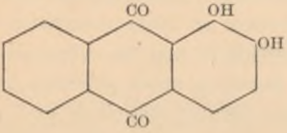
Alizarin crystallises and sublimes in dark-red prisms, which melt at 282°, and are almost insoluble in water, but moderately soluble in alcohol. It is a dihydroxy-derivative of anthraquinone, and has therefore the properties of a dihydric phenol; it dissolves in potash and soda, forming metallic derivatives of the type $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H_2(OM)_2$, which are soluble in water, yielding intensely reddish-violet solutions. With acetic anhydride it gives a *diacetate*, $C_{14}H_6O_2(C_2H_3O_2)_2$, melting at 180°, and when distilled with zinc-dust, it is reduced to anthracene.

The value of alizarin as a dye lies in the fact that it yields magnificently coloured insoluble compounds (called 'lakes') with certain metallic oxides; the ferric compound, for example, is violet black, the lime compound blue, and the tin and aluminium compounds different shades of red (Turkey-red). A short account of the methods used in dyeing with alizarin is given later (p. 504).

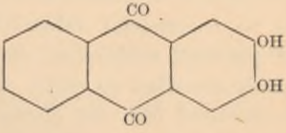
Constitution of Alizarin.—Alizarin may be synthetically prepared by heating a mixture of phthalic anhydride and catechol with sulphuric acid at 150°,

$$C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O + C_6H_4<\begin{smallmatrix}OH\\OH\end{smallmatrix} = C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H_2<\begin{smallmatrix}OH\\OH\end{smallmatrix} + H_2O.$$

As catechol is *o*-dihydroxybenzene, it follows that the two hydroxyl-groups in alizarin must be in the *o*-position to one another, and this substance must, therefore, be represented by one of the following formulæ:



I.

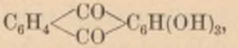


II.

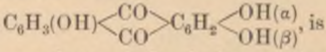
Now alizarin yields two (α^1 and β^1) isomeric mono-nitro-derivatives, $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H(OH)_2 \cdot NO_2$, both of which contain the nitro-group in the same nucleus as the two hydroxyl-groups.

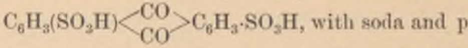
The constitution of alizarin must, therefore, be represented by formula I., as a substance having the constitution II. could only yield one such nitro-derivative, and this formula has been shown to be correct in many other ways which cannot be discussed here.

Besides alizarin, several other dihydroxy- and also trihydroxy-anthraquinones have been obtained, but only those are of value as dyes which contain two hydroxyl-groups in the same positions as in alizarin; two such derivatives, which possess very valuable dyeing properties, may be mentioned.



Purpurin, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)_3$, or $\alpha\beta\alpha^1$-trihydroxyanthraquinone, is contained in madder root, in the form of a glucoside, and may be artificially prepared by oxidising alizarin with manganese dioxide and sulphuric acid. It crystallises in deep-red needles, melts at 252°, and gives, with alumina mordants, a much yellower shade of red than alizarin, and is now used on the large scale for the production of brilliant reds.





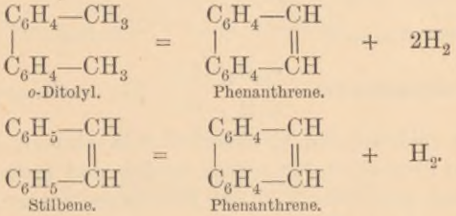
Anthrapurpurin, $C_6H_3(OH)<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH(\alpha)\\OH(\beta)\end{matrix}$, is isomeric with purpurin, and is manufactured by fusing anthraquinone-disulphonic acid, $C_6H_3(SO_2H)<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot SO_3H$, with soda and potassium chlorate (see alizarin, p. 466). It crystallises in yellowish-red needles, melts at 330°, and is very largely employed in dyeing yellow shades of Turkey-red.

Phenanthrene, $C_{14}H_{10}$, an isomeride of anthracene, is a hydrocarbon of considerable theoretical interest, although it has no commercial value. It occurs in large quantities in '50 per cent. anthracene,' from which it may be extracted as already described (p. 457). The resulting crude phenanthrene is converted into the picrate (see below), which is first recrystallised from alcohol, to free it from anthracene picrate, and then decomposed by ammonia, the hydrocarbon being finally purified by recrystallisation.

Phenanthrene crystallises in glistening needles, melts at

99°, and distils at about 340°; it is readily soluble in alcohol, ether, and benzene. When oxidised with chromic acid, it is first converted into *phenanthraquinone*, $C_{14}H_8O_2$, isomeric with anthraquinone, and then into *diphenic acid*, $C_{14}H_{10}O_4$. This acid is decomposed on distillation with lime, yielding carbon dioxide and *diphenyl* (p. 340); it is therefore *diphenyl-dicarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COOH$, and its formation from phenanthrene shows that the latter is also a derivative of diphenyl.

Further evidence as to the constitution of phenanthrene is obtained by studying its methods of formation. It is formed, for example, on passing *o-ditolyl* (prepared from *o*-bromotoluene and sodium) or *stilbene* * through a red-hot tube, and the simplest manner of expressing these two reactions is the following:



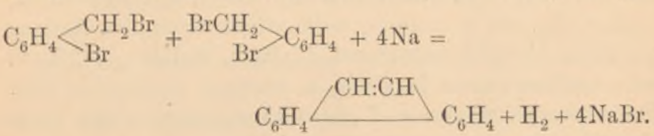
$$\begin{matrix} C_6H_4{-}CH_3 \\ | \\ C_6H_4{-}CH_3 \end{matrix} = \begin{matrix} C_6H_4{-}CH \\ |\qquad \| \\ C_6H_4{-}CH \end{matrix} + 2H_2$$

o-Ditolyl. Phenanthrene.

$$\begin{matrix} C_6H_5{-}CH \\ \| \\ C_6H_5{-}CH \end{matrix} = \begin{matrix} C_6H_4{-}CH \\ |\qquad \| \\ C_6H_4{-}CH \end{matrix} + H_2.$$

Stilbene. Phenanthrene.

Again, phenanthrene is formed, together with anthracene, by the action of sodium on *o*-bromobenzyl bromide (p. 461),



$$C_6H_4{<}\begin{matrix} CH_2Br \\ Br \end{matrix} + \begin{matrix} BrCH_2 \\ Br \end{matrix}{>}C_6H_4 + 4Na =$$

$$C_6H_4\overset{CH:CH}{\diagup\!\!\!-\!\!\!-\!\!\!-\!\!\!\diagdown}C_6H_4 + H_2 + 4NaBr.$$

---

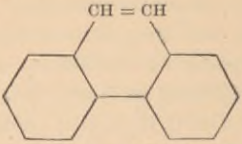
* *Stilbene*, or *diphenylethylene*, $C_6H_5{\cdot}CH:CH{\cdot}C_6H_5$, may be prepared by acting on benzal chloride (p. 349) with sodium,

$$2C_6H_5{\cdot}CHCl_2 + 4Na = C_6H_5{\cdot}CH:CH{\cdot}C_6H_5 + 4NaCl.$$

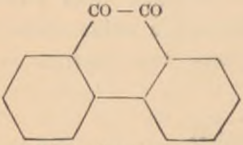
It crystallises in colourless needles, melts at 120°, and, like ethylene, combines with two atoms of bromine, forming *stilbene dibromide*,

$$C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_5 \text{ (m p. 237°)}.$$

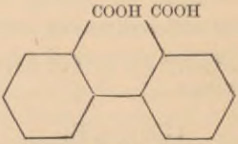
For these and many other reasons, the constitution of phenanthrene is expressed by the formula,



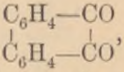
When the hydrocarbon is oxidised to phenanthraquinone, the group –CH = CH– becomes –CO—CO–, and, on further oxidation to diphenic acid, this group is converted into two carboxyl-groups,



Phenanthraquinone.

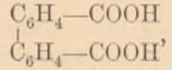
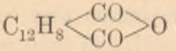


Diphenic Acid.

Phenanthraquinone,  $\begin{array}{l}C_6H_4\text{—}CO\\ \mid \qquad\quad \mid\\ C_6H_4\text{—}CO\end{array}$, like anthraquinone, is formed by oxidising the hydrocarbon with chromic acid. It crystallises from alcohol in orange needles, and melts at 198°. In chemical properties it shows little resemblance to anthraquinone, but is closely related to β-naphthaquinone (p. 456), and is, like the latter, an ortho-diketone (ortho-quinone); it is readily reduced by sulphurous acid to *dihydroxyphenanthrene*, $C_{14}H_8(OH)_2$, and it combines with sodium bisulphite, forming a soluble *bisulphite* compound, $C_{14}H_8O_2$, $NaHSO_3 + 2H_2O$; with hydroxylamine it yields a *dioxime*, $C_{12}H_8(C{:}NOH)_2$. The hydroxy-derivatives of phenanthraquinone, unlike those of anthraquinone, possess no tinctorial properties.

Phenanthraquinone may be readily detected by dissolving a small quantity (0·1 gram) in glacial acetic acid (20 c.c.), adding a few drops of commercial toluene, and then mixing the well-cooled solution with sulphuric acid (1 c.c.). After standing for a few minutes, the bluish-green liquid is poured into water and shaken with ether, when the ether acquires an intense reddish-violet colouration

(Laubenheimer's reaction). Like the indophenin reaction, this test depends on the formation of a colouring matter containing sulphur, produced by the condensation of the phenanthraquinone with the *thiotolene*, $C_4H_3S(CH_3)$, which is contained in the crude toluene (p. 334).

Diphenic acid,  $\begin{array}{l}C_6H_4-COOH\\ |\\ C_6H_4-COOH\end{array}$, obtained by the oxidation of phenanthrene or of phenanthraquinone with chromic acid, crystallises from water in needles, and melts at 229°. When heated with acetic anhydride it is converted into *diphenic anhydride*,  $C_{12}H_8<\begin{array}{l}CO\\CO\end{array}>O$ (m.p. 217°).

This fact is remarkable, because it shows that in the case of derivatives of hydrocarbons which are composed of condensed benzene nuclei, the ortho-position is not the only one which allows of the formation of an anhydride. Naphthalic acid, $C_{10}H_6(COOH)_2$, a derivative of naphthalene in which the carboxyl-groups are in the 1:1'- or peri-position, also forms an anhydride.

CHAPTER XXXII.

PYRIDINE AND QUINOLINE.

Pyridine and quinoline are two very interesting aromatic bases, and many of their derivatives, more especially those which occur in nature, are well-known and important compounds.

Coal-tar, though consisting principally of hydrocarbons and phenols, contains also small quantities of pyridine, quinoline, and numerous other basic substances, such as aniline and isoquinoline; all these bases are dissolved, in the form of sulphates, in the purification of the hydrocarbons, &c., by treatment with sulphuric acid (compare p. 297), and, on afterwards adding excess of soda to the dark acid liquor, they separate again at the surface of the liquid in the form of a dark-brown oil. By repeated fractional distillation a partial separation of the various constituents of this oil may be effected, and crude pyridine, quinoline, &c., may be obtained; on further purification by crystallisation of their salts, or in other ways, some of these bases may be prepared in a state of purity.

Another important source of these compounds is *bone-tar* or *bone-oil*, a dark-brown, unpleasant-smelling liquid formed during the dry distillation of bones in the preparation of bone-black (animal charcoal); this oil contains considerable quantities of pyridine and quinoline, and their homologues, as well as other bases, and these compounds may be extracted from it with the aid of sulphuric acid, and then separated in the manner mentioned above. Bone-oil, purified by distillation, was formerly used in medicine under the name of *Dippel's oil.*

Pyridine and its Derivatives.

Pyridine, C_5H_5N, is formed during the destructive distillation of a great variety of nitrogenous organic substances, hence its presence in coal-tar and in bone-oil; it is also formed when various alkaloids are distilled with potash.

It may be obtained synthetically by passing a mixture of acetylene and hydrogen cyanide through a red-hot tube, a reaction which is very similar to that which occurs in the formation of benzene from acetylene alone (p. 301),

$$2C_2H_2 + HCN = C_5H_5N.$$

Pyridine is conveniently prepared in small quantities by distilling nicotinic acid (p. 479), or other pyridinecarboxylic acids, with lime, just as benzene may be prepared from benzoic and phthalic acids in a similar manner,

$$C_5H_4N{\cdot}COOH = C_5H_5N + CO_2$$
$$C_5H_3N(COOH)_2 = C_5H_5N + 2CO_2.$$

For commercial purposes it is usually prepared by the fractional distillation of the basic mixture, which is separated from bone-oil or coal-tar as already described; the product consists of pyridine, together with small quantities of its homologues.

Pyridine is a colourless, mobile liquid of sp. gr. 1·0033 at 0° ; it boils at 115°, is miscible with water in all proportions, and possesses a pungent and very characteristic odour. It is an exceedingly stable substance, as it is not attacked by boiling nitric or chromic acid, and only with difficulty by halogens; in the latter case, *substitution* products such as *monobromopyridine*, C_5H_4BrN, and *dibromopyridine*, $C_5H_3Br_2N$, are formed. If, however, a solution of pyridine in hydrochloric acid be treated with bromine, a crystalline, unstable, *additive* product, $C_5H_5NBr_2$, is precipitated, even from very dilute solutions, and the formation of this substance is sometimes used as a test for pyridine.

When treated with sodium and alcohol, pyridine is readily reduced, *piperidine* or *hexahydropyridine* (p. 476) being formed,

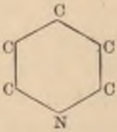
$$C_5H_5N + 6H = C_5H_{11}N.$$

Pyridine is a strong base; like the amines, it turns red litmus blue, and combines with acids to form crystalline salts, such as the *hydrochloride*, C_5H_5N,HCl, and the *sulphate*, $(C_5H_5N)_2,H_2SO_4$. The *platinochloride*, $(C_5H_5N)_2,H_2PtCl_6$, crystallises in orange-yellow needles, and is readily soluble in water; when, however, its solution is boiled, a very sparingly soluble yellow salt, $(C_5H_5N)_2PtCl_4$, separates, a fact which may be made use of for the detection of pyridine even when only small quantities of the base are available. Another test for pyridine (and its homologues) consists in heating a few drops of the base in a test tube with methyl iodide, when a vigorous reaction takes place, and a yellowish additive product, *pyridine methiodide*, C_5H_5N,CH_3I, is produced; if a piece of solid potash be now added, and the contents of the tube again heated, a most pungent and exceedingly disagreeable smell is at once noticed.

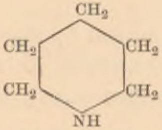
Constitution.—Although pyridine is a powerful base, having a pungent odour, and turning red litmus blue, properties which suggest some relation to the fatty amines, a careful consideration of its molecular formula and chemical behaviour shows at once that it is not analogous to the fatty amines in constitution. It is not a primary, nor a secondary amine, because it does not give the carbylamine reaction, and is not acted on by nitrous acid, and it cannot possibly be a tertiary fatty amine, because no reasonable constitutional formula based on this view could be constructed. If, moreover, it be borne in mind that pyridine is extremely stable, the probability of its being a fatty (open-chain) compound at all seems very remote, because if it were, it would be highly unsaturated, and should be readily oxidised and resolved into simpler substances. The grounds for doubting its relation to any fatty compound are, in fact, much the same as those which led to the conclusion that the constitution of benzene is totally different from that of dipropargyl (p. 304).

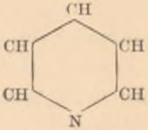
Comparing now the properties of pyridine with those of aromatic compounds, a general analogy is at once apparent; in spite of its great stability, pyridine is really an unsaturated compound, and, like benzene, naphthalene, and other closed-chain compounds, it yields *additive* products under certain conditions, although as a rule it gives *substitution* products.

Considerations such as these led to the conclusion, suggested by Körner in 1869, that pyridine, like benzene, contains a closed-chain or nucleus, as represented by the following formula,



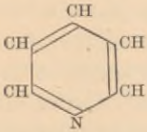
and this view has since been confirmed in a great many ways, notably in the following manner: Piperidine, or hexahydropyridine, the compound which is formed by the reduction of pyridine, and which is reconverted into the latter on oxidation with sulphuric acid (p. 477), has been prepared synthetically by a method (p. 478) which shows it to have the constitution (I.); pyridine, therefore, has the constitution (II.), the relation between the two compounds being the same as that between benzene and hexahydrobenzene.

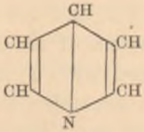

Piperidine (I.).

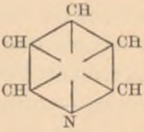

Pyridine (II.).

That the constitution of pyridine is represented by this formula (II.) is also established by a study of the isomerism of pyridine derivatives, and by its relation to quinoline (p. 482); it must, therefore, be regarded as derived from benzene by the substitution of trivalent nitrogen $N\leqslant$ for one of the $CH\leqslant$ groups.

The exact nature of the union of the nitrogen and carbon atoms is not known, and as in the case of benzene, several methods of representation (some of which are shown below) have been suggested; of these, the centric formula is perhaps the best, for reasons similar to those already mentioned in discussing the constitution of benzene (pp. 306, 307).

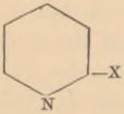

Körner.

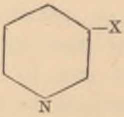

Dewar.

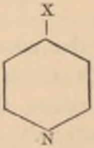

Centric Formula.

Isomerism of Pyridine Derivatives.—The *mono*-substitution products of pyridine, as, for example, the methylpyridines or picolines, exist in *three* isomeric forms; this fact is clearly in accordance with the accepted constitutional formula for pyridine, in which, for the sake of reference, the carbon atoms may be numbered or lettered in the following manner, the symbols C and H being omitted as usual:

These substitution products, being formed by the displacement of any one of the five hydrogen atoms, it is evident that the following three (but not more than three), isomerides may be obtained:







The positions $\alpha\alpha^1$ (or 1, 5) are identical, and so also are the positions $\beta\beta^1$ (or 2, 4), but the position γ (or 3) is different from any of the others.

The *di*-substitution products exist theoretically in *six* isomeric forms, the positions of the substituents in the several isomerides being as follows:

1:2, 1:3, 1:4, 1:5, 2:3, 2:4.

All other positions are identical with one of these; 4:5, for example, is the same as 1:2, and 3:4 is identical with 2:3.

As regards the isomerism of its derivatives, pyridine may be conveniently compared with a mono-substitution product of benzene—aniline, for example—the effect of substituting a nitrogen atom for one of the CH< groups in benzene being the same, in this respect, as that of displacing one of the hydrogen atoms by some substituent.

Derivatives of Pyridine.—**Piperidine,** or hexahydropyridine, $C_5H_{10}NH$, is formed, as already stated, when pyridine is reduced with sodium and alcohol; it is usually prepared from pepper, which contains the alkaloid *piperine* (p. 490), a substance which is decomposed by boiling alkalies yielding piperidine and piperic acid.

Powdered pepper is extracted with alcohol, the filtered solution evaporated, and the residue distilled with potash; after neutralising with hydrochloric acid, the distillate is evaporated to dryness, and the residue extracted with hot alcohol to separate the piperidine hydrochloride from the ammonium chloride which is always present. The filtered alcoholic solution is then evaporated, the residue distilled with solid potash, and the crude piperidine purified by fractional distillation over potash.

Piperidine is a colourless liquid, boiling at 106°, and is miscible with water in all proportions, heat being developed; it has a very penetrating odour, recalling that of pepper. Like pyridine, it is a very strong base, turns red litmus blue, and combines with acids forming crystalline salts; when heated with concentrated sulphuric acid at 300°, it loses six atoms of hydrogen, and is converted into pyridine, part of the sulphuric acid being reduced to sulphur dioxide.

Piperidine behaves like a secondary amine towards nitrous acid, and yields *nitroso-piperidine*, $C_5H_{10}N{\cdot}NO$, an oil, boiling at 218°; like secondary amines, moreover, it interacts with methyl iodide, giving *methylpiperidine*, $C_5H_{10}N{\cdot}CH_3$; it is, therefore, a secondary base (compare p. 483).

The important synthesis of piperidine, which has already been referred to as establishing the constitution of the base, and also that of pyridine, was accomplished by Ladenburg in the following way: *Trimethylene bromide** is heated with potassium cyanide in alcoholic solution, and thus converted into *trimethylene cyanide*,

$$Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Br + 2KCN = CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN + 2KBr,$$

a substance which, on reduction with sodium and alcohol,

---

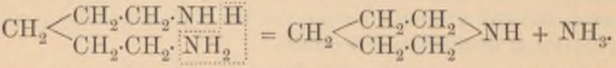
* *Trimethylene bromide*, $C_3H_6Br_2$, is prepared by treating allyl bromide (part i. p. 255) with concentrated hydrobromic acid,

$$CH_2Br{\cdot}CH{:}CH_2 + HBr = CH_2Br{\cdot}CH_2{\cdot}CH_2Br;$$

it is a heavy, colourless oil, and boils at 164°.

yields *pentamethylene diamine*, just as methyl cyanide under similar conditions yields ethylamine,

$CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN + 8H = NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$; during this reduction process, some of the pentamethylene diamine is decomposed into piperidine and ammonia, and the same change occurs, but much more completely, when the hydrochloride of the diamine is distilled,



$$CH_2 \left< \begin{array}{l} CH_2\cdot CH_2\cdot NH \\ CH_2\cdot CH_2\cdot \end{array} \right. \boxed{\begin{array}{l} H \\ NH_2 \end{array}} = CH_2 \left< \begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{array} \right> NH + NH_3.$$

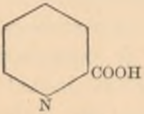
Homologues of Pyridine.—The alkyl-derivatives of pyridine occur in coal-tar and bone-oil, and are, therefore, present in the crude pyridine obtained from the mixture of bases in the manner referred to above; they can only be isolated by repeated fractional distillation and subsequent crystallisation of their salts. The three (α, β, γ) isomeric *methylpyridines* or *picolines*, $C_5H_4N\cdot CH_3$, the six isomeric *dimethylpyridines* or *lutidines*, $C_5H_3N(CH_3)_2$, and the *trimethylpyridines* or *collidines*, $C_5H_2N(CH_3)_3$, resemble the parent base in most ordinary properties, but, unlike the latter, they undergo oxidation more or less readily on treatment with nitric acid or potassium permanganate, and are converted into pyridinecarboxylic acids, just as the homologues of benzene yield benzenecarboxylic acids, the alkyl-groups or side-chains being oxidised to carboxyl-groups,

$$C_5H_4N\cdot CH_3 + 3O = C_5H_4N\cdot COOH + H_2O$$
$$C_5H_3N(CH_3)_2 + 6O = C_5H_3N(COOH)_2 + 2H_2O.$$

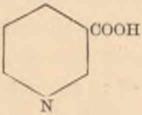
This behaviour is of great use in determining the positions of the alkyl-groups in these homologues of pyridine, because the carboxylic acids into which they are converted are easily isolated, and are readily identified by their melting-points and other properties.

The *pyridinecarboxylic acids* are perhaps, as a class, the most important derivatives of pyridine, chiefly because they are obtained as decomposition products on oxidising many of the alkaloids.

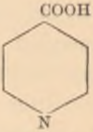
The three (α, β, γ) *monocarboxylic* acids may be prepared by oxidising the corresponding picolines or methylpyridines (see above) with potassium permanganate. The α-carboxylic acid is usually known as *picolinic acid*, because it was first prepared from α-picoline (α-methylpyridine), whereas the β-compound is called *nicotinic acid*, because it was first obtained by the oxidation of nicotine (p. 489); the third isomeride—namely, the γ-carboxylic acid, is called *isonicotinic acid*, and is the oxidation product of γ-picoline.



Picolinic Acid, or
Pyridine-α-carboxylic Acid
(m.p. 136°).



Nicotinic Acid, or
Pyridine-β-carboxylic Acid
(m.p. 229°).



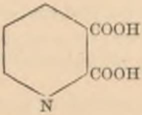
Isonicotinic Acid, or
Pyridine-γ-carboxylic Acid
(sublimes without melting).

These monocarboxylic acids are all crystalline and soluble in water; they have both basic and acid properties, and form salts with mineral acids as well as with bases, a behaviour which is similar to that of glycine (part i. p. 292).

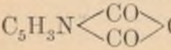
The α-carboxylic acid, and all other pyridinecarboxylic acids which contain a carboxyl-group in the α-position (but only such), give a red, or yellowish-red colouration with ferrous sulphate, a reaction which is of great value in determining the positions of the carboxyl-groups in such compounds.

A carboxyl-group in the α-position, moreover, is usually very readily eliminated on heating; picolinic acid, for example, is much more readily converted into pyridine than nicotinic or isonicotinic acid.

Quinolinic acid, $C_5H_3N(COOH)_2$ (pyridine-$\alpha\beta$-dicarboxylic acid),



a compound produced by the oxidation of quinoline with potassium permanganate, is the most important of the six isomeric dicarboxylic acids. It crystallises in colourless prisms, is only sparingly soluble in water, and gives, with ferrous sulphate, an orange colouration, one of the carboxyl-groups being in the α-position. When heated at 190° it decomposes into carbon dioxide and nicotinic acid, a fact which shows that the second carboxyl-group is in the β-position. On distillation with lime, quinolinic acid, like all pyridinecarboxylic acids, is converted into pyridine.

In its behaviour when heated alone, quinolinic acid differs in a marked manner from phthalic acid—the corresponding benzenedicarboxylic acid—as the latter is converted into its anhydride (p. 426); nevertheless, when heated with acetic anhydride, quinolinic acid gives an anhydride,  $C_5H_3N{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O$, a colourless, crystalline substance, melting at 134°. This fact shows that the carboxyl-groups are united with carbon atoms, which are themselves directly united (as in the case of phthalic acid), and is further evidence in support of the constitutional formula given above.

Quinoline.

Quinoline, C_9H_7N, occurs, together with isoquinoline, in that fraction of coal-tar and bone-oil bases (p. 472) which is collected between 236 and 243°, but as it is difficult to obtain the pure substance from this mixture, quinoline is usually prepared synthetically, by a method devised by Skraup. For this purpose a mixture of aniline and glycerol is heated with a dehydrating agent (sulphuric acid) and an oxidising agent, such as nitrobenzene.*

A mixture of aniline (38 parts), concentrated sulphuric acid (100 parts), nitrobenzene (24 parts), and glycerol (120 parts), is cautiously heated (with reflux apparatus) on a sand-bath, and after the violent reaction which soon sets in has subsided, the mixture is kept boiling

---

* Nitrobenzene is often employed as a mild oxidising agent, as, in presence of an oxidisable substance, it is reduced to aniline,

$$C_6H_5{\cdot}NO_2 + 2H = C_6H_5{\cdot}NH_2 + 2O.$$

for about four hours. It is then cooled, diluted with water, and the unchanged nitrobenzene separated by distillation in steam; soda is then added in excess to liberate the quinoline from its sulphate, and the mixture is again steam-distilled. The quinoline in the receiver is finally separated with the aid of a funnel, dried over solid potash, and purified by fractional distillation.

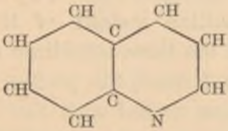
Quinoline is a colourless, highly refractive oil, of sp. gr. 1·095 at 20°, and boils at 239°. It has a peculiar characteristic smell, and is sparingly soluble in water, but it dissolves freely in dilute acids, forming crystalline salts, such as the *hydrochloride*, C_9H_7N,HCl, the *sulphate*, $(C_9H_7N)_2,H_2SO_4$, &c. It also forms double salts, of which the *platinochloride*, $(C_9H_7N)_2,H_2PtCl_6 + 2H_2O$, and the *bichromate*,

$$(C_9H_7N)_2,H_2Cr_2O_7,$$

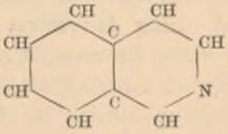
may be mentioned; the latter, prepared by adding potassium bichromate to a solution of quinoline hydrochloride, crystallises from water, in which it is only sparingly soluble, in glistening yellow needles, melting at 164–167°.

Quinoline is a *tertiary* base (compare p. 484), and combines, with methyl iodide, to form the additive product, *quinoline methiodide*, C_9H_7N,CH_3I.

Constitution.—As the relation between pyridine, C_5H_5N, and quinoline, C_9H_7N, on the one hand, is much the same as that between benzene, C_6H_6, and naphthalene, $C_{10}H_8$, on the other, both as regards chemical behaviour and molecular composition (the difference being C_4H_2 in both cases), it might be assumed that quinoline is derived from pyridine, just as naphthalene is derived from benzene; consequently the constitution of quinoline might be expressed by one of the following formulæ:



I.



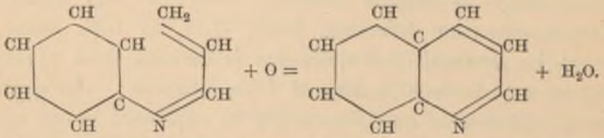
II.

Now, quinoline differs from pyridine, just as naphthalene differs from benzene, in being much more readily oxidised, and when heated with potassium permanganate it yields quinolinic acid, $C_5H_3N(COOH)_2$, a derivative of pyridine (p. 479); this fact proves that quinoline contains a pyridine nucleus; but it also contains a benzene nucleus, as is shown by its formation from aniline by Skraup's method. Its constitution must, therefore, be expressed by one of the above formulæ, as these facts admit of no other interpretation. As, moreover, the carboxyl-groups in quinolinic acid are in the $\alpha:\beta$-position (compare p. 480), formula II. is inadmissible, a conclusion which is obviously necessary to explain the formation of quinoline from aniline. For these and other reasons, the constitution of quinoline is represented by formula I. (the other expressing that of isoquinoline).

The formation of quinoline from aniline and glycerol may be explained as follows: The glycerol and sulphuric acid first interact, yielding acroleïn (part i. pp. 249, 256), which then condenses with aniline (as do all aldehydes), forming *acrylaniline*,

$$C_6H_5{\cdot}NH_2 + CHO{\cdot}CH{:}CH_2 = C_6H_5{\cdot}N{:}CH{\cdot}CH{:}CH_2 + H_2O;$$

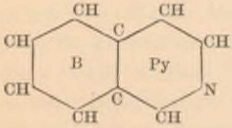
this substance, under the oxidising action of the nitrobenzene, loses two atoms of hydrogen, and is converted into quinoline,



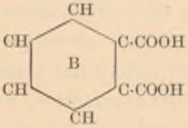
Many derivatives of quinoline may be obtained by Skraup's method, using derivatives of aniline instead of the base itself; when, for example, one of the three toluidines (p. 364) is employed, a *methylquinoline* is formed, the position of the methyl-group—which is, of course, united with the benzene and not with the pyridine nucleus—depending on which of the toluidines is taken.

Isoquinoline, C_9H_7N, occurs in coal-tar quinoline, and may be isolated by converting the fraction of the mixed bases, boiling at 236–243°, into the acid sulphates, C_9H_7N,H_2SO_4, and recrystallising these salts from alcohol (88 per cent.) until the crystals melt at 205°. The sulphate of isoquinoline thus obtained is decomposed by potash, and the base purified by distillation. Isoquinoline is very like quinoline in chemical properties, but it is solid, and melts at 22°; its boiling-point, 241°, is also slightly higher than that of quinoline (239°).

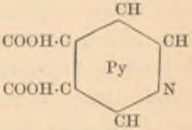
The constitution of isoquinoline is very clearly proved by its behaviour on oxidation with permanganate, when it yields both phthalic acid and *cinchomeronic acid*, $C_5H_3N(COOH)_2$, or pyridine-$\beta\gamma$-dicarboxylic acid; oxidation takes place, therefore, in two directions, in the one case the pyridine (Py), in the other the benzene (B), nucleus being broken up.



Isoquinoline.



Phthalic Acid.



Cinchomeronic Acid.

Secondary and Tertiary Aromatic Bases.—Compounds such as pyridine, piperidine, and quinoline, which owe their basic character to the presence of nitrogen forming part of a closed-chain or nucleus, are classed as secondary or tertiary bases, according as the nitrogen atom is combined with hydrogen, as well as with carbon, or only with the latter.

The *secondary* bases, such as piperidine, which contain an >NH-group, show in some respects the behaviour of secondary amines. When treated with nitrous acid they yield nitroso-derivatives (which give Liebermann's reaction),

$$>NH + HO\cdot NO = >N\cdot NO + H_2O,$$

and when warmed with an alkyl halogen compound, such as methyl iodide, they are converted into alkyl-derivatives by the *substitution* of an alkyl-group for the hydrogen atom of the >NH-group,

$$>NH + CH_3I = >N\cdot CH_3,HI,$$

just as diethylamine, for example, interacts with ethyl iodide, giving triethylamine,

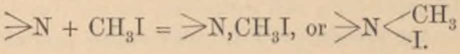
$$(C_2H_5)_2NH + C_2H_5I = (C_2H_5)_2N{\cdot}C_2H_5,HI.$$

These alkyl-derivatives of the secondary bases are themselves tertiary bases, and have the property of forming *additive* products with alkyl halogen compounds, giving salts corresponding with the quaternary ammonium salts (part i. pp. 204, 205),

$$>N{\cdot}CH_3 + CH_3I = >N{\cdot}CH_3,CH_3I, \text{ or } >N(CH_3)_2I.$$

The hydrogen atom of the $>$NH-group in secondary bases is also displaceable by the acetyl-group and by other acid radicles.

The *tertiary* bases, such as pyridine and quinoline, in which the nitrogen atom is not directly united with hydrogen, behave in many respects like the tertiary amines; they do not yield nitroso- nor acetyl-derivatives, but when treated with an alkyl halogen compound they yield *additive* compounds, corresponding with the quaternary ammonium salts, without the formation of any intermediate product,



$$\ge N + CH_3I = \ge N,CH_3I, \text{ or } \ge N<^{CH_3}_{I.}$$

These differences in behaviour make it an easy matter to distinguish between secondary and tertiary aromatic bases of this class.

CHAPTER XXXIII.

ALKALOIDS.

The alkaloids, like the carbohydrates (part i. p. 259), do not form a well-defined group, this term being applied to nearly all *basic nitrogenous substances* which occur in plants, irrespective of any similarity in properties or constitution.

Most alkaloids are composed of carbon, hydrogen, oxygen, and nitrogen, and are crystalline and non-volatile, but a few, notably coniine and nicotine, are composed of carbon, hydrogen, and nitrogen only, and are volatile liquids; with the exception of these liquid compounds, which are readily soluble, the alkaloids are usually sparingly soluble in water, but dissolve much more readily in alcohol, chloroform, ether, and other organic solvents; they are all soluble in acids, with which they usually form well-defined, crystalline salts. Many alkaloids have a very bitter taste, and are excessively poisonous; many, moreover, are extensively used in medicine, and their value in this respect can hardly be overrated.

Generally speaking, the alkaloids are tertiary aromatic bases, but, with few exceptions, their constitutions have not been established, owing partly to their complexity, partly to the difficulties which are experienced in resolving them into simpler compounds which throw any light on the structure of their molecules. Nevertheless, work has been done in this direction, and it is known that many alkaloids are derivatives of pyridine, or of quinoline, because they yield these bases, or their derivatives, when strongly heated with potash, and, on oxidation, usually with potassium permanganate, they give carboxylic acids of pyridine and quinoline.

It is a remarkable fact that by far the greater number of alkaloids contain one or two, sometimes three or more, methoxy-groups ($-O{\cdot}CH_3$), united with a benzene nucleus (as in anisole, $C_6H_5{\cdot}O{\cdot}CH_3$, p. 392), and the determination of the number of such groups in the molecule is of the greatest importance in establishing the constitution of an alkaloid, because in this way some of the carbon and hydrogen atoms are at once disposed of. The method employed for this purpose depends on the fact that all substances containing methoxy-groups are decomposed by hydriodic acid, yielding methyl iodide and a hydroxy-compound (compare anisole) in accordance with the general equation,

$$n(-O{\cdot}CH_3) + nHI = n(-OH) + nCH_3I;$$

by estimating the amount of methyl iodide obtained from a known weight of a given compound, it is easy, therefore, to determine the number of methoxy-groups in the molecule.

This method was first applied by Zeisel, and is of general application, as it affords a means of accurately determining the number of methoxy-groups, not only in alkaloids, but in any other substances in which they occur; it is carried out as follows:

A distilling flask of about 35 c.c. capacity (A, fig. 20), with the side-tube bent as shown, and suspended in a beaker of glycerol, is fixed to the condenser (B) by means of a cork, and connected with an apparatus for generating carbon dioxide.

The condenser, through which water at 50° circulates from the bottle (C), is attached to the 'potash bulbs,' which contain water and about 0·5 gram of amorphous phosphorus; the bulbs are suspended in a beaker of water kept at 60°, and connected, as shown, with two flasks (D, E), containing respectively 50 c.c. and 25 c.c. of an alcoholic solution of silver nitrate (prepared by adding 100 c.c. of absolute alcohol to a solution of 5 grams of silver nitrate in 12 c.c. of water).

In carrying out the estimation, about 0·3 gram of the substance under examination is placed in the flask A, together with 10 c.c. of fuming hydriodic acid, and the temperature of the glycerol bath is gradually raised, until the acid just boils, carbon dioxide, at the rate of about 3 bubbles in 2 seconds, being passed all the time.

The methyl iodide thus formed is carried forward through the condenser into the 'potash bulbs,' where it is freed from hydriodic acid and from small quantities of iodine, which it always contains; it then passes into the alcoholic silver nitrate solution, and is decomposed with separation of silver iodide. The operation, which occupies about two hours, is at an end when the precipitate in the flask settles, and leaves a clear, supernatant liquid.

The contents of flask E are poured into 5 vols. of water and gently warmed; if, as is usually the case, no precipitation takes place after five minutes, the solution is neglected; if, however, a precipitate forms, it must be collected and added to that contained in flask D. The alcoholic liquid in flask D is decanted from the precipitate, mixed with water (300 c.c.) and a few drops of nitric acid, and heated to boiling until free from alcohol; any precipitate is then added to the main quantity, the whole digested for a few minutes with dilute nitric acid, collected on a filter, dried, and weighed.

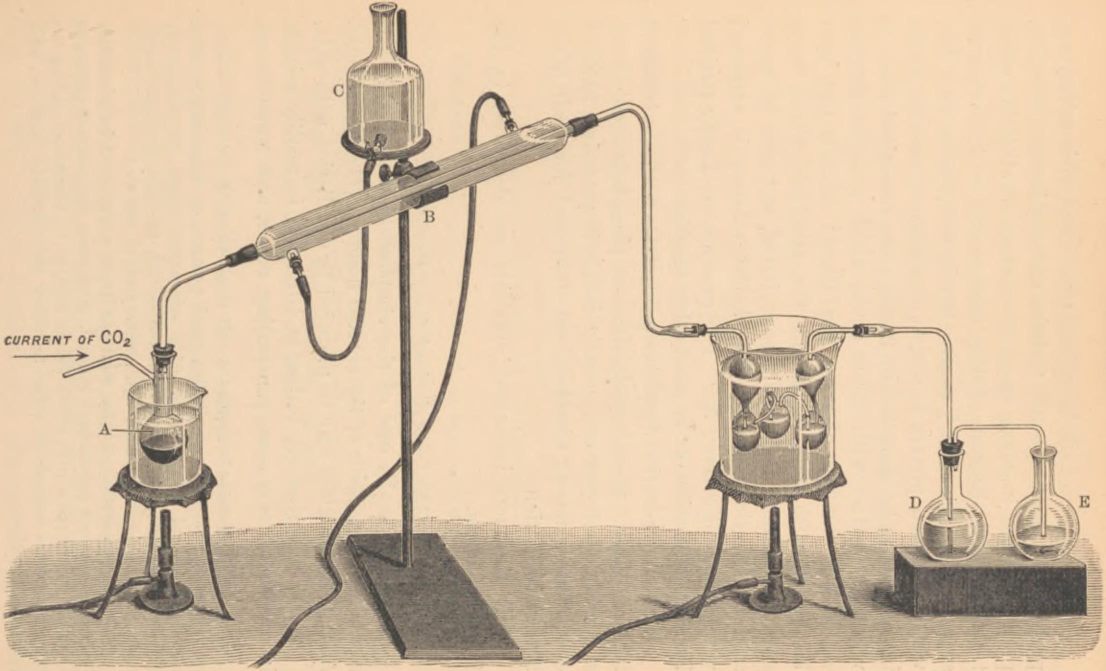


Fig. 20.

The extraction of alkaloids from plants, and their subsequent purification, are frequently matters of considerable difficulty, partly because in many cases a number of alkaloids occur together, partly because of the neutral and acid substances, such as the glucosides,* sugars, tannic acid, malic acid, &c., which are often present in large quantities. Generally speaking, they may be extracted by treating the macerated plant or vegetable product with dilute acids, which dissolve out the alkaloids in the form of salts; the filtered solution may then be treated with soda to liberate the alkaloids, which, being sparingly soluble, are usually precipitated, and may be separated by filtration; if not, the alkaline solution is extracted with ether, chloroform, &c. The products are finally purified by recrystallisation, or in some other manner.

Most alkaloids give insoluble precipitates with a solution of tannic, picric, phosphomolybdic, or phosphotungstic acid, and with a solution of mercuric iodide in potassium iodide,† &c.; these reagents, therefore, are often used for their detection and isolation.

Only the more important alkaloids are described in the following pages.

Alkaloids derived from Pyridine.

Coniine, $C_8H_{17}N$, one of the simplest known alkaloids, is contained in the seeds of the spotted hemlock (*Conium maculatum*), from which it may be prepared by distillation with soda.

It is a colourless oil, boiling at 167°, and is readily soluble in water; it has a most penetrating odour, and turns brown

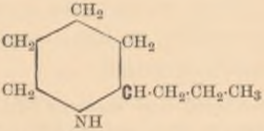
---

* The term *glucoside* is applied to all those vegetable products which, on treatment with acids or alkalies, yield a sugar, or some closely allied carbohydrate and one or more other substances (which are frequently phenols or aromatic aldehydes) as decomposition products (compare amygdalin, p. 405; salicin, p. 404; ruberythric acid, p. 465, &c.).

† For the preparation of these solutions larger works must be consulted. In cases of alkaloid poisoning it is usual, after using the stomach-pump, to wash out the stomach with dilute tannic acid, or to administer strong tea (which contains tannin), in order to render the alkaloids insoluble, and, therefore, harmless.

on exposure to air. Coniine is a strong base, and combines with acids to form salts, such as the *hydrochloride*, $C_8H_{17}N,HCl$, which are readily soluble in water; both the base and its salts are exceedingly poisonous, a few drops of the pure substance causing death in a short time by paralysing the muscles of respiration.

Ladenburg has shown that coniine is dextrorotatory *a-propylpiperidine*,



and has succeeded in preparing it synthetically, the first instance of the synthesis of an optically active alkaloid.

a-Propylpiperidine contains an asymmetric carbon atom (shown in heavy type—compare p. 533), and, therefore, like lactic acid, it exists in three modifications, all of which have been synthetically prepared; the inactive modification may be separated into the two optically active compounds by crystallisation of its tartrate (compare p. 544).

Nicotine, $C_{10}H_{14}N_2$, is present in the leaves of the tobacco plant (*Nicotiana tabacum*), combined with malic or citric acid.

Tobacco leaves are extracted with boiling water, the extract concentrated, mixed with milk of lime, and distilled; the distillate is acidified with oxalic acid, evaporated to a small bulk, decomposed with potash, and the free nicotine extracted with ether. The ethereal solution, on evaporation, deposits the crude alkaloid, which is purified by distillation in a stream of hydrogen.

Nicotine is a colourless oil, which boils at 241°, possesses a very pungent odour, and rapidly turns brown on exposure to air; it is readily soluble in water and alcohol. It is a strong di-acid base, and forms crystalline salts, such as the *hydrochloride*, $C_{10}H_{14}N_2,2HCl$; it combines directly with two molecules of methyl iodide, yielding *nicotine dimethiodide*, $C_{10}H_{14}N_2,2CH_3I$, a fact which shows that it is a di-tertiary base (p. 484). When oxidised with chromic acid, it yields nicotinic acid (pyridine-β-carboxylic acid, p. 479); it is, therefore, a pyridine-derivative, but its constitution has not yet been determined.

Nicotine is exceedingly poisonous, two or three drops taken into the stomach being sufficient to cause death in a few minutes. It shows no very characteristic reactions, but its presence may be detected by its extremely pungent odour (which recalls that of a foul tobacco pipe).

Piperine, $C_{17}H_{19}NO_3$, occurs to the extent of about 8–9 per cent. in pepper, especially in black pepper (*Piper nigrum*), from which it is easily extracted.

The pepper is powdered and warmed with milk of lime for 15 minutes; the mixture is then evaporated to dryness on a water-bath, extracted with ether, the ethereal solution evaporated, and the residual crude piperine purified by recrystallisation from alcohol.

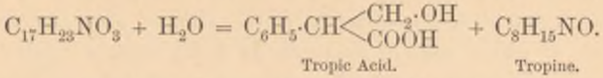
It crystallises in prisms, melts at 128°, and is almost insoluble in water; it is only a very weak base, and when heated with alcoholic potash, it is decomposed into piperidine (p. 476) and piperic acid,

$$C_{17}H_{19}NO_3 + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic Acid.}}{C_{12}H_{10}O_4}.$$

Atropine, or daturine, $C_{17}H_{23}NO_3$, does not occur in nature, although it is prepared from the deadly nightshade (*Atropa belladonna*). This plant contains two isomeric and closely related alkaloids *hyoscyamine* and *hyoscine*, and the former readily undergoes intramolecular change into atropine on treatment with bases.

The plant is pressed, the juice mixed with potash, and extracted with chloroform (1 litre of juice requires 4 grams of potash and 30 grams of chloroform); the chloroform is then evaporated, the atropine extracted from the residue with dilute sulphuric acid, the solution treated with potassium carbonate, and the precipitated alkaloid recrystallised from alcohol.

It crystallises from dilute alcohol in glistening prisms, and melts at 115°; it is readily soluble in alcohol, ether, and chloroform, but almost insoluble in water. When boiled with baryta water it is readily hydrolysed, yielding *tropic acid* and a base called *tropine*, which is a derivative of pyridine,



$$C_{17}H_{23}NO_3 + H_2O = \underset{\text{Tropic Acid.}}{C_6H_5{\cdot}CH{<}\begin{matrix}CH_2{\cdot}OH\\ COOH\end{matrix}} + \underset{\text{Tropine.}}{C_8H_{15}NO.}$$

Atropine is a strong base, and forms well-characterised salts, of which the *sulphate*, $(C_{17}H_{23}NO_3)_2,H_2SO_4$, is readily soluble, and, therefore, most commonly used in medicine; both the base and its salts are excessively poisonous, 0·05—0·2 gram causing death. Atropine sulphate is largely used in ophthalmic surgery, owing to the remarkable property which it possesses of dilating the pupil when its solution is placed on the eye.

Test for Atropine.—If a trace of atropine be moistened with fuming nitric acid, and evaporated to dryness on a water-bath, it yields a yellow residue, which, on the addition of alcoholic potash, gives an intense violet solution, the colour gradually changing to red.

Cocaïne, $C_{17}H_{21}NO_4$, and several other alkaloids of less importance, are contained in coca leaves (*Erythroxylon coca*).

The coca leaves are extracted with hot water (80°), the solution mixed with lead acetate (in order to precipitate tannin, &c.), filtered, and the lead in the filtrate precipitated with sodium sulphate; the solution is then rendered alkaline with soda, the cocaïne extracted with ether, and purified by recrystallisation from alcohol.

Cocaïne crystallises in colourless prisms, melts at 98°, and is sparingly soluble in water; it forms well-characterised salts, of which the *hydrochloride*, $C_{17}H_{21}NO_4,HCl$, is most largely used in medicine. Cocaïne is a very valuable local anæsthetic, and is used in minor surgical operations, as its local application takes away all sensation of pain; it is, however, poisonous, one grain injected subcutaneously having been attended with fatal results.

When heated with acids or alkalies, cocaïne is readily hydrolysed with formation of benzoic acid, methyl alcohol, and ecgonine (a derivative of tetrahydropyridine),

$$C_{17}H_{21}NO_4 + 2H_2O = C_6H_5{\cdot}COOH + CH_3{\cdot}OH + C_9H_{15}NO_3.$$

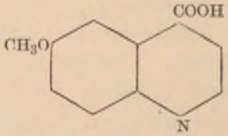
Alkaloids derived from Quinoline.

Quinine, $C_{20}H_{24}N_2O_2$, cinchonine (see below), and several other allied alkaloids, occur in all varieties of cinchona-bark, some of which contain as much as 3 per cent. of quinine. The alkaloids are contained in the bark, combined with tannic and quinic acids.*

The powdered bark is extracted with dilute sulphuric acid, and the solution of the sulphates precipitated with soda. The crude mixture of alkaloids thus obtained is dissolved in alcohol, the solution neutralised with sulphuric acid, and the sulphates, which are deposited, repeatedly recrystallised from water. Quinine sulphate is the least soluble, and separates out first, the sulphates of cinchonine and the other alkaloids remaining in solution; from the pure sulphate, quinine may be obtained as an amorphous powder by adding ammonia.

Quinine crystallises in silky needles, melts at 177°, and is only very sparingly soluble in water; it is only a feeble di-acid base, and generally forms acid salts, such as the *sulphate*, $(C_{20}H_{24}N_2O_2)_2,H_2SO_4 + 8H_2O$; many of its salts are soluble in water, and much used in medicine as tonics, and for lowering the temperature in cases of fever, &c.

Quinine is a di-tertiary base, because it combines with methyl iodide to form *quinine dimethiodide*, $C_{20}H_{24}N_2O_2,(CH_3I)_2$; it is a derivative of quinoline, because, on oxidation with chromic acid, it yields *quininic acid* (methoxyquinoline-γ-carboxylic acid),



Quinine appears to be methoxy-cinchonine, and that it contains one methoxy-group, has been demonstrated by Zeisel's method (p. 486); this view accords with the fact

---

* *Quinic acid*, $C_6H_7(OH)_4{\cdot}COOH$, crystallises in colourless prisms, and melts at 162°. It is a derivative of benzoic acid, being, in fact, hexahydrotetrahydroxybenzoic acid.

that, whereas cinchonine, on oxidation, yields quinoline-γ-carboxylic acid, quinine yields the methoxy-derivative of this acid: in spite, however, of a great amount of laborious investigation, the constitution of quinine is still an unsolved problem.

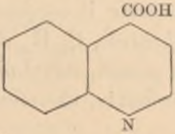
Tests for Quinine.—If a solution of a salt of quinine be mixed with chlorine- or bromine-water, and then ammonia added, a highly characteristic emerald green colouration is produced; quinine is also characterised by the fact that dilute solutions of its salts show a beautiful light-blue fluorescence.

Cinchonine, $C_{19}H_{22}N_2O$, accompanies quinine in almost all the cinchona-barks, and is present in some kinds (in the bark, *China Huanaco*) to the extent of 2·5 per cent.

In order to prepare cinchonine, the mother-liquors from the crystals of quinine sulphate (see above) are treated with soda, and the precipitate dissolved in the smallest possible quantity of boiling alcohol; the crude cinchonine, which separates on cooling, is further purified by converting into the sulphate, and crystallising this salt from water.

Cinchonine crystallises in colourless prisms, melts at 250°, and resembles quinine in ordinary properties; its salts, for example, are antipyretics, but are much less active than those of quinine.

Oxidising agents, such as nitric acid and potassium permanganate, readily attack cinchonine, converting it into a variety of substances, one of the most important of which is *cinchoninic acid*, or quinoline-γ-carboxylic acid,



The formation of this acid not only proves that cinchonine is a quinoline-derivative, but also shows the close relationship existing between quinine and cinchonine (see above).

Strychnine, $C_{21}H_{22}N_2O_2$, and brucine, two highly poisonous alkaloids, are contained in the seeds of *Strychnos nux vomica* and of *Strychnos Ignatii* (Ignatius' beans), but they are usually extracted from the former.

Powdered nux vomica is boiled with dilute alcohol, the filtered solution evaporated to expel the alcohol, and treated with lead acetate to precipitate tannin, &c. The filtrate is then treated with hydrogen sulphide to precipitate the lead, and the filtered solution mixed with magnesia and allowed to stand. The precipitated alkaloids are separated, and warmed with a little alcohol, which dissolves out the brucine; the residual *strychnine* is further purified by recrystallisation from alcohol.

The alcoholic solution of the brucine—which still contains strychnine—is evaporated, and the residue dissolved in dilute acetic acid; this solution is now evaporated to dryness on a water-bath, during which process the strychnine acetate decomposes, with loss of acetic acid and separation of the free base. The stable brucine acetate is dissolved again by adding water, the filtered solution treated with soda, and the precipitated *brucine* purified by recrystallisation from dilute alcohol.

Strychnine crystallises in beautiful rhombic prisms, and melts at 284°; although it is very sparingly soluble in water (1 part in 4000 at 15°), its solution possesses an intensely bitter taste, and is very poisonous. Strychnine is, in fact, one of the most poisonous alkaloids, half a grain of the sulphate having caused death in twenty minutes.

Although strychnine contains two atoms of nitrogen, it is, like brucine, only a mon-acid base, forming salts, such as the *hydrochloride*, $C_{21}H_{22}N_2O_2,HCl$, with one equivalent of an acid; many of the salts are soluble in water. It is, furthermore, a tertiary base, because it combines with methyl iodide to form *strychnine methiodide*, $C_{21}H_{22}N_2O_2,CH_3I$.

When distilled with potash, strychnine yields, among other products, quinoline; probably, therefore, it is a derivative of this base.

Test for Strychnine.—Strychnine is very readily detected, as it shows many characteristic reactions, of which the following is the most important: When a small quantity of powdered strychnine is placed in a large porcelain basin, a little concentrated sulphuric acid added, and then a little powdered potassium bichromate dusted over the liquid, an intense violet solution, which gradually becomes bright-red, and then yellow, is produced.

Brucine, $C_{23}H_{26}N_2O_4$, crystallises in colourless prisms, with 4 mols. H_2O, and melts at 178°. It is more readily soluble in water and in alcohol than strychnine, and, although very poisonous, it is not nearly so deadly as the latter (its physiological effect being only about $\frac{1}{24}$th of that of strychnine). Although it contains two atoms of nitrogen, brucine, like strychnine, is a mon-acid base. The *hydrochloride*, for example, has the composition $C_{23}H_{26}N_2O_4$, HCl; it is also a tertiary base, because it combines with methyl iodide, to form *brucine methiodide*, $C_{23}H_{26}N_2O_4$, CH_3I.

Test for Brucine.—When a solution of a brucine salt is treated with nitric acid, a deep brownish-red colouration is obtained, and, on warming, the solution becomes yellow; if now stannous chloride be added, an intense violet colouration is produced.

This colour reaction serves as a delicate test, both for brucine and for nitric acid, as it may be carried out with very small quantities.

Alkaloids contained in Opium.

The juice of certain kinds of poppy-heads (*Papaver somniferum*) contains a great variety of alkaloids, of which *morphine* is the most important, but *codeïne*, *narcotine*, *thebaïne*, and *papaverine* may also be mentioned. All these compounds are present in the juice in combination with *meconic acid*,* and partly also with sulphuric acid. When incisions are made in

---

* *Meconic acid*, $C_5HO_2(OH)(COOH)_2$, is a hydroxydicarboxylic acid belonging to the fatty series. It crystallises with three molecules of water, and gives, with ferric chloride, an intense dark-red colouration. In cases of suspected opium-poisoning this acid is always tested for, owing to the ease with which it can be detected by this colour reaction.

the poppy-heads, and the juice which exudes is collected and left to dry, it assumes a pasty consistency, and is called *opium*. An alcoholic tincture of opium, containing about 1 grain of opium in 15 minims, is known as *laudanum*.

Preparation of Morphine.—Opium is extracted with hot water, the extract boiled with milk of lime, and filtered from the precipitate, which contains the meconic acid, and all the alkaloids, except morphine. The filtrate is then concentrated, digested with ammonium chloride until ammonia ceases to be evolved (to convert any lime present into soluble calcium chloride), and allowed to stand for some days; the morphine, which separates, is collected and purified by recrystallisation from fusel oil (part i. p. 99).

Morphine, $C_{17}H_{19}NO_3$, crystallises in colourless prisms, with 1 mol. H_2O, and is only slightly soluble in water and cold alcohol, but dissolves readily in potash and soda, from which it is reprecipitated on the addition of acids; it has, in fact, the properties of a phenol. At the same time, it is a monacid base, and forms well-characterised salts with acids. The *hydrochloride*, $C_{17}H_{19}NO_3,HCl + 3H_2O$, crystallises from water in colourless needles, and is the salt most commonly employed in medicine. Morphine has a bitter taste, and is excessively poisonous, one grain of the hydrochloride having been found sufficient to cause death; on the other hand, the system may become so accustomed to the habitual use of opium that, after a time, very large quantities may be taken daily without fatal effects.

Morphine hydrochloride is extensively used in medicine as a soporific, especially in cases of intense pain, which it relieves in a remarkable manner.

Tests for Morphine.—Morphine has the property of liberating iodine from a solution of iodic acid. If a little iodic acid be dissolved in water, and a few drops of a solution of morphine hydrochloride added, a brownish colouration is at once produced, owing to the liberation of iodine, and, on adding some of the solution to starch-paste, the well-known deep-blue colouration is obtained.

A solution of morphine, or of a morphine salt, gives a deep-blue colouration with ferric chloride, but, perhaps, the most delicate test for the alkaloid is the following: If a trace of morphine be dissolved in concentrated sulphuric acid, the solution kept for 15 hours, and then treated with nitric acid, it gives a bluish-violet colour, which changes to blood-red. This reaction is very delicate, and is well shown by 0·01 milligramme of morphine.

The constitution of morphine is still undetermined, but that it is a tertiary base is proved by the fact that, when treated with methyl iodide, it yields *morphine methiodide*,

$$C_{17}H_{19}NO_3,CH_3I.$$

Morphine contains two hydroxyl-groups, one of which is phenolic, the other alcoholic. The third atom of oxygen present in the molecule is not ketonic (that is, present as $>CO$); it must, therefore, be combined with two carbon atoms $-C-O-C-$ (as in ordinary ether). It is to the presence of the phenolic hydroxyl-group that morphine owes its property of dissolving in alkalies, and giving a blue colour with ferric chloride.

If the base be heated with potash and methyl iodide, *methylmorphine*, $C_{17}H_{17}NO(OCH_3)\cdot OH$, is produced, a substance which is identical with *codeïne*, an alkaloid which accompanies morphine in opium. Codeïne is insoluble in alkalies, and is, therefore, not a phenol; it behaves, however, like an alcohol, and gives, with acetic anhydride, *acetylcodeïne*, $C_{17}H_{17}NO(OCH_3)\cdot C_2H_3O_2$.

It is very remarkable that morphine is a derivative of phenanthrene, as derivatives of this hydrocarbon are very seldom met with in nature. If morphine be distilled with zinc-dust, a considerable quantity of this hydrocarbon is obtained, together with pyridine, quinoline, and other substances.

Alkaloids related to Uric Acid.

Caffeïne, theïne, or methyltheobromine, $C_8H_{10}N_4O_2$, occurs in coffee-beans ($\frac{1}{2}$ per cent.), in tea (2 to 4 per cent.), in kola-nuts (2·5 per cent.), and in other vegetable products.

Tea (1 part) is macerated with hot water (4 parts), milk of lime (1 part) added, and the whole evaporated to dryness on a water-bath; the caffeïne is then extracted from the residue by means of chloroform, the extract evaporated, and the crude base purified by recrystallisation from water.

Caffeïne crystallises in long, colourless needles, with 1 mol. H_2O, melts at 225°, and at higher temperatures sublimes undecomposed; it has a bitter taste, and is sparingly soluble in cold water and alcohol. Caffeïne is a feeble base, and forms salts only with strong acids; the *hydrochloride*, $C_8H_{10}N_4O_2,HCl$, is at once decomposed on treatment with water, with separation of the base.

The constitution of caffeïne has been determined by E. Fischer, who has shown that this substance and uric acid are very closely allied; caffeïne is, therefore, an example of an alkaloid which is not a derivative of pyridine or quinoline.

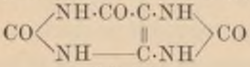
Tests for Caffeïne.—If a trace of caffeïne be evaporated with concentrated nitric acid, it gives a yellow residue (amalinic acid), which, on the addition of ammonia, becomes intensely violet (murexide reaction); this reaction is also shown by uric acid (part i. p. 292). A solution of caffeïne in chlorine water yields, on evaporation, a yellowish-brown residue, which dissolves in dilute ammonia, with a beautiful violet-red colouration.

Theobromine, $C_7H_8N_4O_2$, occurs in cocoa-beans, from which it may be obtained by treatment with lime, and extraction with alcohol. It crystallises from water, and shows the greatest resemblance to caffeïne in properties; the latter is, in fact, methyltheobromine, and may be obtained directly from theobromine in the following way:

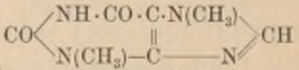
Theobromine contains an $>NH$ group, the hydrogen of which is readily displaced by metals (as in succinimide, part i. p. 238), and when treated with an ammoniacal silver nitrate solution, it yields *silver theobromine*. This substance interacts readily with methyl iodide with formation of caffeïne,

$$\underset{\text{Silver Theobromine.}}{C_7H_7N_4O_2Ag} + CH_3I = \underset{\text{Caffeïne.}}{C_7H_7N_4O_2{\cdot}CH_3} + AgI.$$

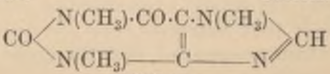
The relationship between uric acid, theobromine, and caffeïne is expressed by the following graphic formulæ:



Uric Acid.



Theobromine.



Caffeïne.

Antipyrine, Kairine, and Thalline.

These three nitrogenous compounds, which do not occur in nature, may be briefly described here as examples of what may be termed 'artificial alkaloids;' they are employed in medicine, as substitutes for quinine, for lowering the body-temperature in cases of fever.

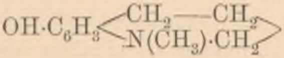
Antipyrine, $C_{11}H_{12}N_2O$, was first obtained by Knorr by treating ethyl acetoacetate (part i. p. 189) with phenylhydrazine (p. 376), and then heating the product (*phenylmethylpyrazolone*) with methyl iodide,

$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + C_6H_5\cdot NH\cdot NH_2 = C_{10}H_{10}N_2O + C_2H_5\cdot OH + H_2O$$

$$C_{10}H_{10}N_2O + CH_3I = C_{11}H_{12}N_2O,HI.$$

It is a colourless, crystalline compound, melts at 113°, and is readily soluble in water and alcohol; it is a strong mon-acid base, and its salts dissolve freely in water. Its aqueous solution gives a deep-red colouration with ferric chloride, and a bluish-green colouration with nitrous acid.

Kairine, or hydroxymethyltetrahydroquinoline,

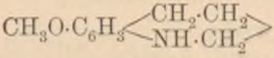


$$OH\cdot C_6H_3\left<\begin{array}{l}CH_2—CH_2\\N(CH_3)\cdot CH_2\end{array}\right>$$

may be obtained indirectly from *o*-amidophenol, which is first converted into hydroxyquinoline by Skraup's reaction (p. 482); this product is then reduced with tin and hydrochloric acid, and the tetrahydrohydroxyquinoline thus obtained is converted into its methyl-derivative by treating it with methyl iodide.

Kairine is a crystalline compound, melting at 114°. It is a strong base, and forms crystalline salts, of which the *hydrochloride*, $C_{10}H_{13}NO,HCl + H_2O$, is used in medicine.

Thalline, or methoxytetrahydroquinoline,



$$CH_3O\cdot C_6H_3\left<\begin{array}{l}CH_2\cdot CH_2\\NH\cdot CH_2\end{array}\right>$$

is isomeric with kairine, and is obtained by reducing the methoxyquinoline which is prepared from *p-methoxyaniline*, $C_6H_4(OCH_3)\cdot NH_2$, by Skraup's reaction; it is a crystalline compound, melting at 42°, and is used in the form of its sulphate or tartrate. With ferric chloride and other oxidising agents it gives a green precipitate.

Antifebrin, or acetanilide, another important febrifuge, has already been described (p. 362).

Choline, Betaïne, Neurine, and Taurine.

Certain nitrogenous substances which occur in the animal kingdom may also be referred to in this chapter, because they are basic compounds of great physiological importance; they really belong, however, to different classes of the fatty series.

Choline, or hydroxyethyltrimethylammonium hydroxide, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$, occurs in the blood, bile, brain-substance, yolk of egg, and in other parts of animal organisms, usually in the form of *lecithin* (a compound of choline, glycerol, phosphoric acid, and various fatty acids); it also occurs in mustard and in hops. It may be prepared synthetically by warming trimethylamine with ethylene oxide (part i. p. 223) in aqueous solution,

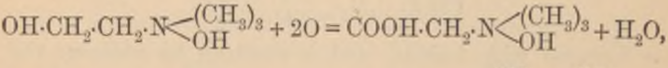
$$N(CH_3)_3 + C_2H_4O + H_2O = C_5H_{15}NO_2.$$

It is a crystalline, very hygroscopic, strongly basic substance, its aqueous solution having an alkaline reaction, and absorbing carbon dioxide from the air; when treated with hydrochloric acid it yields the corresponding chloride,

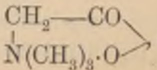
$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH + HCl = OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3Cl + H_2O,$$

but when boiled with water the base is decomposed into glycol and trimethylamine.

Betaïne, $C_5H_{11}NO_2$, is formed when choline undergoes mild oxidation; the acid, which is first produced by the conversion of the $-CH_2{\cdot}OH$ group into carboxyl,



$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}N{<}\genfrac{}{}{0pt}{}{(CH_3)_3}{OH} + 2O = COOH{\cdot}CH_2{\cdot}N{<}\genfrac{}{}{0pt}{}{(CH_3)_3}{OH} + H_2O,$$

loses one molecule of water, forming betaïne,  a salt-like compound, which has a neutral reaction, a somewhat sweet taste, and crystallises from dilute alcohol with 1 mol. H_2O.

When treated with hydrochloric acid, betaïne is converted into the *chloride*, $COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl$, and this compound may also be obtained synthetically by heating trimethylamine with chloracetic acid. Betaïne occurs in beet-juice, and is present in large quantities in the mother-liquors obtained in the preparation of beet-sugar.

Neurine, or vinyltrimethylammonium hydroxide,

$$CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH,$$

can be obtained by heating choline with hydriodic acid, and then treating the product with silver hydroxide,

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH + 2HI = CH_2I{\cdot}CH_2{\cdot}N(CH_3)_3I + 2H_2O$$

$$CH_2I{\cdot}CH_2{\cdot}N(CH_3)_3I + 2AgOH = CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH + 2AgI + H_2O\,;$$

it is formed, together with choline and numerous other bases, during the putrefaction of animal albuminoid matter.*

Neurine is only known in solution as a strongly basic, very soluble, and exceedingly poisonous substance, but some of its salts, as, for example, the *chloride*, $CH_2{:}CH{\cdot}N(CH_3)_3Cl$, are crystalline.

Taurine, or amidoethylsulphonic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$, occurs in the combined state in ox-gall and in many other animal secretions. It crystallises in colourless prisms, melts and decomposes at about 240°, and is readily soluble in water, but insoluble in alcohol; it has a neutral reaction, and is only a feeble acid, because the presence of the amido-group neutralises the effect of the sulphonic group to such an extent that it forms salts only with strong bases. When treated with nitrous acid, the amido-group is displaced by hydroxyl,

---

* The bases produced during the putrefaction of animal albuminoid matter are known collectively as *ptomaïnes*, and many of them are highly poisonous.

just as in the case of primary amines, and *hydroxyethylsulphonic acid* (isethionic acid) is formed,

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H + HO{\cdot}NO = OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H + N_2 + H_2O;$$

the last-named compound is one of the few examples of fatty sulphonic acids.

CHAPTER XXXIV.

DYES AND THEIR APPLICATION.

Although nearly all fatty compounds, and the majority of those belonging to the aromatic series, are colourless, most of the principal dyes used at the present day are aromatic compounds, the primary source of which is coal-tar.

That a dye must be a coloured substance is, of course, obvious, but a coloured substance is not necessarily a dye, in the ordinary sense of the word, unless it is also capable of fixing itself, or of being fixed, in the fabric to be dyed, in such a way that the colour is not removed by rubbing or by washing with water; azobenzene, for example, is intensely coloured, but it would not be spoken of as a dye, because it does not fulfil the second condition.

True dyes, in the sense just defined, may be roughly divided into two classes with respect to their behaviour with a *given* fabric: (*a*) Those which fix themselves on the fabric, and (*b*) those which do so only with the aid of a mordant.

If a piece of *silk* or *wool* be dipped into a solution of picric acid, it is dyed yellow, and the colour is not removed on subsequently washing with water, but is fixed in the fibre. If, however, a piece of *calico* or other *cotton* material be treated in the same way, the picric acid does not fix itself, and is completely removed on washing with water. A given substance may, therefore, be a dye for certain materials, but not for others; the animal fabrics, silk and wool, fix picric acid, and are dyed by it, but the vegetable fabric, cotton, does not—a behaviour which is repeatedly met with in the case of other colouring matters (see below).

Now, since picric acid is soluble in water, it is evident that it must have undergone some change when brought into contact with the silk or wool, otherwise it would be dissolved out of the fabric on washing with water. Materials such as wool, cotton, silk, &c., consist of minute fibres, which may be very roughly described as long, cylindrical, or flattened tubes (except in the case of silk, the fibres of which are solid), the walls of which, like parchment paper and animal membrane, allow of the passage of water and of dissolved crystalloids by diffusion, but not of colloid substances, or, of course, of matter in suspension. If, therefore, the picric acid were present in the fibre, *as* picric acid, it would, on washing, rapidly pass into the water by diffusion; as this is not the case, it must be assumed that it has actually combined with some substance in the silk or wool, and has been converted into a yellow compound, which is either insoluble or a colloid.

The nature of the insoluble compound formed when a material is dyed in this way is not known, but there are reasons for supposing that certain constituents of the fibre unite with the dye to form an insoluble salt. This seems probable, from the fact that nearly all dyes which thus fix themselves directly on the fabric are, to some extent, either basic or acid in character. Azobenzene, as already mentioned, is not a dye, probably, because it is a neutral substance; if, however, some group, such as an amido-, hydroxyl-, or sulphonic-group, which confers basic or acid properties, be introduced into the molecule of azobenzene, then the resulting derivative is a dye, because it has the property of combining directly with the fibres of certain materials (compare p. 522).

Another fact which leads to the same conclusion may be quoted. Certain dyes—as, for example, rosaniline—are salts of bases which are themselves colourless, and yet some materials may be dyed simply by immersion in *colourless* solutions of these bases, the same colour being obtained as with the coloured salt (that is, the dye itself); this can only be explained by assuming that some constituent of the fibre combines with the colourless base, forming with it a salt of the same colour as the dye.

Some fibres, especially silk and wool, seem to contain both acid and basic constituents, as they are often dyed directly both by basic and by acid dyes; cotton, on the other hand, seems to be almost free from both, as, except in rare cases, it does not combine with colouring matters.

Granting, then, that the fixing of a dye within the fibre is the result of its conversion into some insoluble compound, it seems reasonable to suppose that, even if a colouring matter be incapable of fixing itself in the fibre of the material, it might still be employed as a dye, provided that, after it had once passed through the walls of the fibre, it could be there converted into some insoluble compound by other means; this principle is applied in the case of dyes of the second class, which are fixed in the material with the aid of *mordants.*

Mordants are substances which (usually after first undergoing some preliminary change) combine with dyes, forming insoluble coloured compounds; the colour of the dyed fabric in such cases depends, of course, on that of the compound thus produced, and not on that of the dye itself, so that by using different mordants, different shades or colours are obtained.

As an example of dyes of the second class, alizarin may be taken, as it illustrates very clearly the use of mordants.

If a piece of calico be dipped into a solution of alizarin, it is coloured *yellow*, but the colour is not fixed, and is easily got rid of again on washing with soap and water; if, however, a piece of calico, which has been previously mordanted with a suitable aluminium salt (in the manner described below), be treated in the same way, it is dyed a fast *red*, the alizarin having combined with the aluminium salt in the fibre to form a red insoluble compound; if, again, the calico had been mordanted with a ferric salt instead, it would have been dyed a fast *dark purple.*

Substances very frequently employed as mordants are certain salts of iron, aluminium, chromium, and tin, more especially those, such as the acetates, sulphocyanides, and alums, which undergo decomposition on treatment with water or with steam, yielding either an insoluble basic salt or an insoluble metallic hydroxide.

The process of mordanting usually involves two operations: firstly, the fabric is passed through, or soaked in, a solution of the mordant, in order that its fibres may become impregnated with the metallic salt; secondly, the fabric is treated in such a way that the salt is decomposed within the fibres, and there converted into some insoluble compound.

This second operation, the fixing of the mordant, so that it will not be washed out when the fabric is brought into the dye-bath, is accomplished in many ways. One of the simplest is to pass the mordanted material through a solution of some weak alkali (ammonia, sodium carbonate, lime) or of some salt, such as sodium phosphate or arsenate, which interacts with the metallic salt in the fibre, forming an insoluble metallic hydroxide, phosphate, arsenate, &c. Another method, applicable more especially in the case of mordants which are salts of *volatile acids*, consists in exposing the fabric to the action of steam, at a suitable temperature; under these conditions the metallic salt dissociates, the acid volatilises with the steam, and an insoluble hydroxide or basic salt remains in the fibre.

In the case of silk and woollen fabrics, the operations of mordanting and fixing the mordant may often be carried out simultaneously, by soaking the materials in a boiling dilute solution of the mordant; under these conditions, the metallic salt is partially dissociated, and deposited in the fibre in an insoluble form; silk may sometimes be simply soaked in a cold, concentrated solution of the mordant, and then washed with water to cause the dissociation of the metallic salt.

In cases where only parts of the fabric are to be dyed, as, for example, in *calico-printing*, the solution of the mordant is mixed with the dye, and with some thickening substance, such as starch, dextrin, gum, &c., and printed on the fabric in the required manner, the thickening being used to prevent the mordant spreading to other parts; during the subsequent steaming process, the metallic hydroxide which is produced combines with and fixes the dye.

All these processes are identical in principle, the object being to deposit some insoluble metallic compound within the fibre; when, now, the mordanted material is treated with a solution of a suitable dye, the latter unites with the metallic hydroxide, forming a coloured compound which is fixed in the fibre. The coloured substances produced by the combination of a dye with a metallic hydroxide are termed *lakes*, and those dyes which form lakes are called *acid* dyes.

Tannin (p. 440) is an example of a different class of mordants—namely, of those which are employed with *basic dyes*, such as malachite green (p. 509) and rosaniline (p. 513): its use depends on the fact that, being an acid, it combines with dyes of a basic character, forming with them insoluble coloured salts (tannates), which are thus fixed in the fibre. The fabric is mordanted by first passing it through a solution of tannin, and then through a weak solution of tartar emetic, or stannic chloride, which converts the tannin into an insoluble antimony, or tin tannate, and thus fixes it in the fibre.

All colouring matters are converted into colourless compounds on reduction, and in many cases such a radical change in composition takes place, that the reduction product cannot be directly reconverted into the dye by oxidation; a nitro-group, for example, may be reduced to an amido-group, or a hydroxyl-group may be displaced by hydrogen, or the molecule may be resolved into two simpler molecules, as in the case of amidoazobenzene, which, when treated with *powerful* reducing agents, yields aniline and *p*-phenylenediamine,

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2 + 4H = C_6H_5{\cdot}NH_2 + NH_2{\cdot}C_6H_4{\cdot}NH_2.$$

In very many cases, however, the colourless reduction product differs from the dye in composition, simply in containing two or more additional atoms of hydrogen, and may be readily reconverted into the dye by oxidising agents; such reduction products are called *leuco-compounds*.

Amidoazobenzene, for example, the hydrochloride or oxalate of which is the dye *aniline yellow* (p. 524), on treatment with *mild* reducing agents, such as zinc-dust and acetic acid, yields amidohydrazobenzene, which is only slightly coloured,

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2 + 2H = C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2.$$

The last-named substance is readily oxidised on shaking its alcoholic solution with precipitated (yellow) mercuric oxide, with regeneration of amidoazobenzene, and is, therefore, *leuco*-amidoazobenzene; many examples of leuco-compounds will be met with in the following pages.

When an insoluble dye yields a soluble leuco-compound, which is very readily reconverted into the dye on oxidation, it may be applied to fabrics in a special manner, as, for example, in the case of dyeing with indigo blue. Indigo blue, $C_{16}H_{10}N_2O_2$ (p. 527), is insoluble in water, but on reduction it is converted into a readily soluble leuco-base, $C_{16}H_{12}N_2O_2$, known as *indigo white*: in dyeing with indigo, a solution of indigo white is prepared by reducing indigo, suspended in water, with grape-sugar and soda, or ferrous sulphate and soda, and the fabric is then passed through this solution, whereupon the indigo white diffuses through the walls into the fibres; on subsequent exposure to the air the indigo white is reconverted into indigo blue by oxidation, and the insoluble dye is thus fixed in the fabric.

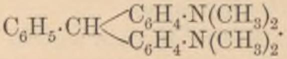
Some of the more important dyes will now be described: as, however, it would be impossible to discuss fully the constitutions of these compounds, it must be understood that the formulæ employed in the following pages are those commonly accepted, and that most of them have been satisfactorily established.

Derivatives of Triphenylmethane.

Triphenylmethane, $C_6H_5 \cdot CH(C_6H_5)_2$ (p. 340), or, more strictly speaking, triphenyl carbinol, $C_6H_5 \cdot C(C_6H_5)_2 \cdot OH$, is the parent substance of a number of dyes, which are of very great technical importance, on account of their brilliancy; as examples, malachite green, pararosaniline, and rosaniline may be described.

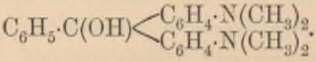
Three distinct classes of substances are constantly met with in studying the triphenylmethane group of colouring matters—namely, the **leuco-base**, the **colour-base**, and the **dye** itself.

The *leuco-base* (p. 507) is an amido-derivative of triphenylmethane; in the case of malachite green, for example, the leuco-base is tetramethyldiamidotriphenylmethane,



$$C_6H_5 \cdot CH \begin{matrix} \diagup C_6H_4 \cdot N(CH_3)_2 \\ \diagdown C_6H_4 \cdot N(CH_3)_2 \end{matrix}.$$

The *colour-base* is a derivative of triphenyl carbinol, and is produced from the leuco-base by oxidation, just as triphenyl carbinol results from the oxidation of triphenylmethane (p. 341); tetramethyldiamidotriphenyl carbinol, for example, is the colour-base of malachite green,

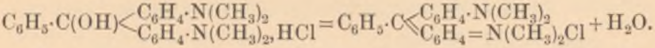


$$C_6H_5 \cdot C(OH) \begin{matrix} \diagup C_6H_4 \cdot N(CH_3)_2 \\ \diagdown C_6H_4 \cdot N(CH_3)_2 \end{matrix}.$$

Both the leuco-base and the colour-base are usually colourless, and the latter also yields colourless, or only slightly coloured, salts on treatment with *cold* acids; when *warmed* with acids, however, the colour-base is at once converted into highly coloured salts, which constitute the dye, water being eliminated,

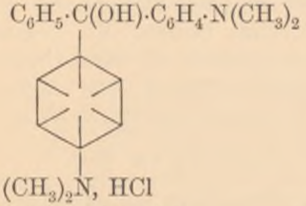
$$\underset{\text{Malachite Green Base.}}{C_{23}H_{26}N_2O} + HCl = \underset{\text{Chloride of Malachite Green.}}{C_{23}H_{25}N_2Cl} + H_2O.$$

This loss of water must be assumed to be due to combination taking place between the hydroxyl-group and the hydrogen atom of the acid employed, and the conversion of the colourless, into the coloured, salt may be expressed in the following way:

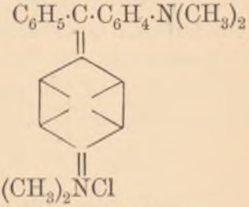


$$C_6H_5\cdot C(OH)<\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2,HCl\end{matrix} = C_6H_5\cdot C<\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4=N(CH_3)_2Cl\end{matrix} + H_2O.$$

This change resembles the conversion of colourless hydroquinone into highly coloured quinone (and also that of *p*-amidophenol into quinone-chlorimide, p. 416), as will be more readily understood if it be represented thus:



Hydrochloride of Colour-base.

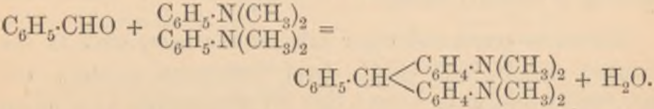


Chloride of Malachite Green.

Exactly similar changes may be assumed to take place in the formation of the pararosaniline and rosaniline dyes, and, in fact, in the case of many other colouring matters, some of which are described later.

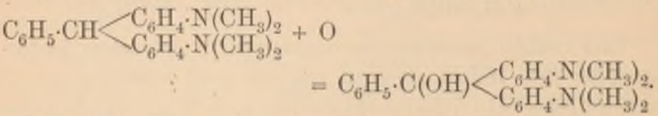
Malachite green (of commerce) is a double salt, formed by the combination of the chloride of tetramethyldiamidotriphenyl carbinol with zinc chloride, and the first step in its manufacture is the preparation of *leuco-malachite green* or *tetramethyl-p-diamidotriphenylmethane*, $C_6H_5\cdot CH<\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2\end{matrix}$.

Leuco-malachite green is obtained by the action of dehydrating agents, generally zinc chloride, on a mixture of benzaldehyde (1 mol.) and dimethylaniline (2 mols.),



$$C_6H_5\cdot CHO + \begin{matrix}C_6H_5\cdot N(CH_3)_2\\ C_6H_5\cdot N(CH_3)_2\end{matrix} = C_6H_5\cdot CH<\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2\end{matrix} + H_2O.$$

It is a colourless, crystalline substance, which, when treated with oxidising agents, such as manganese dioxide and sulphuric acid, or lead dioxide and hydrochloric acid, yields *tetramethyldiamidotriphenyl carbinol*, just as triphenylmethane, under similar circumstances, yields triphenyl carbinol,



$$C_6H_5\cdot CH{<}\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2\end{matrix} + O = C_6H_5\cdot C(OH){<}\begin{matrix}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2\end{matrix}.$$

This oxidation product is a colourless base, and dissolves in *cold* acids, yielding colourless solutions of its salts; when, however, such solutions are warmed, the colourless salts decompose, and lose one molecule of water, intensely green solutions of the dye being obtained; the formation of the chloride, for example, is expressed by the equation

$$C_{23}H_{26}N_2O + HCl = C_{23}H_{25}N_2Cl + H_2O,$$

and its double salt, with zinc chloride (or the oxalate of the base), constitutes the malachite green (Victoria green, benzaldehyde green) of commerce.

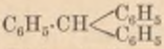
Preparation of Malachite Green.—Dimethylaniline (10 parts) and benzaldehyde (4 parts) are heated with zinc chloride (4 parts) in a porcelain basin, or enamelled iron pot, for two days at 100°, with constant stirring; the product is then submitted to distillation in steam, to get rid of the unchanged dimethylaniline, and allowed to cool. The leuco-compound is now separated from the aqueous solution of zinc chloride, washed with water, dissolved in as little hydrochloric acid as possible, the solution diluted considerably with water, and the calculated quantity of freshly precipitated lead peroxide, (PbO_2), added. The filtered dark-green solution is then mixed with sodium sulphate, to precipitate any lead, again filtered, and the colouring matter precipitated in the form of its zinc double salt, $3C_{23}H_{25}N_2Cl,2ZnCl_2 + 2H_2O$, by the addition of zinc chloride and common salt; this salt is finally purified by recrystallisation.

Malachite green, and other salts of the base, such as the oxalate, $2C_{23}H_{24}N_2,3C_2H_2O_4$, form deep-green crystals, and are readily soluble in water; they are decomposed by alkalies, with separation of the *colour-base*, tetramethyldiamidotriphenyl carbinol.

Malachite green dyes silk and wool directly an intense dark-bluish green, but cotton must first be mordanted with tannin and tartar emetic (p. 506), and then dyed in a bath gradually raised to 60°.

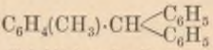
Many other dyes, closely allied to malachite green, are prepared by condensing benzaldehyde with tertiary alkylanilines (p. 366). *Brilliant green*, for example, is finally obtained when diethylaniline is employed instead of dimethylaniline in the above-described process, whereas *acid green* is obtained from benzaldehyde and ethylbenzylaniline,* $C_6H_5\cdot N(C_2H_5)\cdot C_7H_7$, in a similar manner. The salts of these two colouring matters are very sparingly soluble in water, and, therefore, of little use as dyes; for this reason, the bases are treated with anhydrosulphuric acid, and thus converted into a mixture of readily soluble sulphonic acids, the sodium salts of which constitute the commercial dyes. Silk and wool are dyed in a bath acidified with sulphuric acid (hence the name acid green), and very bright greens are obtained, but these dyes are not suitable for cotton.

Pararosaniline and rosaniline are exceedingly important dyes, which, like malachite green, are derived from triphenylmethane. Whereas, however, malachite green is a derivative of *diamido*-triphenylmethane, the rosanilines are all *triamido*-triphenylmethane derivatives, as will be seen from the following table:



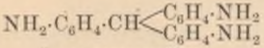
$C_6H_5\cdot CH{<}\begin{matrix}C_6H_5\\C_6H_5\end{matrix}$

Triphenylmethane.



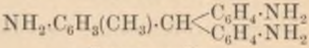
$C_6H_4(CH_3)\cdot CH{<}\begin{matrix}C_6H_5\\C_6H_5\end{matrix}$

Tolyldiphenylmethane
(Methyltriphenylmethane).



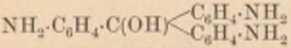
$NH_2\cdot C_6H_4\cdot CH{<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{matrix}$

Leuco-pararosaniline
(Paraleucaniline).
Triamidotriphenylmethane.



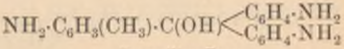
$NH_2\cdot C_6H_3(CH_3)\cdot CH{<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{matrix}$

Leuco-rosaniline
(Leucaniline).
Triamidotolyldiphenylmethane.



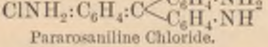
$NH_2\cdot C_6H_4\cdot C(OH){<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{matrix}$

Pararosaniline Base.
Triamidotriphenyl Carbinol.



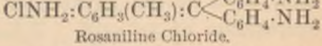
$NH_2\cdot C_6H_3(CH_3)\cdot C(OH){<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{matrix}$

Rosaniline Base.
Triamidotolyldiphenyl Carbinol.



$ClNH_2{:}C_6H_4{:}C{<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH\end{matrix}$

Pararosaniline Chloride.



$ClNH_2{:}C_6H_3(CH_3){:}C{<}\begin{matrix}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{matrix}$

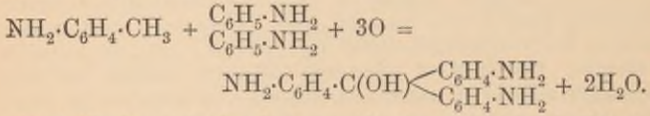
Rosaniline Chloride.

---

* Produced by treating aniline with benzylchloride and ethyl bromide successively.

In all these compounds, the amido-groups have been proved to be in the *para*-position to the methane carbon atom.

Pararosaniline (of commerce) is the chloride of triamidotriphenyl carbinol, a base which is most conveniently prepared by oxidising a mixture of *p*-toluidine (1 mol.) and aniline (2 mols.) with arsenic acid, or nitrobenzene (compare rosaniline, p. 513).



$$NH_2{\cdot}C_6H_4{\cdot}CH_3 + \begin{matrix}C_6H_5{\cdot}NH_2\\ C_6H_5{\cdot}NH_2\end{matrix} + 3O = NH_2{\cdot}C_6H_4{\cdot}C(OH)\left\langle\begin{matrix}C_6H_4{\cdot}NH_2\\ C_6H_4{\cdot}NH_2\end{matrix}\right. + 2H_2O.$$

Probably the *p*-toluidine is first oxidised to *p*-amidobenzaldehyde, $NH_2{\cdot}C_6H_4{\cdot}CHO$, which then condenses with the aniline (as in the case of the formation of leuco-malachite green), to form leuco-pararosaniline; this compound is then converted into the pararosaniline base by further oxidation.

The salts of pararosaniline have a deep magenta colour, and are soluble in warm water; they dye silk, wool, and cotton, under the same conditions as described in the case of malachite green; pararosaniline is, however, not so largely used as rosaniline.

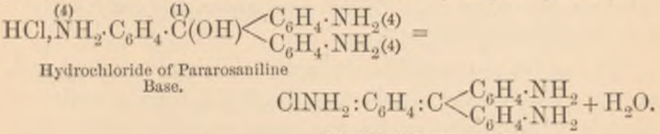
Triamidotriphenyl carbinol, the pararosaniline colour-base, is obtained, as a colourless precipitate, on adding alkalies to a solution of the chloride, or of some other salt; it crystallises from alcohol in colourless needles, and, when treated with acids, gives the intensely coloured pararosaniline salts.

Leuco-pararosaniline, paraleucaniline or triamidotriphenylmethane, $NH_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2$, is prepared by reducing triamidotriphenyl carbinol with zinc-dust and hydrochloric acid,

$$NH_2{\cdot}C_6H_4{\cdot}C(OH)(C_6H_4{\cdot}NH_2)_2 + 2H = NH_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2 + H_2O.$$

It crystallises in colourless plates, melts at 148°, and forms salts, such as the hydrochloride, $C_{19}H_{19}N_3,3HCl$, with three equivalents of an acid. When the hydrochloride is treated with nitrous acid, it is converted into a tri-diazo-compound, $CH(C_6H_4{\cdot}N{:}NCl)_3$, which, when boiled with water, yields *aurin*, $C_{19}H_{14}O_3$ (p. 518), and when heated with alcohol, is converted into triphenylmethane, just as diazobenzene chloride, under similar conditions, yields phenol or benzene.

Constitution of Pararosaniline.—Since triphenylmethane can be obtained from pararosaniline in this way, the latter is a derivative of this hydrocarbon (an important fact, first established by E. and O. Fischer in 1878); moreover, pararosaniline may be prepared from triphenylmethane, as follows: Triphenylmethane is converted into trinitrotriphenylmethane, $NO_2\cdot C_6H_4\cdot CH(C_6H_4\cdot NO_2)_2$—a compound in which, it has been shown, that all the nitro-groups are in the *p*-position to the methane carbon atom*—with the aid of fuming nitric acid; this nitro-compound, on reduction, yields a substance which is identical with leuco-pararosaniline, and which, on oxidation, is readily converted into the colour-base, triamidotriphenyl carbinol; this base, when treated with acids, yields salts of pararosaniline, with elimination of water (compare p. 511):

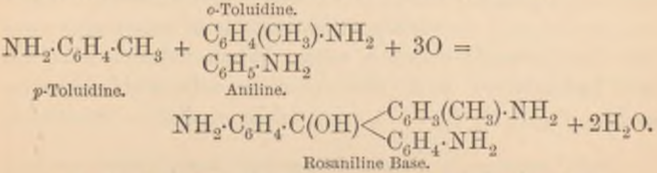


$$HCl,\overset{(4)}{N}H_2\cdot C_6H_4\cdot \overset{(1)}{C}(OH)<\begin{matrix}C_6H_4\cdot NH_{2(4)}\\ C_6H_4\cdot NH_{2(4)}\end{matrix} = ClNH_2:C_6H_4:C<\begin{matrix}C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix} + H_2O.$$

Hydrochloride of Pararosaniline Base.

Chloride of Pararosaniline.

Rosaniline (of commerce), fuchsine, or magenta, is the chloride (or acetate) of triamidotolyldiphenyl carbinol, a base which is produced by the oxidation of equal molecular proportions of aniline, *o*-toluidine, and *p*-toluidine (with arsenic acid, mercuric nitrate, nitrobenzene, &c.), the reaction being similar in all respects to the formation of the pararosaniline base from aniline (2 mols.) and *p*-toluidine (1 mol.),



$$NH_2\cdot C_6H_4\cdot CH_3 + \begin{matrix}C_6H_4(CH_3)\cdot NH_2\\ C_6H_5\cdot NH_2\end{matrix} + 3O = NH_2\cdot C_6H_4\cdot C(OH)<\begin{matrix}C_6H_3(CH_3)\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix} + 2H_2O.$$

o-Toluidine.

p-Toluidine.

Aniline.

Rosaniline Base.

---

* The proofs of this statement are too complex to be given here.

Rosaniline is usually manufactured at the present time by what is termed the '*nitrobenzene process*,' the '*arsenic acid process*'—in which the oxidising agent is arsenic acid—being now little used.

To the requisite mixture of aniline, *o*-toluidine, and *p*-toluidine* (38 parts), hydrochloric acid (20 parts) and nitrobenzene (20 parts) are added, and the whole is gradually heated to 190°, small quantities of iron-filings (3–5 parts) being added from time to time (see below). At the end of five hours the reaction is complete, and steam is then led through the mass to drive off any unchanged aniline, toluidine, or nitrobenzene, after which the residue is powdered and extracted with boiling water, under pressure; lastly, the extract is mixed with salt, and the crude rosaniline chloride which separates purified by recrystallisation.

In this reaction the nitrobenzene acts only indirectly as the oxidising agent; the ferrous chloride, produced by the action of the hydrochloric acid on the iron, is oxidised by the nitrobenzene to ferric chloride, which in its turn oxidises the mixture of aniline and toluidines to rosaniline, and is itself again reduced to ferrous chloride; the action is, therefore, continuous, and only a small quantity of iron is necessary.

The salts of the rosaniline base with one equivalent of acid, as, for example, the chloride, $C_{20}H_{20}N_3Cl$, form magnificent crystals, which show an intense green metallic lustre; they dissolve in warm water, forming deep red solutions, and dye silk, wool, and cotton a brilliant magenta colour, the conditions of dyeing being the same as in the case of malachite green.

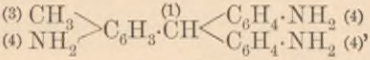
The addition of alkalies to the saturated solution of the chloride of rosaniline destroys the colour, and causes the precipitation of the colour-base, *triamidotolyldiphenyl carbinol*, $C_{20}H_{20}N_3 \cdot OH$ (p. 511), which crystallises in colourless needles, and, on warming with acids, is at once reconverted into the intensely coloured salts. When reduced with tin and hydrochloric acid, the rosaniline salts yield *leuco-rosaniline*, $C_{20}H_{21}N_3$ (p. 511), a colourless, crystalline substance,

---

* Crude 'aniline-oil,' a mixture of these three bases, is sometimes used instead of the pure compounds.

which, when treated with oxidising agents, is again converted into rosaniline.

The *constitution of rosaniline* has been deduced in the same way as that of pararosaniline (p. 513), since, by means of the diazo-reaction, leuco-rosaniline has been converted into diphenyl-*m*-tolylmethane, $CH_3\cdot C_6H_4\cdot CH(C_6H_5)_2$; leuco-rosaniline has, therefore, the constitution

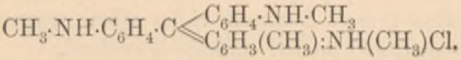


$$\left.\begin{matrix}(3)\ CH_3\\(4)\ NH_2\end{matrix}\right> C_6H_3\cdot\overset{(1)}{CH}<\begin{matrix}C_6H_4\cdot NH_2\ (4)\\C_6H_4\cdot NH_2\ (4)'\end{matrix}$$

and the rosaniline salts are derived from this base, just as those of pararosaniline and of malachite green are derived from leuco-pararosaniline and leuco-malachite green respectively.

Derivatives of Pararosaniline and Rosaniline.

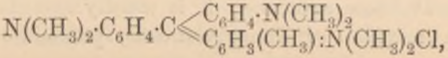
The hydrogen atoms of the three amido-groups in pararosaniline and rosaniline may be displaced by methyl- or ethyl-groups, by heating the dye with methyl or ethyl iodide (chloride or bromide); under these conditions, tri-alkyl substitution products are obtained as primary products, one of the hydrogen atoms of each of the amido-groups being displaced. When, for example, rosaniline chloride is heated with methyl iodide or chloride, it yields, in the first place, the chloride of *trimethyl*-rosaniline,



$$CH_3\cdot NH\cdot C_6H_4\cdot C<\begin{matrix}C_6H_4\cdot NH\cdot CH_3\\C_6H_3(CH_3){:}NH(CH_3)Cl.\end{matrix}$$

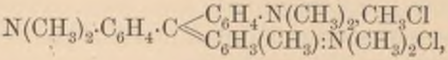
This compound is a reddish-violet dye; the corresponding *triethyl*-rosaniline chloride is the principal constituent of *Hofmann's violet*, *dahlia*, *primula*, &c. dyes, which have now been superseded by more brilliant violets.

By the long-continued action of the methyl halogen compounds on rosaniline salts, the chloride of *hexamethyl*-rosaniline,



$$N(CH_3)_2\cdot C_6H_4\cdot C<\begin{matrix}C_6H_4\cdot N(CH_3)_2\\C_6H_3(CH_3){:}N(CH_3)_2Cl,\end{matrix}$$

is obtained. This substance is a magnificent, bluish-violet dye, but is now little used; it is a tertiary base, and, like dimethylaniline, it combines directly with methyl chloride, forming an additive compound of the constitution



$$N(CH_3)_2\cdot C_6H_4\cdot C\left\langle\begin{array}{l} C_6H_4\cdot N(CH_3)_2,CH_3Cl \\ C_6H_3(CH_3){:}N(CH_3)_2Cl, \end{array}\right.$$

which, curiously enough, is green, and was formerly used under the name '*iodine green*' (so called because it was first produced with methyl iodide).

Starting, then, from rosaniline, which is a brilliant red dye, and substituting methyl-groups for hydrogen, the colour first becomes reddish-violet, and then bluish-violet, as the number of alkyl-groups increases. This change is more marked when ethyl-groups are introduced, and, still more so, when phenyl- or benzyl-groups are substituted for hydrogen, as, in the latter case, pure blue dyes are produced (see below); in fact, by varying the number and character of the substituting groups, almost any shade from red to blue can be obtained.

Lastly, it is interesting to note that, when a violet dye, like hexamethylrosaniline, combines with an alkyl halogen compound, it is converted into a bright green dye, which, however, is somewhat unstable, and, on warming, readily decomposes into the alkyl halogen compound and the original violet dye. A piece of paper, for example, which has been dyed with 'iodine green' becomes violet when warmed over a bunsen burner, and methyl chloride is evolved.

The alkyl-derivatives of pararosaniline and of rosaniline are no longer prepared by heating the dyes with alkyl halogen compounds, but are obtained by more economical methods. The dyes of this class now actually manufactured, examples of which are described below, are, with few exceptions, derivatives of pararosaniline.

Methylviolet appears to consist principally of the chloride of *pentamethyl*-pararosaniline; it is usually manufactured by heating a mixture of dimethylaniline, potassium chlorate, and copper chloride (or sulphate), at 50–60°, for about 8 hours;* the product is treated with hot water, the copper removed by passing sulphuretted hydrogen, the solution concentrated, and the dye precipitated by the addition of salt.

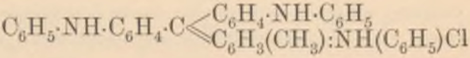
Methylviolet comes into the market in the form of hard lumps, which have a green metallic lustre; it is readily soluble in alcohol and hot water, forming beautiful violet solutions, which dye silk, wool, and cotton, under the same conditions as employed in the case of malachite green (p. 511).

When rosaniline is treated with aniline at 100°, in the presence of some weak acid, such as acetic, benzoic, or stearic acid (which combines with the ammonia), phenyl-groups displace the hydrogen atoms of the amido-groups, just as in the formation of diphenylamine from aniline and aniline hydrochloride (p. 368),

$$C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}NH_2,HCl = (C_6H_5)_2NH + NH_3,HCl.$$

Here, as in the case of the alkyl-derivatives of rosaniline, the colour of the product depends on the number of phenyl-groups which have been introduced; the mono- and di-phenyl-derivatives are reddish-violet and bluish-violet respectively, whereas triphenylrosaniline is a pure blue dye, known as *aniline blue.*

Aniline blue,



$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}C_6H_4{\cdot}NH{\cdot}C_6H_5\\C_6H_3(CH_3){:}NH(C_6H_5)Cl\end{matrix}$$

(triphenylrosaniline chloride), is prepared by heating rosaniline with benzoic acid and an excess of aniline at 180° for about 4 hours, and until the mass dissolves in dilute acids, forming a pure blue solution. The product, which contains the aniline blue in the form of the colour-base, is then treated with hydrochloric acid, whereupon the chloride crystallises out in an almost pure condition.

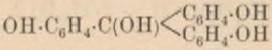
---

* The changes which take place during this remarkable process are doubtless very complex, and cannot be discussed here.

Aniline blue is very sparingly soluble in water, and, in dyeing with it, the operation has to be conducted in alcoholic solution. In order to get over this difficulty, the insoluble dye is treated with anhydrosulphuric acid, and thus converted into a mixture of sulphonic acids, the sodium salts of which are readily soluble, and come into the market under the names '*alkali blue*,' '*water blue*,' &c.

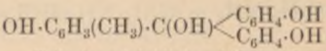
In dyeing silk and wool with these colouring matters, the material is first dipped into alkaline solutions of the salts, when a light-blue tint is obtained, and it is not until it has been immersed in dilute acid (to liberate the sulphonic acid), that the true blue colour is developed. Cotton is dyed in the same way, but must first be mordanted with tannin.

The tri-hydroxy-derivatives of triphenyl carbinol and of tolyldiphenyl carbinol, which correspond with the tri-amido-compounds described above, are respectively represented by the following formulæ:



$$OH\cdot C_6H_4\cdot C(OH)\begin{array}{l}\diagup C_6H_4\cdot OH\\ \diagdown C_6H_4\cdot OH\end{array}$$

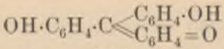
Trihydroxytriphenyl Carbinol.



$$OH\cdot C_6H_3(CH_3)\cdot C(OH)\begin{array}{l}\diagup C_6H_4\cdot OH\\ \diagdown C_6H_4\cdot OH\end{array}$$

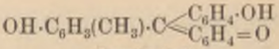
Trihydroxytolyldiphenyl Carbinol.

These compounds may be obtained from the corresponding tri-amido-derivatives (the colour-bases of pararosaniline and of rosaniline) with the aid of the diazo-reaction; in other words, the amido-compounds are treated with nitrous acid, and the solutions of the diazo-salts are then heated. The hydroxy-compounds thus produced are, however, unstable, and readily lose one molecule of water, yielding coloured compounds—*aurin* and *rosolic acid*—which correspond with the pararosaniline and rosaniline dyes in constitution,



$$OH\cdot C_6H_4\cdot C\begin{array}{l}\diagup C_6H_4\cdot OH\\ \diagdown\!\!\diagdown C_6H_4=O\end{array}$$

Aurin.



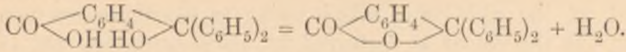
$$OH\cdot C_6H_3(CH_3)\cdot C\begin{array}{l}\diagup C_6H_4\cdot OH\\ \diagdown\!\!\diagdown C_6H_4=O\end{array}$$

Rosolic Acid.

These substances are of little use as dyes owing to the difficulty of fixing them.

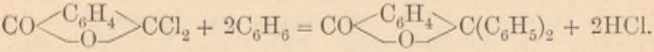
The Phthaleïns.

The phthaleïns, like malachite green and the rosanilines, are derivatives of triphenylmethane, inasmuch as they are substitution products of *phthalophenone*, a compound formed from *triphenylcarbinol-o-carboxylic acid*, by loss of one molecule of water,*



$$\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{OH\ HO}\end{matrix}>\mathrm{C(C_6H_5)_2} = \mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{C(C_6H_5)_2} + \mathrm{H_2O}.$$

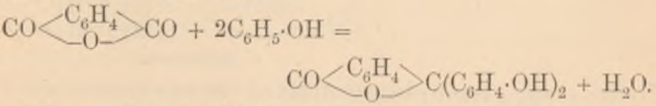
Phthalophenone is readily prepared by acting on a mixture of phthalyl chloride (p. 426) and benzene, with aluminium chloride,



$$\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{CCl_2} + 2\mathrm{C_6H_6} = \mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{C(C_6H_5)_2} + 2\mathrm{HCl}.$$

It crystallises in colourless needles, melts at 115°, and dissolves in alkalies, yielding salts of triphenylcarbinol-*o*-carboxylic acid. This acid, on reduction with zinc-dust in alkaline solution, is converted into *triphenylmethane-o-carboxylic acid*, $\mathrm{COOH{\cdot}C_6H_4{\cdot}CH(C_6H_5)_2}$, from which, by distillation with lime, *triphenylmethane* is obtained—a proof that the phthaleïns are derivatives of this compound.

Phenolphthaleïn, or dihydroxyphthalophenone, $C_{20}H_{14}O_4$, is prepared by heating phthalic anhydride (3 parts) with phenol (4 parts) and powdered zinc chloride (5 parts), at 115–120° for 8 hours; the product is washed with water, dissolved in soda, and the phenolphthaleïn precipitated from the filtered solution with acetic acid,

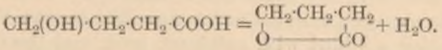


$$\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{CO} + 2\mathrm{C_6H_5{\cdot}OH} = \mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{C(C_6H_4{\cdot}OH)_2} + \mathrm{H_2O}.$$

---

* Compounds produced in this way from one molecule of a hydroxy-acid, by loss of water, are called *lactones*. Many hydroxy-acids, notably those belonging to the fatty series, yield lactones, but only when the hydroxyl-group is in the γ- or δ-position (part i. p. 164).

γ-Hydroxybutyric acid, for example, cannot be isolated, because when set free from its salts, by the addition of a mineral acid, it at once decomposes with formation of its lactone,



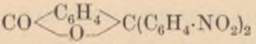
$$\mathrm{CH_2(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH} = \begin{matrix}\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2}\\ \mathrm{O\text{———}CO}\end{matrix} + \mathrm{H_2O}.$$

γ-Butyrolactone.

The fatty lactones are mostly neutral volatile liquids, but those belonging to the aromatic series are crystalline solids; all lactones dissolve in alkalies, yielding salts of the hydroxy-acids from which they are derived.

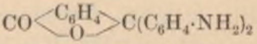
Phenolphthaleïn separates from alcohol in small yellowish crystals, and melts at 250°; its solutions are coloured a deep pink on the addition of alkali, owing to the formation of a salt, but the colour is destroyed by acids, hence the use of phenolphthaleïn as an indicator in alkalimetry; it is, however, of no value as a dye.

That phenolphthaleïn is dihydroxyphthalophenone, and, therefore, a derivative of triphenylmethane, may be proved in the following way. Phthalophenone, when treated with nitric acid, yields dinitrophthalophenone, which, on reduction, is converted into diamidophthalophenone: from this substance, by treatment with nitrous acid, phenolphthaleïn is produced.



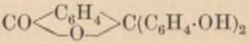
$$CO{<}\substack{C_6H_4\\ O}{>}C(C_6H_4\cdot NO_2)_2$$

Dinitrophthalophenone.



$$CO{<}\substack{C_6H_4\\ O}{>}C(C_6H_4\cdot NH_2)_2$$

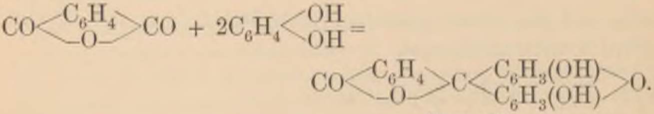
Diamidophthalophenone.



$$CO{<}\substack{C_6H_4\\ O}{>}C(C_6H_4\cdot OH)_2$$

Phenolphthaleïn.

Fluoresceïn, $C_{20}H_{12}O_5$, is a very important dye-stuff, produced by heating together phthalic anhydride and resorcinol,



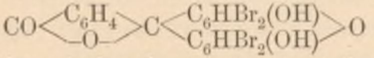
$$CO{<}\substack{C_6H_4\\ O}{>}CO + 2C_6H_4{<}\substack{OH\\ OH} = CO{<}\substack{C_6H_4\\ O}{>}C{<}\substack{C_6H_3(OH)\\ C_6H_3(OH)}{>}O.$$

Fluoresceïn.

In this change, two hydrogen atoms of the two benzene rings unite with the oxygen atom of one of the >CO groups of the phthalic anhydride (as in the formation of phenolphthaleïn), a second molecule of water being eliminated from the hydroxyl-groups of the two resorcinol molecules.

Phthalic anhydride (5 parts) and resorcinol (7 parts) are heated together at 200° until the mass has become quite solid; the dark product is then washed with hot water, dissolved in soda, the filtered alkaline solution acidified with sulphuric acid, and the fluoresceïn extracted with ether.

Fluoresceïn crystallises from alcohol in dark-red crusts; it is almost insoluble in water, but dissolves readily in alkalies, forming dark reddish-brown solutions, which, when diluted, show a most magnificent yellowish-green fluorescence (hence the name fluoresceïn). In the form of its sodium salt, $C_{20}H_{10}O_5Na_2$, fluoresceïn comes into the market as the dye '*uranin.*' Wool and silk are dyed yellow, and at the same time show a beautiful fluorescence, but the colours are faint, and soon fade, hence fluoresceïn has a very limited application alone, and is generally mixed with other dyes, in order to impart fluorescence. The great value of fluoresceïn lies in the fact that its derivatives are very important dyes.



Eosin, $\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{C_6HBr_2(OH)}\\ \mathrm{C_6HBr_2(OH)}\end{matrix}>\mathrm{O}$ (tetrabromofluoresceïn), is formed when fluoresceïn is treated with bromine, four atoms of hydrogen in the resorcinol nuclei being displaced.

Fluoresceïn is treated with the calculated quantity of bromine in acetic acid solution, and the eosin which separates is collected, washed with a little acetic acid, and dissolved in dilute potash. The filtered solution is then acidified, and the eosin extracted with ether.

Eosin separates from alcohol in red crystals, and is almost insoluble in water, but dissolves readily in alkalies, forming deep-red solutions, which, on dilution, exhibit a beautiful green fluorescence, but not nearly to the same extent as solutions of fluoresceïn.

Eosin comes into the market in the form of its potassium salt, $C_{20}H_6Br_4O_5K_2$ (a brownish powder), and is much used for dyeing silk, wool, cotton, and especially paper, which fixes the dye without the aid of a mordant. Silk and wool are dyed with eosin directly in a bath acidified with a little acetic acid; but cotton must first be mordanted with zinc, lead, or aluminium salts. The shades produced are a beautiful pink, and the materials also show a very beautiful fluorescence.

Tetriodofluoresceïn, $C_{20}H_8I_4O_5$, is also a valuable dye. Its sodium salt, $C_{20}H_6I_4O_5Na_2$, comes into the market under the name '*erythrosin.*'

Many other phthaleïns have been prepared by condensing phthalic acid and its derivatives with other phenols, and then treating the products with bromine or iodine.

Azo-dyes.

The azo-dyes contain the azo-group, –N:N–, to each of the nitrogen atoms of which a benzene or naphthalene nucleus is directly united. Azobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_5$, the simplest of all azo-compounds, is not a dye, although it is intensely coloured (compare p. 502), and this is true also of other neutral azo-compounds; if, however, one or more hydrogen atoms in such compounds be displaced by amido-, hydroxyl-, or sulphonic-groups, the products, as, for example,

Amidoazobenzene,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$,
Hydroxyazobenzene,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$,
Azobenzenesulphonic acid,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H$,

are yellow or brown dyes.

Azo-dyes are usually prepared by one of two general methods—namely, by treating a *diazo-chloride* with an *amido-compound*,*

$$C_6H_5{\cdot}N{:}NCl + C_6H_5{\cdot}N(CH_3)_2 = \underset{\text{Dimethylamidoazobenzene Hydrochloride.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2,HCl},$$

$$\underset{p\text{-Diazotoluene Chloride.}}{CH_3{\cdot}C_6H_4{\cdot}N{:}NCl} + \underset{o\text{-Toluidine.}}{CH_3{\cdot}C_6H_4{\cdot}NH_2} =$$

$$\underset{\text{Amidoazotoluene Hydrochloride.}}{CH_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(CH_3){\cdot}NH_2,HCl},$$

or by treating a *diazo-chloride* with a *phenol*,

$$C_6H_5{\cdot}N{:}NCl + C_6H_5{\cdot}OH = \underset{\text{Hydroxyazobenzene.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH} + HCl,$$

$$C_6H_5{\cdot}N{:}NCl + C_6H_4(OH)_2 = \underset{\text{Dihydroxyazobenzene.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_3(OH)_2} + HCl.$$

In the first case the products—amidoazo-compounds—are *basic* dyes, whereas in the second case they are *acid* dyes.

---

* In cases where a diazoamido-compound is first produced (p. 374), an excess of the amido-compound is employed and the mixture warmed until the intramolecular change into the amidoazo-compound is complete.

Another method of some general application for the direct preparation of azo-dyes containing a sulphonic-group, consists in treating diazobenzenesulphonic acid, or its anhydride (p. 384), with an amido-compound or with a phenol:

$$SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OH + C_6H_5{\cdot}NH_2 = \underset{\text{Amidoazobenzenesulphonic Acid.}}{SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2} + H_2O$$

$$SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OH + C_6H_5{\cdot}OH = \underset{\text{Hydroxyazobenzenesulphonic Acid.}}{SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH} + H_2O.$$

As, however, the yield is generally a poor one, such dyes are usually prepared by sulphonating the amidoazo- or hydroxyazo-compounds.

In all these reactions the diazo-group, $C_6H_5{\cdot}N{:}N{-}$, displaces hydrogen of the benzene nucleus from the *p*-position to one of the amido- or hydroxyl-groups; substances such as *p*-toluidine, in which the *p*-position is occupied, either do not interact with diazo-chlorides or only do so with great difficulty.

The technical operations incurred in the production of azo-colours are, as a rule, very simple. In combining diazo-compounds with phenols, for example, the amido-compound (1 mol.) is dissolved in water and hydrochloric acid (2 mols.), the solution well cooled with ice, and gradually mixed with the calculated quantity of sodium nitrite (1 mol.); this solution of the diazo-salt is then slowly run into the *alkaline* solution of the phenol, or its sulphonic acid, care being taken to keep the solution slightly alkaline, otherwise the liberated hydrochloric acid prevents combination taking place. After a short time the solution is mixed with salt, which causes the colouring matter to separate in flocculent masses; the product is then collected in filter-presses and dried, or sent into the market in the form of a paste.

The combination of diazo-compounds with amido-compounds is generally brought about by simply mixing the aqueous solution of the diazo-compound with that of the salt of the amido-compound (compare foot-note, p. 522), and then precipitating the colouring matter by the addition of common salt; in some cases, however, the reaction takes place only in alcoholic solution.

Acid azo-colours (that is, hydroxy- and sulphonic-derivatives) are taken up by animal fibres directly from an acid bath, and are principally employed in dyeing wool; they can be fixed on cotton with the aid of mordants (tin and aluminium salts being generally employed), but, as a rule, only with difficulty; nevertheless some acid dyes, notably those of the *congo-group* (p. 526), dye cotton directly without a mordant.

Basic azo-dyes are readily fixed on cotton which has been mordanted with tannin, and are very largely used in dyeing calico and other cotton goods.

At the present time a great many azo-colours are manufactured, but only a few of the more typical can be mentioned here.

Aniline yellow, a salt of amidoazobenzene (p. 375),

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2,$$

is now no longer used in dyeing, because the colour is not fast, and is in many ways inferior to other readily obtainable yellow dyes.

Chrysoïdine (diamidoazobenzene), $C_6H_5{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$, is produced by mixing molecular proportions of diazobenzene chloride and *m*-phenylenediamine (p. 364) in aqueous solution. The hydrochloride crystallises in reddish needles, is moderately soluble in water, and dyes silk and wool directly, and cotton mordanted with tannin, an orange-yellow colour.

Bismarck brown, $NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$ (triamidoazobenzene), is prepared by treating *m*-phenylenediamine hydrochloride with nitrous acid, one half of the base being converted into the diazo-compound, which then interacts with the other half, producing the dye,

$$NH_2{\cdot}C_6H_4{\cdot}N{:}NCl + C_6H_4(NH_2)_2 = NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2,HCl.$$

The hydrochloride is a dark-brown powder, and is largely used in dyeing cotton (mordanted) and leather a dark brown.

Helianthin (dimethylamidoazobenzenesulphonic acid) is very easily prepared by mixing aqueous solutions of diazobenzenesulphonic acid and dimethylaniline hydrochloride,

$$SO_3H\cdot C_6H_4\cdot N{:}N\cdot OH + C_6H_5\cdot N(CH_3)_2 = SO_3H\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N(CH_3)_2 + H_2O.$$

The sodium salt (methylorange) is a brilliant orange-yellow powder, and dissolves freely in hot water, forming a yellow solution, which is coloured red on the addition of acids, hence its use as an indicator. It is seldom employed as a dye, on account of its sensibility to traces of acid.

Resorcin yellow (tropæölin O) is prepared by combining diazobenzenesulphonic acid and resorcinol, and has the constitution $SO_3H\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(OH)_2$. Its sodium salt is a moderately brilliant orange-yellow dye, and is not readily acted on by acids; it is chiefly employed, mixed with other dyes of similar constitution, in the production of olive-greens, maroons, &c.

By using various benzene derivatives, and combining them as in the above examples, *yellow* and *brown* dyes of almost any desired shade can be obtained; in order, however, to produce a *red* azo-dye, a compound, containing at least one naphthalene nucleus, must be prepared. This can be readily done by combining a benzenediazo-compound with a naphthylamine, naphthol, naphthalenesulphonic acid, &c., just as described above. The dyes thus obtained give various shades of reddish-brown or scarlet, and are known collectively as 'Ponceaux' or 'Bordeaux.'

When, for example, diazoxylene chloride is combined with β-naphthol, a scarlet dye (scarlet R) of the composition $C_6H_3(CH_3)_2\cdot N{:}N\cdot C_{10}H_5(OH)\cdot SO_3Na$ is formed; another scarlet dye (Ponceau 3R) is produced by the combination of diazocumene chloride with β-naphtholdisulphonic acid, and has the composition $C_6H_2(CH_3)_3\cdot N{:}N\cdot C_{10}H_4(SO_3Na)_2\cdot OH$.

Rocellin, $SO_3Na\cdot C_{10}H_6\cdot N{:}N\cdot C_{10}H_6\cdot OH$, a compound produced by combining β-naphthol with the diazo-compound of naphthionic acid (p. 455), may be mentioned as an example of an azo-dye containing two naphthalene nuclei. It gives beautiful red shades, very similar to those obtained with the natural dye, cochineal, which rocellin and other allied azo-colours have, in fact, almost superseded.

Within the last few years a great number of exceedingly valuable colouring matters have been prepared from benzidine, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ (p. 379), and its derivatives.

Benzidine may be compared with two molecules of aniline, and when diazotised it yields the salt of a di-diazo- or *tetrazo-diphenyl*, $ClN{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{:}NCl$. This substance interacts with amido-compounds, phenols, and their sulphonic acids, just as does diazobenzene chloride (but with double the quantity), producing a variety of most important colouring matters, known as the dyes of the *congo-group*.

Congo-red, a dye produced by the combination of tetrazo-diphenyl chloride with naphthionic acid, is one of the most valuable compounds of this class. Its sodium salt,

$$SO_3Na{\cdot}(NH_2)C_{10}H_5 \vdots N{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{:}N \vdots C_{10}H_5(NH_2){\cdot}SO_3Na,$$

is a scarlet powder, which, on the addition of acids, turns blue, owing to the liberation of the free sulphonic acid.

The congo-dyes possess the unusual property of combining with unmordanted cotton, producing brownish-red shades which are fast to soap. They are much used for dyeing cotton, but they become dull in time in any atmosphere which contains traces of acid fumes, as, for example, in the air of manufacturing towns, owing to the liberation of the blue sulphonic acids.

The **Benzopurpurins** are also exceedingly valuable dyes of the congo-group; they are produced by combining tetrazo-ditolyl salts* with the sulphonic acids of α- and β-naphthylamine, and are, therefore, very similar to congo-red in con-

---

* *Tolidine*, $NH_2{\cdot}(CH_3)C_6H_3{\cdot}C_6H_3(CH_3){\cdot}NH_2$, is produced from nitrotoluene by reactions similar to those by which benzidine is produced from nitrobenzene; when its salts are treated with nitrous acid they yield salts of tetrazoditolyl, just as benzidine gives salts of tetrazodiphenyl.

stitution. They dye unmordanted cotton splendid scarlet shades, and are used in very large quantities.

Various Colouring Matters.

Martius' yellow (dinitro-α-naphthol), $C_{10}H_5(NO_2)_2{\cdot}OH$, is obtained by the action of nitric acid on α-naphtholmono-, or di-sulphonic acid, the sulphonic group or groups being eliminated during nitration. The commercial dye is the sodium salt, $C_{10}H_5(NO_2)_2{\cdot}ONa$; it is readily soluble in water, and dyes silk and wool directly an intense golden yellow.

When α-naphthol-trisulphonic acid is nitrated, only two of the sulphonic groups are eliminated, and the resulting substance has the formula $C_{10}H_4(NO_2)_2(OH){\cdot}SO_3H$; it is, in fact, the sulphonic acid of Martius' yellow. This valuable dye-stuff is called **naphthol yellow,** and comes into the market in the form of its potassium salt, $C_{10}H_4(NO_2)_2(OH){\cdot}SO_3K$; it is very largely used, as the yellow shades are faster to light than those of Martius' yellow.

Methylene blue, $C_{16}H_{18}N_3SCl$, was first prepared by Caro, in 1876, by the oxidation of dimethyl-*p*-phenylenediamine (p. 367) with ferric chloride in presence of sulphuretted hydrogen.

Nitrosodimethylaniline (p. 367) is reduced in strongly acid solution with zinc-dust, or with sulphuretted hydrogen, and the solution of dimethyl-*p*-phenylenediamine thus obtained is treated with ferric chloride in presence of excess of sulphuretted hydrogen. The intensely blue solution thus obtained is mixed with salt and zinc chloride, which precipitate the colouring matter as a zinc double salt, in which form it comes into the market.

Methylene blue is readily soluble in water, and is a valuable cotton-blue, as it dyes cotton, mordanted with tannin, a beautiful blue, which is very fast to light and soap; it is not much used in dyeing silk or wool.

Indigo, $C_{16}H_{10}N_2O_2$, is a natural dye, which has been used from the earliest times. It is contained in the leaves of the indigo plant (*Indigofera tinctoria*) and in woad (*Isatis tinctoria*) in the form of the glucoside 'indican;' when the leaves are macerated with water, this glucoside undergoes fermentation, and indigo separates as a blue scum.

Indigo comes into the market in an impure condition in the form of dark-blue lumps, and, especially when rubbed, shows a remarkable copper-like lustre; it is insoluble in water and most other solvents, but dissolves readily in hot aniline, from which it crystallises on cooling; it sublimes, when heated, in the form of a purple vapour, and condenses as a dark-blue crystalline powder, which consists of pure 'indigotin,' the principal and most valuable constituent of commercial indigo.

Reducing agents convert indigo into its leuco-compound, *indigo white*, which, in contact with air, is rapidly reconverted into indigo, a property made use of in dyeing with this substance (p. 507); concentrated sulphuric acid dissolves indigo with formation of *indigodisulphonic acid*, $C_{16}H_8N_2O_2(SO_3H)_2$, the sodium salt of which is used in dyeing under the name 'indigo carmine.'

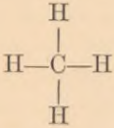
Indigo has been synthetically produced by Baeyer by various reactions, two of the more important of which are mentioned on pp. 408 and 433.

CHAPTER XXXV.

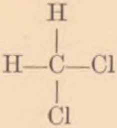
STEREO-ISOMERISM.

The constant use of graphic formulæ in studying carbon compounds was strongly recommended in an early chapter (part i. p. 53), because, as was then pointed out, such formulæ afford a fairly sure and complete summary of the chemical properties of the substances which they represent, whereas the ordinary molecular formulæ express little, and are besides more difficult to remember. The true significance of graphic formulæ was also explained; the lines which are drawn between any two atoms simply express the conclusion that, as far as can be ascertained experimentally, these particular atoms are directly united, without attempting to give the slightest indication of the nature of this union, or of the direction in which the force of affinity is exerted.

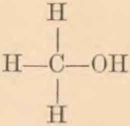
When, therefore, formulæ such as the following



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}$$



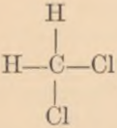
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}Cl} \\ | \\ \mathrm{Cl} \end{array}$$



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H} \end{array}$$

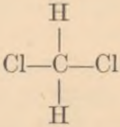
are employed, it must not be supposed that they give any idea whatever of the actual form of the molecule, or intend to indicate that all the atoms in the molecule lie in one plane (that is, the plane of the paper); such an assumption is unsupported by facts, and is, moreover, shown to be incorrect by many considerations, of which the following may be mentioned.

(*a*) Experience has shown that methylene chloride, CH_2Cl_2, exists in only *one* form, and all attempts to obtain an isomeride have failed; yet, if a compound of this composition were actually represented by the above plane formula, it should be capable of existing in *two* isomeric forms—namely,



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}Cl} \\ | \\ \mathrm{Cl} \end{array}$$

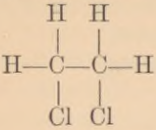
and



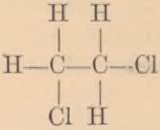
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{Cl{-}C{-}Cl} \\ | \\ \mathrm{H} \end{array}$$

because in one case the chlorine atoms would be adjacent, in the other they would be separated by hydrogen atoms, and the relative positions of all the atoms not being identical, the substances themselves could not be so.

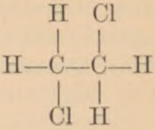
(*b*) Again, only *two* isomeric dichlorethanes—namely, $CH_2Cl{\cdot}CH_2Cl$ and $CH_3{\cdot}CHCl_2$, are known, whereas, if ethane and its derivatives were actually composed of atoms, all of which lie in one plane, the following *five* isomeric dichlorethanes should be capable of existence :



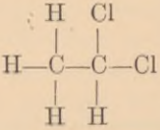
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & \\ & \mathrm{Cl} & & \mathrm{Cl} & \end{array}$$



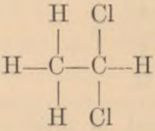
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{Cl} \\ & | & & | & \\ & \mathrm{Cl} & & \mathrm{H} & \end{array}$$



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{Cl} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & \\ & \mathrm{Cl} & & \mathrm{H} & \end{array}$$



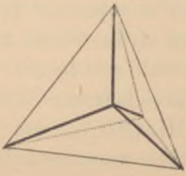
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{Cl} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{Cl} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{Cl} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{Cl} & \end{array}$$

These, and a great many other similar cases, show conclusively that the atoms in the molecule of a carbon compound cannot lie in one plane; were this so, it would be impossible to explain the fact that a large number of isomerides which, theoretically, would be capable of existence, have never yet been prepared.

If, then, an attempt be made to account satisfactorily for the known isomerism of carbon compounds, it is found that this can be done by assuming that each of the several atoms or groups with which a carbon atom is united is situated at some point on one of four different lines, which are symmetrically arranged in the space around the carbon atom. In other words, it may be supposed that the carbon atom is situated in the centre of an imaginary regular tetrahedron, and that its four affinities (those forces by virtue of which it unites with four atoms or groups) act in the directions of straight lines drawn from the centre of the tetrahedron to the four corners, as represented by the dark lines in the following figure :

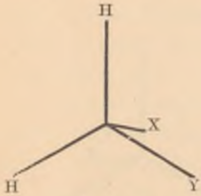


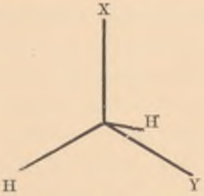
Now this highly important theory, which was advanced by Le Bel and van't Hoff, independently, in 1874, is not based solely on the fact that it explains the non-existence of a larger number of isomerides of a given substance than is actually known; it is also supported by positive evidence of a very weighty character, and, indeed, may be shown to accord well with all known facts.

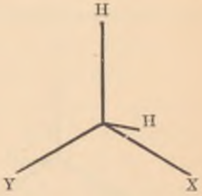
If, then, this theory be applied in the case of some of the simplest organic compounds, it leads to the following conclusions:

(1) Assuming that one of the hydrogen atoms in marsh-gas, CH_4, is displaced by an atom X, there can only be *one* substitution product of the type CH_3X, because all the hydrogen atoms are identically situated.

(2) Only *one* di-substitution product of the type CH_2XY, such as CH_2Cl_2 or CH_2ClBr (in which X and Y are either identical or dissimilar), is also possible, formulæ such as







being *absolutely* identical, although they may appear to be different on paper.

Points such as these can only be clearly understood by actually handling models made to represent arrangements of this kind;* it will then be seen at once that, in whatever manner the positions of the different atoms H H X Y are

---

* In order to facilitate the study of stereochemistry, sets of models similar to those recommended by Friedländer have been specially prepared at the authors' request by Messrs Baird and Tatlock (14 Cross Street, Hatton Garden, London, E.C.), from whom they may be obtained at a cost of eighteen pence. Such sets contain sufficient models for the study of the isomerism of the tartaric acids, but larger sets adapted for the study of the sugars may also be obtained.

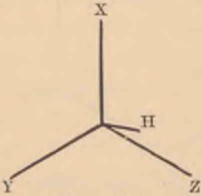
varied, only one arrangement is possible, the apparent difference which exists on paper vanishing at once on rotating the models.

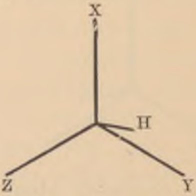
(3) In the case of the tri-substitution products of methane, also, *one* form only is possible, where any two of the substituting atoms, or groups of atoms, are *the same*, as, for example, in the compounds

$CHCl_3$ $(CH_3)_2CH{\cdot}OH$ $(C_2H_5)_2CH{\cdot}CH_2{\cdot}OH$.

In all these cases there is perfect agreement between fact and theory, compounds of the given types being known in *one* form only.

(4) If, however, three atoms in marsh-gas be substituted by three *different* groups, compounds of the type C, H, X, Y, Z*—in which the carbon atom is united with four different atoms or groups—being obtained, then it is possible to construct *two*, but only two, different arrangements, which cannot be made to coincide by rotation, or in any other way; these two forms may be represented by the following figures:





In working with the models this is very clearly seen, by first inserting the red, white, blue, and yellow balls into the two india-rubber carbon models, in such a way as to produce identical arrangements; by then interchanging any two of the balls in one of the models, a form will be obtained which is different from, and which, therefore, cannot be made to coincide with, the other form by rotating.

These two arrangements are related to one another, in the same way as an *object* to its *mirror-image*—that is to say, if one be held before a mirror, the position of X, Y, and Z in relation to H in the mirror-image will be found to be

---

* Or C, *r*, *b*, *w*, *y*; compare foot-note, p. 536.

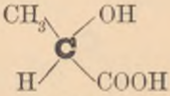
identical with those in the other viewed directly, an interesting point, which again is much more clearly seen by using models; for the sake of convenience, one of these arrangements may be denoted by +, the other by −, the actual choice being immaterial.

When, therefore, a carbon atom is united to *four different* atoms or groups, H, X, Y, and Z, the compound which is produced may, theoretically, exist in two distinct modifications, related to one another in the same way as an object to its mirror-image. Any carbon atom united in this way is called an '**asymmetric carbon atom,**' on account of its unsymmetrical or asymmetrical nature.

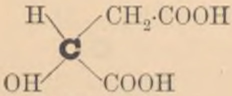
Now certain substances, such as active amyl alcohol, sarcolactic acid, malic acid,* and mandelic acid (p. 440), which have already been described, have the property of rotating the plane of polarised light, and experience has shown that all substances which have this property, when in a liquid state, or in solution, exist in (at least) *two forms*, one of which rotates the plane of polarisation to the right, the other doing so to precisely the same extent to the left.

On considering the constitutional formulæ of such optically active organic substances, one remarkable fact is brought to light—namely, that the molecule always contains at least *one* asymmetric carbon atom, as is indicated in the following formulæ, in which the symbol of this particular carbon atom is printed in heavy type:

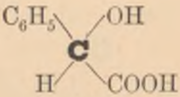
Active Amyl Alcohol.



Lactic Acid.



Malic Acid.



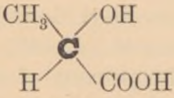
Mandelic Acid.

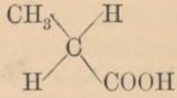
---

* These three compounds are described in part i. pp. 105, 227, 239.

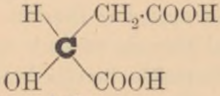
That this property of rotating the plane of polarised light is due to the presence in the molecule of an asymmetric carbon atom is practically proved by the fact that all optically active compounds of known constitution contain a carbon atom united in this way, and also by the fact that if by any means the asymmetric character of the carbon atom be destroyed, the power of rotating the plane of polarised light also disappears.

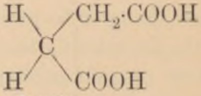
Sarcolactic acid, for example, is optically active, but when reduced with hydriodic acid, it yields propionic acid, which is inactive, because it does not contain a carbon atom united with four different atoms or groups.


Active.

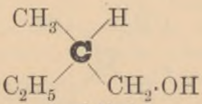

Inactive.

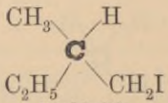
Malic acid, again, is optically active, but, on reduction, inactive succinic acid is formed,

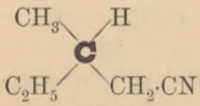

Active.

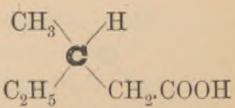

Inactive.

A still more instructive case is afforded by active amyl alcohol, and the following derivatives :

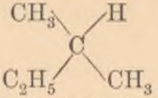

Amyl Alcohol.


Amyl Iodide.


Amyl Cyanide.


Methylethylpropionic Acid.

These substances, prepared from active amyl alcohol by the usual series of reactions, are themselves optically active, because they still contain an asymmetric carbon atom; if, however, the iodide be reduced to the hydrocarbon



Dimethylethylmethane.

the asymmetric character of the carbon atom is destroyed, and a substance is formed which is optically inactive.

This relation between the presence of an asymmetric carbon atom and the property of rotating the plane of polarised light, was first pointed out by Le Bel and van't Hoff, and is now supported by such a mass of evidence that it may be regarded as established.

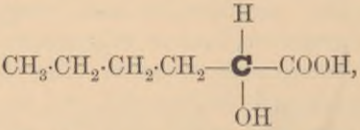
Considering now some of the simplest optically active substances—namely, those containing *only one* asymmetric carbon atom, it may be repeated that they invariably exist in two optically active forms, one of which is dextrorotatory (*d* or +), the other levorotatory (*l* or −) to exactly the same extent. These two forms are called *optical*, *physical*, or *stereochemical isomerides;* they have the same chemical properties and chemical constitution, because their molecules differ only as regards the arrangement in space. They have also the same melting-point and boiling-point, and are identical in other physical properties, except that they almost invariably differ to a greater or less extent in crystalline form, inasmuch as the crystals of the one are to those of the other as an object to its mirror-image (p. 540).

When any substance containing *one* asymmetric carbon atom is prepared synthetically, the product is found to be optically *inactive.* When, for example, lactic acid is produced from α-bromopropionic acid, or malic acid from bromosuccinic acid (part i. pp. 226 and 240), the product in each case has no action on polarised light.

This is due to the fact that the product contains equal quantities of the *d* and *l* forms, and the action on polarised light of the one is exactly counterbalanced by that of the other. This can be proved by simply dissolving together equal quantities of the *d* and *l* forms, and then evaporating the solution, when an inactive product, identical with that produced synthetically, is obtained.

When, moreover, this inactive product is a solid, it is found, as a rule, to differ very considerably from the active forms in physical properties; it has a different melting-point (usually a higher one), different solubility, and a different crystalline form, and is spoken of as the *racemic* (inactive or *i.r.*) modification of the compound. Liquid racemic modifications are not known, and it is doubtful whether they are capable of existing.

The above statements refer simply to compounds containing only one asymmetric carbon atom. No matter how many carbon atoms the molecule may contain, or what the nature of the other atoms may be, as long as only one of the carbon atoms is combined with four different atoms or groups, the compound exists only in the above three optically different forms—namely, *d*, *l*, and *i.r.*; a substance of the constitution



$$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{-}\underset{\substack{|\\ OH}}{\overset{\substack{H\\ |}}{\mathbf{C}}}{-}COOH,}$$

for example, would not form a larger number of optical isomerides than a simple substance such as lactic acid.

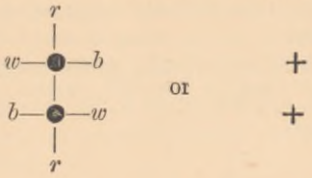
When, however, a compound contains *two* asymmetric carbon atoms, a larger number of modifications may exist in accordance with the above theory, as will be seen at once by constructing models in the following manner:

I. Make two *identical* asymmetric carbon atoms, **C**, *r*, *b*, *w*, *y*,[*] each of which, for convenience, may be designated +; now remove *y* from both models, join the two open ends by means

---

[*] The letters *r*, *b*, *w* and *y* refer to the red, blue, white, and yellow balls in the sets of models.

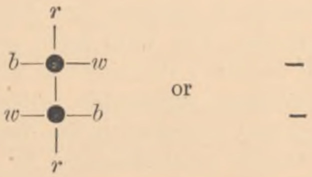
of the rod, and lay the model on the table, so that the two red balls point upwards. This is one possible modification, a plane figure of which may be obtained by pressing the red balls outwards on the table, when it will appear like this:



Modification I.

The removal of one of the balls, representing one of the atoms or groups, and the substitution for it of the more complex group (**C**, *r*, *b*, *w*), still leaves each carbon atom asymmetrical; in other words, each is now combined with the four different groups (*b*), (*w*), (*r*), and (C, *r*, *b*, *w*), instead of with (*r*), (*b*), (*w*), and (*y*).

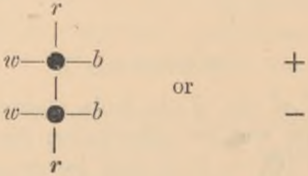
II. Repeat the above operations, starting, however, with two *identical* asymmetric carbon atoms, **C**, *r*, *b*, *y*, *w*, which are the mirror-images of those taken in (I.), and which may, therefore, be called – ; the plane representation of this model will be



Modification II.

This form is quite different from I., because the one cannot possibly be converted into the other by rotation; if, for example, II. be turned over, the positions of *b* and *w* will correspond with those in I., but although the flat images would be the same, the two are not identical, because *r*, *r* will now point downwards in II., whereas they pointed upwards in I.; if, in fact, this model (II.) be held before a mirror, it will be seen that it is *not* identical with its mirror-image, but that its mirror-image *is* identical with I. viewed directly.

III. If now two *different* asymmetric carbon atoms, C, *r*, *b*, *w*, *y*, and C, *r*, *b*, *y*, *w*, or + and −, be joined in the same manner as before, another modification will be obtained which is quite different from I. and II., and which may be represented thus:



Modification III.

No other forms different from these three can be constructed. It is evident, then, that a compound containing *two* asymmetric carbon atoms may form *three* distinct modifications. One of these (I.) will be dextrorotatory, because it contains two *identical* (+) asymmetric carbon atoms; the other (II.) will be levorotatory to exactly the same extent, because it contains two *identical* (−) asymmetric carbon atoms. The third form, on the other hand, will be optically inactive; the molecule which it represents contains two *different* asymmetric carbon atoms, one + and the other −, and consequently the dextrorotatory action of the one is exactly counterbalanced by the levorotatory action of the other; in other words, the rotatory power of one *part* of this molecule is compensated or neutralised by that of the other part; such a compound is said to be inactive by *internal compensation*.

There is, however, a fourth modification which has not yet been considered in the present case; by dissolving equal quantities of the two active (*d* and *l*) forms, and then evaporating, an inactive or *racemic* modification may be obtained, just as in the case of the lactic acids, &c., and this form is said to be inactive by *external compensation*, the action of two *separate* molecules counterbalancing one another.

In order to decide which two of the above three forms represent the active (*d* and *l*) modifications of the substance, it is only necessary to determine which two models behave to each other as object to mirror-image. This will be found to be the case with the forms I. and II., which are therefore the active forms; on the other hand, the form III. coincides with its own mirror-image, and is, therefore, inactive.

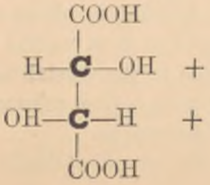
The same conclusions are arrived at by disconnecting and then comparing the asymmetric carbon atoms, when it is easy to see that one of the models is composed of two *different* arrangements; this, therefore, is the form which is inactive by internal compensation.

Stereo-isomerism of the Tartaric Acids.

One of the best examples of the stereo-isomerism of substances containing two asymmetric carbon atoms is that of the tartaric acids, $\text{COOH}\cdot\mathbf{C}\text{H(OH)}\cdot\mathbf{C}\text{H(OH)}\cdot\text{COOH}$. As will be seen from the constitutional formula, there are two carbon atoms, each of which is united with four different atoms or groups—namely, $\{\text{COOH}\}$, $\{\text{H}\}$, $\{\text{OH}\}$, and $\{\text{CH(OH)}\cdot\text{COOH}\}$, and consequently, theoretically, there should be four physically isomeric forms of this acid.

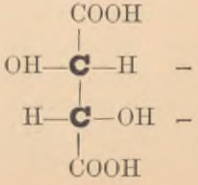
As a matter of fact, four modifications are known—namely, dextrotartaric, levotartaric, mesotartaric and racemic acid, (part i. p. 245).

Dextrotartaric acid and levotartaric acid are the two optically active modifications, and may be respectively represented by the formulæ,



$$\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\mathbf{C}-\text{OH} \quad + \\ | \\ \text{OH}-\mathbf{C}-\text{H} \quad + \\ | \\ \text{COOH} \end{array}$$

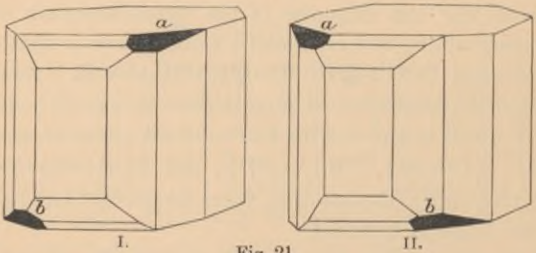
and



$$\begin{array}{c} \text{COOH} \\ | \\ \text{OH}-\mathbf{C}-\text{H} \quad - \\ | \\ \text{H}-\mathbf{C}-\text{OH} \quad - \\ | \\ \text{COOH} \end{array}$$

The one rotates the plane of polarisation to the right to exactly the same extent as the other to the left; but in all other respects they are identical, except for slight differences in crystalline form. They possess the same melting-point, and the same solubility in various solvents; their metallic salts have the same composition, and crystallise with the same number of molecules of water. Their ethereal salts melt and boil at the same temperature; all their salts, like the acids themselves, are optically active to the same extent, but in opposite directions.

In addition to this difference in their action on polarised light, these two active tartaric acids and the corresponding salts show a slight difference in crystalline form, which is exhibited very clearly in the case of the well-defined crystals of their sodium ammonium salts, $C_4H_4O_6Na(NH_4) + 4H_2O$.

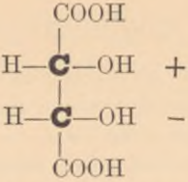


I. II.

Fig. 21.

If these crystals be examined, it will be found that certain faces (those which are darkened in the figures) which are on the *right-hand* side of the crystals of the dextrorotatory acid, are on the *left-hand* side of those of the levorotatory acid. The two kinds of crystals are, in fact, related as an object to its mirror-image, as will be seen by holding I. before a mirror, when the darkened faces will appear as in II. viewed directly, and *vice versâ*. A similar difference in the crystalline form is observed in the case of other optically active substances, and such crystals are said to be *enantiomorphous*.

Mesotartaric acid, $C_4H_6O_6$, is the *simple* optically inactive form of tartaric acid; that is to say, it is inactive by internal compensation (see above), and may be represented by the formula,



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H-}\mathbf{C}\mathrm{-OH} \quad + \\ | \\ \mathrm{H-}\mathbf{C}\mathrm{-OH} \quad - \\ | \\ \mathrm{COOH} \end{array}$$

It differs from the two optically active forms in many respects, as, for example, in melting-point, solubility, and crystalline form. It might, in fact, be regarded as quite a different substance from an examination of its *physical* properties, and of those of its salts, although, in *chemical* properties, it is identical with the active forms. On the other hand, mesotartaric acid resembles racemic acid very closely in physical properties, but, unlike the latter, *it cannot be resolved into two optically active modifications*, because it is a simple substance.

Racemic acid, $C_4H_6O_6, C_4H_6O_6$, is the *double* inactive form of tartaric acid, and is simply composed of equal quantities of dextro- and levo-tartaric acids; that is to say, it is inactive by external compensation (see above), and may be represented by the formula $\left\{ \begin{array}{l} C_4H_6O_6 + + \\ C_4H_6O_6 - - \end{array} \right.$. It also behaves as if it were a distinct substance, as far as physical properties are concerned, which is all the more remarkable when it is borne in mind that racemic acid is obtained on evaporating a solution of equal quantities of the two active modifications, and that it *can be again separated into these two forms* by the methods given below.

It will be seen from the above examples that the existence of physical isomerides, and the number of such modifications, is in complete accordance with the theory of Le Bel and van't Hoff, and a great many other cases might be mentioned in which the agreement is quite as perfect.

As the number of asymmetric carbon atoms increases, the number of isomerides naturally becomes larger, so that a substance such as saccharic acid (part i. pp. 264, 270),

$$\mathrm{COOH}\cdot\mathbf{C}\mathrm{H(OH)}\cdot\mathbf{C}\mathrm{H(OH)}\cdot\mathbf{C}\mathrm{H(OH)}\cdot\mathbf{C}\mathrm{H(OH)}\cdot\mathrm{COOH},$$

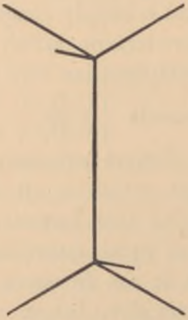
which contains four asymmetric carbon atoms, is capable of existing in ten optically isomeric forms (which may be constructed with the aid of models).

As in the case of chemical isomerism, however, all the theoretically possible isomerides of a given substance have not always been actually obtained owing to experimental difficulties; dimethylsuccinic acid,

$$\mathrm{COOH}\cdot\mathbf{C}\mathrm{H(CH_3)}\cdot\mathbf{C}\mathrm{H(CH_3)}\cdot\mathrm{COOH},$$

for example, like tartaric acid, should exist in four forms, but only two are known, both of which are optically inactive, the two active forms not having yet been isolated.

An examination of the models of substances containing two asymmetric carbon atoms—that is, of substances derived from the symbol,



might lead to the supposition that they should exist in more than four modifications.

In the first place, the model could be so arranged that the directions of the affinities of the two carbon atoms would be as shown in the figure. If, then, one of the carbon atoms were slowly rotated about an axis, an infinite number of forms would be produced, all of which would be different, because they would represent different relative positions in space of the atoms constituting the molecule. It would be just the same even if the substance did not contain an asymmetrical carbon atom; ethane, $CH_3{\cdot}CH_3$, or ethylene chloride, $CH_2Cl{\cdot}CH_2Cl$, for example, could in this way be represented as existing in an infinite number of modifications.

This objection, however, at once disappears on considering the matter a little more carefully.

In a compound represented by the above symbol (by attaching atoms or groups to the corners of the imaginary tetrahedra), the atoms or groups united with one of the carbon atoms must exert a certain attraction or repulsion on those united with the other, those which have the greatest affinity for each other striving to approach as nearly as possible, until a certain position of equilibrium, which is the resultant of all the mutual attractions, is reached.

This position may be disturbed by the application of heat or of some other force, but on removing the disturbing element, the original form will be restored, so that, under given conditions, the compound only exists in one form, unless, of course, it contains asymmetric carbon atoms.

Resolution of Racemic Modifications.

The racemic modification of tartaric acid and the corresponding forms of other optically active substances—namely, of those which are inactive because they are composed of equal quantities of the two opposed active forms—may sometimes be resolved into their components by one or other of the following methods:

(1) By crystallisation of the salt formed by the combination of a *racemic* acid or base with an optically *inactive* substance. This method was first employed by Pasteur in the case of racemic (tartaric) acid, and depends on the fact that if a solution of sodium ammonium racemate be allowed to crystallise at a particular temperature (below 28°), enantiomorphous crystals (right- and left-handed, as shown in the fig., p. 540) are deposited. If now these crystals are sorted mechanically, the right-handed ones being placed in one vessel, the left-handed ones in another, a separation of the

racemic acid into its constituents is accomplished, one kind of crystals being those of the salt of the dextro-acid, the other those of the salt of the levo-acid. If, however, crystallisation take place at temperatures above 28°, only one kind of crystal is deposited—namely, crystals of sodium ammonium racemate, which do *not* exist in enantiomorphous forms, and which, indeed, belong to quite a different crystalline system. This method of separation is not applicable in all cases, because, as a rule, the crystals of the salts of the two active components are not sufficiently well defined to allow of their mechanical separation, even if they are deposited separately.

(2) A second method, also discovered by Pasteur, consists in fractionally crystallising the salt formed from a racemic acid or base with an optically *active* substance. This method depends on the fact, that the two constituents of the racemic modification, form, with one and the same optically active substance, salts which *differ in solubility*, and which, therefore, can be separated by fractional crystallisation in the ordinary way. If, for example, racemic acid be combined with the optically active base cinchonine (p. 493) or strychnine (p. 494), the product may be resolved into the salts of the dextro- and levo-acids; in a similar manner the inactive modification of coniine (p. 489) may be resolved into its constituents by fractional crystallisation of the salt which it forms with dextrorotatory tartaric acid.

(3) Another method of separation, quite different in principle from the foregoing, depends on the fact that if certain organisms, such as *penicillium glaucum*, be placed in a solution of a racemic modification, they feed on and, therefore, destroy one—usually the dextro—modification, the result being that, after a time, the solution contains only the levo-isomeride.

ORGANIC CHEMISTRY.

APPENDIX.

THE CONSTITUENTS OF PLANTS AND ANIMALS.

INTRODUCTORY.

It has been pointed out in Chapter I. that the peculiar composition of those substances which are obtained directly or indirectly from animals and plants led chemists at first to regard them as essentially different from those compounds which occur in the mineral world, and to conclude that all animal and vegetable products owed their formation to the existence of a 'vital' force. The synthesis of urea by Wöhler in 1828, and that of numerous other vegetable and animal products which followed in due course, made it necessary, however, for all chemists to abandon this idea; and recent work (particularly that of Emil Fischer, who has succeeded in building up many such complex substances as those of the sugar and uric acid groups) has shown that, in time, perhaps, there will be few, if any, animal or vegetable products which the chemist will be unable to prepare in his laboratory. That time, however, is certainly still a long way off, because the greater part of all living organisms is composed of a mixture of substances most of which are of great complexity; further, many or most of these compounds are very unstable, and readily break up into simpler—but still very complex—decomposition products; they are also, as a rule, insoluble in water and other liquids, and do not crystallise. All these properties make the investigation of such substances a task of the greatest difficulty; but still progress is being made, and physiological chemistry, which deals with the formation, properties, and relationships of the compounds found in organised nature, is attracting more and more attention.

A few of the substances which occur in plants and animals have already been described in some detail; notably those very important compounds, mostly vegetable in origin, which belong to the group of carbohydrates (part i. p. 259), and a few nitrogenous substances such as urea and uric acid (part i. p. 289 *et seq.*), which are formed in, and excreted by, animals. Most of these substances are comparatively simple in composition, and have only a moderately high molecular weight; they are soluble in water or other liquids; they can be obtained in a state of purity in crystals, and both their empirical and molecular formulæ have been determined by one or other of the methods already described; in fact, substances such as these offer no unsurmountable difficulties to the investigator, and so in most cases their constitution has been determined, and it has then been possible to prepare them synthetically.

Two or three noteworthy exceptions, however, may be mentioned. The two compounds, starch (part i. p. 271) and cellulose (part i. p. 273), which play such an important part in the vegetable world, and which form such a large proportion by weight of all plants, are both well-known substances in one sense of the word—that is to say, their ordinary properties, their behaviour under various conditions, and their *empirical* formulæ have been determined. But the *molecular* formulæ of starch and cellulose are still unknown. So far it has only been proved that they are both highly complex substances, which break up into simpler ones (dextrin, maltose, glucose) under certain conditions; and from the study of these and other decomposition products it has been inferred that the molecular formula of starch, for example, is at least $(C_6H_{10}O_5)_{200}$; it may, however, be much more complex, and the molecular formula of cellulose is possibly even greater than that of starch.

These are but two instances of the great complexity of certain vegetable products, and the fact that so much is already known of the ordinary properties of these two compounds is principally due to their comparative stability, and to the comparative readiness with which they can be separated from the other compounds with which they are generally associated in nature.

The Principal Constituents of Plants.

The Carbohydrates.

Although, then, owing to our incomplete knowledge of the structure of the more complex vegetable substances, a clear and satisfactory system of classification is quite impossible at present, the sugars, starches, and celluloses, which are the principal constituents of all plants, are conveniently placed together in one large group, and are classed as 'carbohydrates' (part i. p. 259). It is, however, a difficult task to give an exact definition of a carbohydrate, as this term is applied to substances having widely different physical and chemical properties; and the real relation between them must remain uncertain until more is known of their structure or constitution.

A carbohydrate might be defined as a substance consisting of carbon, hydrogen, and oxygen, and containing the last two elements in the same proportion as that in which they occur in water. This definition, no doubt, would be sufficiently exact, but unfortunately it would include many very simple compounds, such as acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, &c., which have no relation whatever to the principal naturally-occurring members of the group. For this reason the term is usually taken to include only the more complex substances which fulfil the above definition; and further, only those in which *most* of the oxygen atoms in the molecule are present in the form of *hydroxyl*-groups, the remaining oxygen atom or atoms being combined as in ketones $>CO$, aldehydes $-CHO$, or ethers $\geqslant C-O-C \leqslant$. A carbohydrate, then, is usually a polyhydric alcohol, and at the same time an aldehyde or ketone (compare glucose and fructose, part i. pp. 264–5); whilst the more complex ones are also anhydrides or ethers (cane-sugar, maltose, milk-sugar, part i. pp. 260–270), formed from two or more molecules of the simpler carbohydrates, with elimination of one or more molecules of water.

Ordinary *starch*, obtained from potatoes, wheat, and other forms of grain, has already been described in the chapter on carbohydrates. There are, however, various kinds of starches found in the vegetable and animal kingdoms; all these substances have the empirical formula $C_6H_{10}O_5$, and although they resemble ordinary starch in many respects, they differ from it in others.

Inulin $(C_6H_{10}O_5)_n$, for instance (part i. p. 265), is a starch which is found in artichokes, dahlia tubers, chicory, and many other plants; it is readily soluble in hot water, is coloured *yellow* by iodine, and when boiled with very dilute sulphuric acid it is converted into fructose (part i. p. 265).

Glycogen, or animal starch $(C_6H_{10}O_5)_n$, is another starch which occurs in the liver, muscle, and white corpuscles, and is a substance of great physiological importance; it resembles ordinary starch in that it is a white, tasteless, odourless powder; but it gives a red colouration with iodine, and is almost entirely soluble in water to an opalescent liquid; on hydrolysis with dilute mineral acids it yields glucose.

Dextrin, or soluble starch, as has been already stated (part i. p. 272), is a mixture of various compounds, formed by the *partial* hydrolysis of starch by the action of dilute mineral acids or of diastase. When the highly-complex starch molecule is broken down it is not immediately resolved into monoses or dioses (part i. p. 274); but it gives at first various polyoses, which are soluble in water, and which, on further hydrolysis with acids or diastase, are converted into glucose or maltose. These polyoses have not yet been thoroughly investigated; but two of those which are best known have been named *amylo-dextrin* and *malto-dextrin* respectively.

The starches and the dextrins may therefore be regarded as forming two subdivisions of the carbohydrate group.

The **gums**, such as gum-arabic, form another subdivision of this large group, the term 'gum' being applied to those carbohydrates which are amorphous, and which on treatment with water either dissolve, giving a sticky solution, or swell up to a jelly-like, sticky mass; they have usually the empirical formula $C_6H_{10}O_5$. *Gum-arabic* occurs in the bark of various species of acacia, and in many other plants; it is a mixture of at least two gums, one of which on hydrolysis yields the sugar arabinose (part i. p. 258),

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CHO.$$

Wood gum, or *xylan*, is another gum which occurs in many plants, more especially in the oak and beech, and in straw; on hydrolysis with dilute sulphuric acid it gives the sugar xylose, $C_5H_{10}O_5$ (part i. p. 258), which is optically isomeric with arabinose.

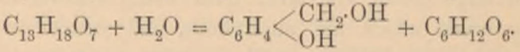
The Glucosides.

The name *glucoside* (compare footnote, p. 488) is applied to a group of vegetable substances which have generally a very high molecular weight, and which seem to have only one property in common—namely, that under the influence of a dilute acid, or of those unorganised ferments which are called *enzymes* (compare part i. p. 98), they are resolved into two or more substances, one of which is a sugar (generally glucose—hence the name). Since these glucosides give not only different sugars, but also other decomposition products which have absolutely no relation to one another, they are only placed together provisionally, until their true nature is known.

Amygdalin, $C_{20}H_{27}NO_{11}$ (p. 405), and *salicin*, $C_{13}H_{18}O_7$ (p. 404), are perhaps two of the best-known members of this group; the former, on hydrolysis, is resolved into benzaldehyde, hydrocyanic acid, and glucose,

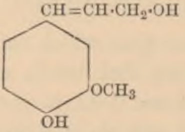
$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5{\cdot}CHO + 2C_6H_{12}O_6 + HCN;$$

whereas the latter, under similar circumstances, is converted into *saligenin* (orthohydroxybenzyl alcohol) and glucose,

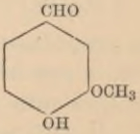


$$C_{13}H_{18}O_7 + H_2O = C_6H_4\left<\begin{matrix}CH_2{\cdot}OH\\OH\end{matrix}\right. + C_6H_{12}O_6.$$

Coniferin, $C_{16}H_{22}O_8$, is an important glucoside which occurs in the coniferæ; on hydrolysis with acids or with emulsin (part i. p. 279) it is decomposed, giving glucose and *coniferyl alcohol*. The last-named compound, on oxidation with chromic acid, is converted into *vanillin*, the essential and sweet-smelling constituent of the vanilla bean.



Coniferyl Alcohol.



Vanillin.

Digitalin, $C_{29}H_{46}O_{12}$, is a glucoside occurring in the leaves of *Digitalis purpurea* and *lutea;* it is of great medicinal importance owing to its action on the heart. On hydrolysis with concentrated hydrochloric acid it yields glucose and other compounds. Digitalin is one of the comparatively few substances which do not contain nitrogen and yet have a pronounced physiological action.

Essential Oils.

Nearly all plants contain in their seeds, fruit, flowers, leaves, stems, or roots various substances having a characteristic smell and taste; these odoriferous principles or essences are not carbohydrates, as the latter are characteristically odourless, and if they have any taste it is sweet, more or less like that of ordinary cane-sugar. Moreover, unlike the fatty vegetable oils—such as olive, linseed, palm oil, &c., which consist of *non-volatile* glycerides (part i. p. 166)—these odoriferous or ethereal oils are readily volatile. By distilling the macerated plant-part in a current of steam, it is generally possible to separate the odoriferous constituents, which collect as oil in the receiver.

The volatile oils thus obtained are usually called *essential oils*, and many of those which possess a pleasant odour or taste are used in the manufacture of essences and perfumes; many of them are also used in medicine.

A few examples of these essential oils have already been given, such as oil of winter-green (part i. p. 88), oil of mustard (part i. p. 256), oil of bitter almonds (p. 405), and oil of aniseed (p. 410); but they are so numerous that it would be impossible to mention even the more important ones.

Now, most essential oils are complex mixtures of various substances; and, although the characteristic properties of any one such oil are usually due to the presence of one definite compound, this compound is generally mixed with smaller quantities of many others. It often happens, therefore, that two or more essential oils may have one or more constituents in common, and yet differ entirely in smell and other properties, because each contains in addition some highly odoriferous compound which does not occur in the others.

The most abundant and perhaps the most generally known of all the essential oils is the substance called '*turpentine*,' which is obtained in very large quantities by making shallow cuts in the stems of the pine-trees or coniferæ and collecting the sap or juice which flows out.

Turpentine consists of a solution of various solids—called *resins*—in a liquid called *oil of turpentine*; and on distilling crude turpentine in a current of steam the essential oil passes over, leaving a residue of resin or *colophony* (violin resin).

Oil of turpentine thus obtained is a colourless, mobile liquid of sp. gr. about 0·86, boiling at about 158–160°; it is, however, a mixture, and is not constant in composition or in physical properties, but shows considerable variations in character according to the species of pine from which it has been obtained. The oil has a well-known, not unpleasant odour, which is probably not due to its principal constituent, but to small quantities of substances formed from it by oxidation. On exposure to moist air, oil of turpentine gradually changes; it darkens in colour, becomes more viscous, and is converted into resin and a variety of oxidation products, ozone and hydrogen peroxide being also produced during these changes.

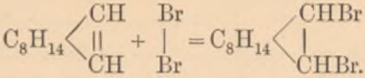
Oil of turpentine is practically insoluble in water, but is miscible with most organic liquids; it is an excellent solvent for many substances which are insoluble in water, such as phosphorus, sulphur, and iodine, and it also dissolves resins and caoutchouc; it is used on the large scale in the preparation of varnishes and oil paints.

The Terpenes.

The principal constituent of oil of turpentine is a definite compound called pinene, a substance which not only occurs in all pine-trees, but also in a great many other essential oils —as, for example, in those of laurel, lemon, parsley, sage, and thyme.

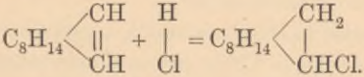
Pinene is a hydrocarbon of the molecular formula $C_{10}H_{16}$; it is a colourless, mobile liquid, having an odour of 'turpentine,' and is specifically lighter than water (sp. gr. 0·858 at 20°). It boils at 155°, and is readily volatile in steam.

Pinene, like ethylene, combines directly with two atoms of bromine, yielding a crystalline *dibromide;* it must, therefore, be regarded as an *unsaturated* hydrocarbon, and the formation of its dibromide may be expressed as follows,



$$C_8H_{14}\Big\langle\begin{matrix}CH\\ \|\\ CH\end{matrix} + \begin{matrix}Br\\ |\\ Br\end{matrix} = C_8H_{14}\Big\langle\begin{matrix}CHBr\\ |\\ CHBr.\end{matrix}$$

It also combines with one molecule of hydrogen chloride, when the dry gas is passed into it at low temperatures, a reaction which affords further evidence that pinene is an unsaturated compound,



$$C_8H_{14}\Big\langle\begin{matrix}CH\\ \|\\ CH\end{matrix} + \begin{matrix}H\\ |\\ Cl\end{matrix} = C_8H_{14}\Big\langle\begin{matrix}CH_2\\ |\\ CHCl.\end{matrix}$$

This product, *pinene hydrochloride*, $C_{10}H_{17}Cl$, is a crystalline compound melting at 125°; it has an odour like that of camphor (p. 563), and is often called 'artificial camphor.'

Pinene also combines directly with nitrosyl chloride (NOCl), giving a crystalline compound, $C_{10}H_{16}NOCl$, melting at 103°, which is called *pinene nitrosochloride.*

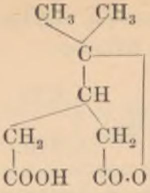
These additive compounds are of great use in detecting and recognising pinene, which, being a liquid, is not so easily identified as these crystalline solids of definite melting-point.

When pinene dibromide is heated alone at a moderately high temperature it is converted into cymene (p. 339) and hydrogen bromide,

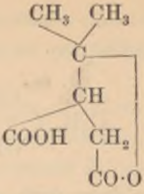
$$C_{10}H_{16}Br_2 = CH_{14} + 2H_{10}Br\,;$$

cymene is also produced, together with various other hydrocarbons, when pinene is heated with iodine.

Pinene readily undergoes oxidation, yielding various products according to the conditions of the experiment; among these may be mentioned terephthalic acid (p. 427) and two other important oxidation products—namely, terpenylic and terebic acids, the constitutional formulæ of which are as follows,



Terpenylic Acid.



Terebic Acid.

Terpenylic acid, $C_8H_{12}O_4$, is a *lactone* (p. 519, footnote) and at the same time a monocarboxylic acid; it is a crystalline compound melting at 90°.

Terebic acid, $C_7H_{10}O_4$, is also a crystalline lactonic monocarboxylic acid (m.p. 175°), and is closely related to terpenylic acid, from which it can be obtained by oxidising with potassium permanganate.

As the constitutions of these two acids have been settled beyond doubt, their formation from pinene throws a good deal of light on the constitution of this important vegetable product (compare p. 558).

Three different pinenes are known. Two of these compounds are optically active, and are identical in every respect, except that they rotate the plane of polarisation of polarised light in opposite directions, but of course to the same extent; these two forms are distinguished as dextrorotatory or *d*-pinene and levorotatory or *l*-pinene. The third modification is an externally compensated mixture of the two optically active forms, and is known as inactive or *i*-pinene.

d-Pinene can be obtained by fractional distillation of the oil of turpentine obtained from Burmese turpentine, whereas *l*-pinene is prepared from French turpentine in a similar manner; it is very difficult, however, to obtain either of these compounds in a state of purity. *i*-Pinene, on the other hand, can easily be obtained in a pure condition, by decomposing the nitrosochloride of either of the optically active modifications with aniline; this is a very interesting fact, as it shows how easily some optically active substances may be converted into externally compensated mixtures.

Camphene, $C_{10}H_{16}$, is a solid hydrocarbon which occurs in a number of essential oils (ginger-, citronella-, spike-, valerian-oil), and which can also be obtained artificially from various naturally-occurring compounds; it melts at 48°, boils at 160°, and is practically insoluble in water.

Camphene is formed when pinene hydrochloride is heated at 200° with sodium acetate and glacial acetic acid, or distilled with lime; although this change is apparently a very simple one, it does not consist merely in the elimination of hydrogen chloride, as represented by the following equation,

$$C_{10}H_{17}Cl = C_{10}H_{16} + HCl;$$

but it is almost certain that various intramolecular changes take place at the same time, and that the ten carbon atoms in camphene are united to one another in a different manner from that in which they are combined in pinene.

Camphene can also be obtained indirectly from camphor (p. 563) by the method described later.

Camphene resembles pinene inasmuch as it unites directly with one molecule of hydrogen chloride, forming a crystalline product, *camphene hydrochloride*, $C_{10}H_{17}Cl$, which melts at 149–151°; it also combines directly with two atoms of bromine, giving *camphene dibromide*, $C_{10}H_{16}Br_2$. It is, however, much more stable than pinene, and is only oxidised with difficulty; on treatment with chromic acid it gives camphor (p. 563).

Camphene, like pinene, exists in two optically active (*d*- and *l*-) forms, and in one externally compensated (inactive or *i*-) modification.

Limonene, $C_{10}H_{16}$, like pinene, is an important constituent of essential oils, and occurs in those of lemon, lime, lavender, caraway, bergamot, celery, turpentine, and many others; it is a colourless, pleasant-smelling, mobile liquid, boiling at 175°. It combines directly with *four* atoms of bromine to form a crystalline *limonene tetrabromide*, $C_{10}H_{16}Br_4$, which melts at 104°; it also unites with two molecules of hydrogen chloride or hydrogen bromide, yielding the crystalline compounds $C_{10}H_{18}Cl_2$ and $C_{10}H_{18}Br_2$ respectively. On oxidation with concentrated sulphuric acid it yields *cymene*.

Three different, optically isomeric, modifications of limonene, corresponding with the three pinenes, are known, and they all occur naturally in plants; *d*-limonene, for instance, is found in lemon oil, whereas *l*-limonene occurs in pine-needle oil and in Russian oil of peppermint. These two compounds differ only as regards their action on polarised light, and each gives rise to optically active derivatives which are related in the same way as the parent substances.

The third isomeride, *i*-limonene, is an externally compensated mixture of the two optically active forms, and, before its relation to the latter was known, it was named *dipentene*. Dipentene is, of course, identical with limonene in chemical properties, and it is formed when either of the optically active modifications is heated at 250–300°; it is also produced when pinene or camphene is treated in a similar manner—a fact which seems to show that there is a close relationship between these three hydrocarbons. Further, when either of the active limonenes is caused to combine with *two* molecules of hydrogen chloride or bromide, the product $C_{10}H_{18}Cl_2$ or $C_{10}H_{18}Br_2$ is optically *inactive*, and is named *dipentene dihydrochloride* or *dihydrobromide* as the case may be; in the formation of these derivatives the asymmetric carbon atom in limonene (compare formula, p. 560) probably loses its asymmetric character, so that the derivatives in question are *not* externally compensated compounds. Dipentene is produced when equal quantities of the two active modifications are mixed; it occurs naturally in *Oleum cinæ*.

Pinene, camphene, and limonene are three of the most important members of a group of substances of vegetable origin which are classed together as the **terpenes** (from the word 'turpentine').

The term terpene, however, like the word carbohydrate, cannot be very accurately defined. It is usually applied to a number of *hydrocarbons* which occur in essential oils, and which have the molecular formula $C_{10}H_{16}$. These terpenes are all readily volatile, and they are all *unsaturated* compounds; they all combine directly with bromine, hydrogen chloride, hydrogen bromide, and nitrosyl chloride, or at least with one or other of these reagents, forming crystalline additive products which serve for their isolation and identification. But whereas some of the terpenes combine directly with only *two* atoms of bromine or *one* molecule of hydrogen bromide, others unite with *four* atoms of bromine or *two* molecules of hydrogen bromide. This difference in behaviour admits of a classification of the terpenes into two groups, as follows:

GROUP I.—Terpenes which combine with Br_2 or with HBr.
Pinene. Camphene.

GROUP II.—Terpenes which combine with $2Br_2$ or with 2HBr.
Limonene.

Several other members of each of these groups are known, but as they cannot be described here their names are not given.

Constitution of the Terpenes.

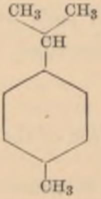
The behaviour of the terpenes towards bromine and the halogen acids affords a most important starting-point from which to consider the constitution of these natural products; for, if the terpenes were *open-chain* hydrocarbons of the molecular formula $C_{10}H_{16}$, they should unite directly with *six* atoms of bromine or with *three* molecules of a halogen acid, because they would necessarily contain either three double (or ethylenic) bindings, or one ethylenic and one treble (or acetylenic) binding.

This will be made clearer by considering the following formulæ, which represent two (unknown) open-chain hydrocarbons of the molecular formula $C_{10}H_{16}$.

$$CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$
$$CH{\vdots}C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

As, therefore, some of the terpenes unite directly with only *two*, others with only *four* atoms of bromine, it must be concluded that they are not open-chain hydrocarbons.

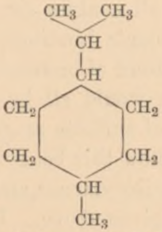
Now, it has also been found that many of the terpenes are very easily transformed into comparatively simple derivatives of benzene, and that various other compounds closely related to, or obtained from, the terpenes are also changed into benzene derivatives under the influence of heat or of chemical agents. Among the benzene derivatives which are thus produced, the most frequently found is the well-known hydrocarbon *cymene* or p-*isopropylmethylbenzene*, $C_{10}H_{14}$ (p. 339), which, as will be seen, contains only two atoms of hydrogen less than the terpenes, and which is represented by the following constitutional formula,



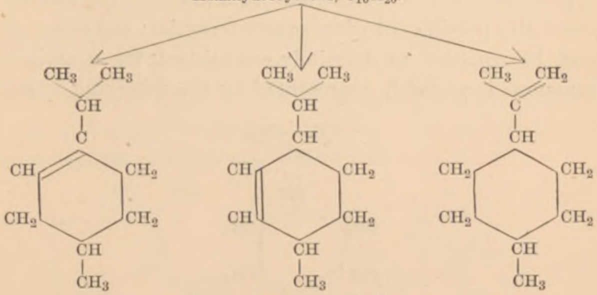
Cymene or Para-methylisopropylbenzene.

This conversion of terpenes and their derivatives into cymene, and also the fact that cymene itself often occurs together with the terpenes in essential oils, have led to the conclusion that the terpenes are probably derivatives of, or closely related to, cymene—that is to say, that they probably contain the same 'skeleton' of carbon atoms as that which occurs in cymene. Further investigation, more especially the study of their oxidation products, many of which have been proved to contain remnants of this same skeleton of carbon atoms (compare p. 554), has only served to confirm this view; and although it cannot be said that the constitution of any terpene is definitely established, it is very probable that many of these hydrocarbons are related to cymene in a fairly simple manner.

A few of the facts and arguments bearing on this conclusion may be briefly set out as follows:—In order to convert a saturated hydrocarbon such as hexahydrocymene, $C_{10}H_{20}$ (which stands in the same relation to cymene as hexahydrobenzene does to benzene: compare p. 309), into an unsaturated hydrocarbon of the composition $C_{10}H_{16}$, *four* atoms of hydrogen must be removed. Suppose, now, that in the first place only *two* of these hydrogen atoms are taken away, and that they are lost by any one pair of *neighbouring* carbon atoms, various isomeric hydrocarbons of the molecular formula $C_{10}H_{18}$, such as the following, would be obtained,

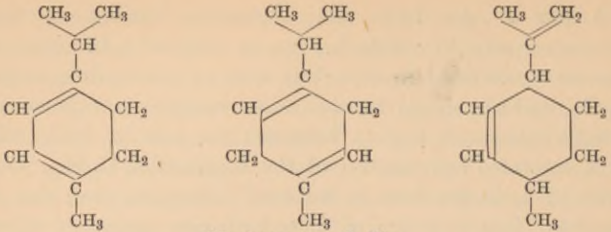


Hexahydrocymene, $C_{10}H_{20}$.



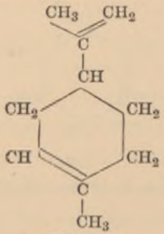
Tetrahydrocymenes, $C_{10}H_{18}$.

By repeating this process—that is to say, by again removing two atoms of hydrogen in a similar manner, hydrocarbons of the molecular formula $C_{10}H_{16}$ would be obtained, as, for example, the following,



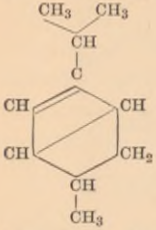
Dihydrocymenes, $C_{10}H_{16}$.

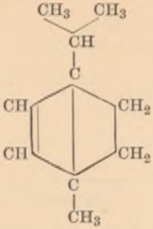
All compounds such as these, obtained by taking away *four* atoms of hydrogen from *hexa*hydrocymene, would be regarded as *dihydrocymenes*—that is to say, cymene *plus* two atoms of hydrogen; they would all contain one closed chain and two double linkings or ethylenic bindings, and they would combine directly with four atoms of bromine or with two molecules of a halogen acid; they would all be readily converted into cymene by the action of suitable reagents. Probably, then, those terpenes which show this behaviour—namely, those of Group II.—are true dihydrocymenes, and are represented by formulæ such as those just given above. In the case of limonene, it is even possible to choose one from amongst the numerous theoretically possible dihydrocymene formulæ; and although it cannot be regarded as definitely established, the constitution of limonene is probably represented by the following formula,

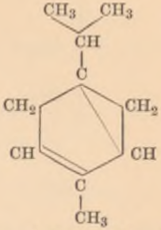


Limonene.

But now, instead of removing the last pair of hydrogen atoms from neighbouring carbon atoms of the hydrocarbons $C_{10}H_{18}$, two hydrogen atoms from other parts of the closed chain may be taken away; there would then be formed hydrocarbons $C_{10}H_{16}$ such as the following,

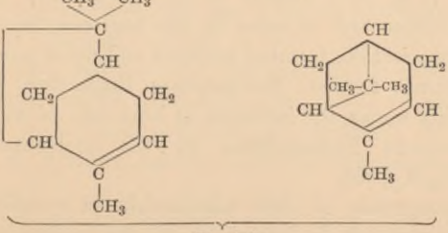






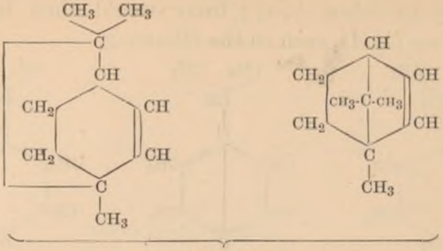
Now, these formulæ represent substances which, although they would not be actually regarded as dihydrocymenes (because they contain two closed chains), are yet related to the dihydrocymenes in a comparatively simple manner; moreover, substances such as these would probably combine directly with *two* atoms of bromine or with *one* molecule of a halogen acid; they would probably be converted into cymene by the action of vigorous reagents, *one* of the closed chains being broken. It is thought, therefore, that those terpenes which behave in this way—namely, those of Group I.—contain two closed chains, and that the arrangement of their carbon atoms is not far removed from that which obtains in cymene.

For reasons such as these, and for many others which cannot be discussed here, the following constitutional formulæ have been provisionally assigned to pinene and camphene, the two most important members of Group I.,



*Pinene.**

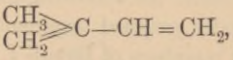
* These two formulæ are *identical*.



*Camphene.**

Sesquiterpenes and Polyterpenes.

The terpenes of the molecular formula $C_{10}H_{16}$ are often accompanied in nature by other unsaturated hydrocarbons of higher molecular weight, which are no doubt related to the terpenes more or less closely. Some of these more complex hydrocarbons have the same empirical formula (C_5H_8) as the terpenes, and their molecular formula is therefore $(C_5H_8)_n$, generally $C_{15}H_{24}$ or $C_{20}H_{32}$. It has been suggested, therefore, that all these compounds, including the terpenes, are polymeric modifications of some simple hydrocarbon (C_5H_8); and this view finds some slight support in the fact that the hydrocarbon *isoprene*,



$$\begin{array}{l}CH_3\\CH_2\end{array}\!\!\geqslant C-CH=CH_2,$$

a liquid (b.p. 37°) formed in the destructive distillation of india-rubber and of some of the terpenes, readily undergoes polymerisation, forming terpenes and other more complex hydrocarbons; further, the terpenes themselves polymerise very readily under the influence of heat and of strong acids, giving various hydrocarbons of the molecular formula $C_{20}H_{32}$, $C_{30}H_{48}$, &c.

In consequence of this relationship in composition the naturally-occurring hydrocarbons of the molecular formula

---

* These two formulæ are *identical*.

$C_{15}H_{24}$ have been named the *sesquiterpenes*, whilst the more complex ones still have been named the *polyterpenes*.

The two best-known sesquiterpenes are *cadinene* and *caryophyllene*, both of which are viscous liquids, boiling at about 274° and 255° respectively.

Cadinene occurs in the essential oils of cubeb, juniper, camphor, &c., and caryophyllene in oil of cloves.

Compounds closely related to the Terpenes.

Although the terpenes are such constant and important constituents of most ethereal or essential oils, the specific odour or taste of the latter is usually due to the presence of one or more compounds which contain *oxygen* as well as carbon and hydrogen; the compounds in question are usually *ketones* (such as camphor and menthone: see below), phenols (such as thymol and carvacrol: p. 397), or alcohols (such as borneol and menthol: see below), or ethereal salts of these alcohols, and most of them are closely related to the terpenes in constitution. Some of the more important of these naturally-occurring terpene derivatives are described in the following pages.

Camphor, $C_{10}H_{16}O$, is a constituent of essential oil of camphor, and is obtained from the leaves of the camphor-tree (*Laurus camphora*), which grows in Japan, by distilling with steam. It is a soft, crystalline solid, melting at 175° and boiling at 204°; it is very volatile, sublimes readily even at ordinary temperatures, and has a highly characteristic smell. It is only sparingly soluble in water, but sufficiently so to impart to it a distinct taste and smell (*Aqua camphoræ*), and it dissolves readily in alcohol and most ordinary organic solvents; it is extensively used in medicine, in the manufacture of xylonite, and also in the preparation of a few explosives.

Camphor can be obtained by oxidising camphene (p. 555) with potassium dichromate and sulphuric acid,

$$C_{10}H_{16} + O = C_{10}H_{16}O;$$

a fact which shows that it is very nearly related to this terpene; it is also produced when the secondary alcohol, borneol (p. 567), is oxidised with nitric acid,

$$C_{10}H_{18}O + O = C_{10}H_{16}O + H_2O.$$

These methods of formation and its whole chemical behaviour prove that camphor is a *ketone;* with hydroxylamine, for instance, camphor interacts readily, giving a crystalline oxime, *camphoroxime* (m.p. 118°),

$$C_{10}H_{16}O + NH_2{\cdot}OH = C_{10}H_{16}{:}N{\cdot}OH + H_2O;$$

and on reduction it is converted into borneol, just as acetone is transformed into the secondary alcohol, isopropyl alcohol,

$$C_{10}H_{16}O + H_2 = C_{10}H_{17}{\cdot}OH.$$

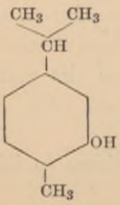
When camphor is heated with iodine it is converted into carvacrol or hydroxycymene (p. 397),

$$C_{10}H_{16}O + I_2 = C_{10}H_{14}O + 2HI;$$

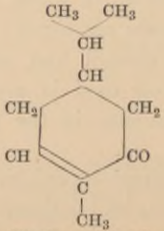
and when distilled with phosphorus pentoxide it is transformed into cymene (p. 339),

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O.$$

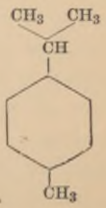
These last two facts seem to show that camphor is very closely related to cymene and carvacrol, and when written in the form of equations, the two reactions appear to be extremely simple; at one time the following constitutional formula was assigned to camphor on account of its supposed relation to these two benzene derivatives,



Carvacrol.



Kekulé's Formula for Camphor.

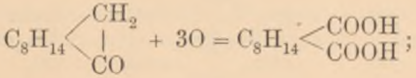


Cymene.

There are, however, many other important facts which show clearly that camphor is not a true cymene or carvacrol derivative, as represented above, and that its conversion into these benzene derivatives is not nearly so simple a change as it appears to be.

In the first place, camphor behaves like a *saturated* ketone, and forms substitution, not additive, products when treated with bromine, chlorine, &c., whereas in accordance with Kekulé's formula it would be an unsaturated compound; in the second place, camphor gives rise to a number of oxidation products of known constitution, and the formation of these substances cannot be accounted for on the basis of the constitutional formula given above.

The first product of the oxidation of camphor with boiling nitric acid is a dicarboxylic acid of the composition $C_{10}H_{16}O_4$, called camphoric acid,

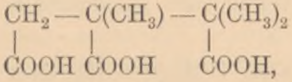


$$C_8H_{14}\left<\begin{matrix}CH_2\\ |\\ CO\end{matrix}\right. + 3O = C_8H_{14}\left<\begin{matrix}COOH\\ COOH\end{matrix}\right.;$$

and this compound on further oxidation yields a tricarboxylic acid, $C_9H_{14}O_6$, called camphoronic acid,

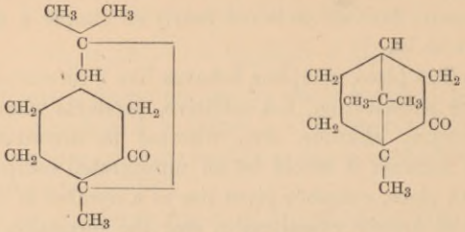
$$C_{10}H_{16}O_4 + 5O = C_9H_{14}O_6 + CO_2 + H_2O.$$

Now, it has been proved that camphoronic acid has the following constitution,



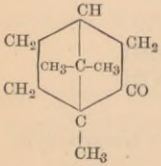
$$\begin{array}{lll} CH_2 - & C(CH_3) - & C(CH_3)_2 \\ | & | & | \\ COOH & COOH & COOH, \end{array}$$

by preparing it synthetically by a series of simple reactions (see below); and as an acid of this constitution could not possibly be obtained by the oxidation of a true cymene or carvacrol derivative, it follows that camphor has not the constitution assigned to it by Kekulé; nevertheless, it is doubtless very closely related to cymene, as Kekulé supposed, and its constitution is probably expressed by the following formula or by some modification of it,

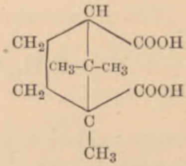


Bredt's Formula for Camphor.*

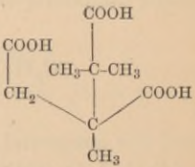
The relation between camphor, camphoric acid, and camphoronic acid may be indicated by the following formulæ,



Camphor.



Camphoric Acid.



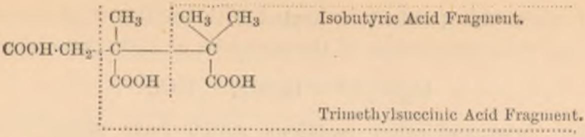
Camphoronic Acid.

Camphoric acid, $C_8H_{14}<\begin{matrix}COOH\\COOH\end{matrix}$, the first oxidation product of camphor, is a crystalline substance melting at 187°; it is readily converted into its anhydride $C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>O$ (m.p. 221°).

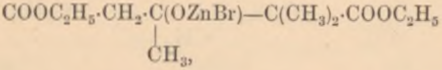
Camphoronic acid, $C_6H_{11}(COOH)_3$, is a crystalline compound which melts at 137° and is readily soluble in water; when submitted to dry distillation it is decomposed into trimethylsuccinic acid, isobutyric acid, carbon dioxide, water, and carbon,

---

* These formulæ are *identical;* many other formulæ for camphor have been suggested.

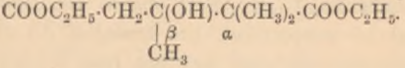


Camphoronic acid has been prepared synthetically in the following manner:—Ethylic acetoacetate, $COOC_2H_5{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, condenses with ethylic bromisobutyrate, $(CH_3)_2{\cdot}CBr{\cdot}COOC_2H_5$, and zinc to form a compound,



$$COOC_2H_5{\cdot}CH_2{\cdot}\underset{\displaystyle CH_3,}{\underset{|}{C}}(OZnBr)\text{—}C(CH_3)_2{\cdot}COOC_2H_5$$

which, when treated with dilute acids, yields ethylic β-hydroxy-ααβ-trimethylglutarate, $COOC_2H_5{\cdot}CH_2{\cdot}\underset{\displaystyle CH_3}{\underset{|\beta}{C}}(OH){\cdot}\underset{\alpha}{C}(CH_3)_2{\cdot}COOC_2H_5$.



By treatment first with phosphorus trichloride and then with potassium cyanide, the hydroxyl group is replaced by the cyanogen group, and the product on hydrolysis yields camphoronic acid.

Borneol, $C_{10}H_{17}{\cdot}OH$, occurs in combination with acetic acid as *bornyl acetate*, $C_{10}H_{17}{\cdot}O{\cdot}CO{\cdot}CH_3$, in many essential oils—as, for example, in those of thyme, valerian, and pine-needles; it also occurs in a free condition in the oils of spike and rosemary; its principal source, however, is the *Dryobalanops camphora*, a tree growing in Borneo and Sumatra.

Borneol can be obtained by reducing the ketone, camphor, with sodium and alcohol (see above). It is rather like camphor in physical properties, but it is more distinctly crystalline; and, although it has an odour something like that of camphor, it also smells faintly of peppermint. It melts at 203°, boils at 212°, and is readily volatile in steam.

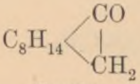
Borneol is a secondary alcohol; when treated with phosphorus pentachloride it is converted into bornyl chloride,

$$C_{10}H_{17}{\cdot}OH + PCl_5 = C_{10}H_{17}Cl + POCl_3 + HCl;$$

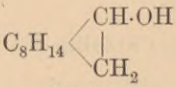
and when this product is heated with aniline it gives camphene, with elimination of the elements of hydrogen chloride,

$$C_{10}H_{17}Cl = C_{10}H_{16} + HCl.$$

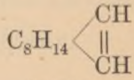
From these, and other reactions which have already been described, it will be obvious that camphor, borneol, and camphene are closely related to one another, as may be indicated by the following formulæ,



Camphor.



Borneol.

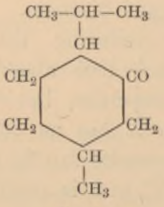


Camphene.

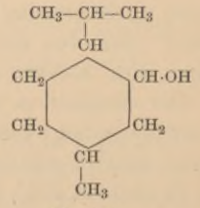
Menthone, $C_{10}H_{18}O$, is one of the numerous constituents of oil of peppermint, the essential oil of *Mentha piperita*, which also contains menthol (see below), pinene, cadinene (p. 563), and many other compounds.

Menthone is a colourless liquid, boiling at 206°, and its chemical behaviour stamps it as a ketone; on reduction with sodium and alcohol it is converted into the secondary alcohol, menthol.

Menthone is a ketone derived from hexahydrocymene, and it may be called *ketohexahydrocymene;* its constitution and that of menthol are expressed by the following formulæ,



Menthone.



Menthol.

Menthol, $C_{10}H_{19}{\cdot}OH$, is a secondary alcohol related to menthone in just the same way as borneol is related to camphor; it occurs in oil of peppermint both in the free state and as *menthyl acetate*, $C_{10}H_{19}\cdot O\cdot CO\cdot CH_3$, an ethereal salt. Menthol is a crystalline solid melting at 142°, and it is principally to the presence of this alcohol that oil of peppermint owes its very powerful odour.

On reduction with hydriodic acid, menthol is converted into hexahydrocymene; this and many other facts afford evidence that its constitution is represented by the graphic formula given above.

Camphor and the other terpene derivatives mentioned above, like the terpenes themselves, are capable of existing in various optically different modifications, as each contains at least one asymmetric carbon atom; the compounds found in nature are nearly always optically active, and, excepting dipentene (p. 556), the externally compensated mixture of the two forms is seldom obtained directly from living organisms.

The foregoing account of the properties of some of the principal compounds occurring in the vegetable kingdom may perhaps be briefly summarised as follows:—Firstly, most of the well-known substances obtained from plants are composed of carbon, hydrogen, and oxygen, except a few, which consist of the first two elements only (the terpenes). Secondly, many of them can be easily purified by crystallisation, distillation, &c., and can thus be obtained in a condition suitable for analysis and further investigation. Thirdly, with a few exceptions, such as starch, cellulose, and the gums—which, however, constitute the great proportion of all dry vegetable matter—these compounds are not very highly complex, and their constitution or molecular structure is known.

It must be borne in mind, however, that in a work of this scope only the best-known compounds of the vegetable kingdom can be considered, and in consequence of this fact a false impression may have been produced by the above description; it is merely *because* more is known of the simpler than of the more complex compounds that the former have been described and the latter passed over. It must also be remembered that although, for convenience, the compounds of the vegetable kingdom are classed apart from those of the animal kingdom, there is no sharp line of division between the two, and that many compounds—as a rule, the more complex ones—occur both in animals and plants, and are probably equally important to both.

If thus restricted to the simpler compounds, the above summary of the properties of vegetable, as distinct from animal, products may be accepted.

Substances found principally in the Animal Kingdom.

Passing now to the consideration of substances occurring principally in animals, the first point to notice is that they generally contain *nitrogen*, and very often *sulphur* or *phosphorus*, in addition to carbon, hydrogen, and oxygen. Speaking very generally, they are also more unstable than vegetable products, and undergo decomposition very easily under the influence of chemical agents, or as the result of the action of organisms, which bring about the numerous and complex changes collectively named *putrefaction;* this instability is shown more particularly by the complex substances called proteïds (p. 594), which occur in plants as well. Partly on account of their instability, it is generally a matter of the greatest difficulty to separate these complex substances in a condition even approximating purity; further, as they are generally non-volatile and non-crystalline, the ordinary methods of purification cannot be applied to them.

In consequence of these properties comparatively little is known of the most important constituents of the animal kingdom except that they are unusually complex; there are, on the other hand, many comparatively simple substances obtained from animal matter which have been carefully studied, and the constitution of which has been satisfactorily established. Animal substances, in fact, like those of the vegetable kingdom, may be classed into the two groups:

(*a*) Comparatively simple compounds of known constitution.
(*b*) Complex substances of unknown constitution.

The differences between glucose and starch, for example, illustrate the kind of difference between these two groups of compounds of animal origin.

In the vegetable kingdom the simplest, and consequently best known, compounds are those which, like oxalic acid and other vegetable acids, may be regarded as products of excretion, or decomposition products of the more complex starches, celluloses, &c. It is the same in the animal world; the products excreted, or those resulting from the breaking down of the more complex compounds, are often crystalline and comparatively simple, as, for example, urea and uric acid.

Whereas, then, the investigation of some of the constituents of animals is very well advanced, there are others about which so little is known that any satisfactory system of classification is out of the question; it is possible, however, to classify those compounds of known constitution, and to subdivide them into various groups according to their chemical relationships.

Lecithine and the Ptomaines.

The first group which will be considered contains four important simple compounds which are derivatives of the quaternary base, *ethyltrimethylammonium hydroxide*, $CH_3{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$; they are all closely related to one another, and, as will be seen from their constitutional formulæ, the relationship between them is the same as that between ethyl alcohol, acetaldehyde, acetic acid, and ethylene.

Choline, $CH_2(OH){\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$.
Muscarine, $CHO{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$.
Betaïne, $COOH{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$.
Neurine, $CH_2{=}CH{\cdot}N(CH_3)_3{\cdot}OH$.

These four compounds and the two primary *diamines*, putrescine and cadaverine, which are also described in this section, are decomposition products of more complex compounds, and most of them are formed during the putrefaction of animal matter; they are nearly all poisonous, and are classed as the **ptomaines** or **toxines**.

One much more complex substance is also described here—namely, *lecithine*—which may be regarded as an ethereal salt of the alcohol, choline, and which is considered first because many of the ptomaines are produced from it as the result of putrefactive decomposition.

Lecithine (*Protagon*), $C_{44}H_{90}NPO_9$, is a substance containing phosphorus, which is very widely distributed throughout the animal and vegetable kingdoms. It is found in small quantities in bile and in most organs of the body, and is especially prominent in the brain substance, the blood-corpuscles, and in the nerve tissues; it occurs in considerable quantities in yolk of egg (hence the name from λεχιθος, yolk of egg), and is also found in plants, particularly in the seeds.

Preparation from Yolk of Egg.—The colouring matter of the yolk is first removed by extracting with ether, and the residue is then well washed with water and digested with absolute alcohol at 40–50°; after filtering, the solution is evaporated at a low temperature and the residue again extracted with warm absolute alcohol. On cooling the alcoholic solution to $-10°$, the lecithine separates, and is collected and washed with cold alcohol.

Lecithine is a waxy, apparently crystalline, very hygroscopic substance, soluble in alcohol and ether; in contact with water it swells up and forms a kind of emulsion. Its constitution is indicated by the change which it undergoes on treatment with acids or baryta water, when it is decomposed into stearic acid,[*] glycerophosphoric acid,[†] and choline,

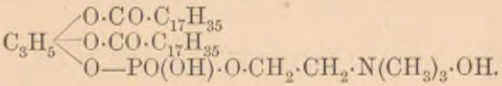
---

[*] Some forms of lecithine yield palmitic or oleïc acid instead of stearic acid.

[†] *Glycerophosphoric acid*, $C_3H_5(OH)_2 \cdot O \cdot PO(OH)_2$, is a thick syrup, prepared by combining glycerol with metaphosphoric acid.

$$C_{44}H_{90}NPO_9 + 3H_2O = \underset{\text{Stearic Acid.}}{2C_{18}H_{36}O_2} + \underset{\text{Glycero-phosphoric Acid.}}{C_3H_9PO_6} + \underset{\text{Choline.}}{C_5H_{15}NO_2};$$

it is thus probable that the constitution of lecithine is represented by the following formula,*



$$C_3H_5\begin{cases} O{\cdot}CO{\cdot}C_{17}H_{35} \\ O{\cdot}CO{\cdot}C_{17}H_{35} \\ O{-}PO(OH){\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH. \end{cases}$$

Choline, or *hydroxyethyltrimethylammonium hydroxide*, $CH_2(OH){\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$, sometimes called *sinkaline* or *bilineurine*, has just been mentioned as one of the decomposition products of lecithine. It is widely distributed in the animal and vegetable kingdoms, and was discovered by Strecker in bile (χολή); its constitution was established by Baeyer. Choline is contained in hops, and is a constituent of the alkaloid sinapine which occurs in mustard-seeds. It is also produced in corpses, as the result of putrefactive changes.

Preparation.—Lecithine is boiled for one hour with baryta water; the barium is then precipitated with carbonic anhydride, and, after filtering, the filtrate is evaporated and the residue extracted with absolute alcohol. The alcoholic extract is mixed with platinum chloride, and the platinochloride of choline, which separates in crystals, is collected, dissolved in water, and decomposed by sulphuretted hydrogen. The filtrate from the platinum sulphide yields, on evaporation, chloride of choline, $C_5H_{14}NOCl$.

Choline is a syrupy mass which crystallises with difficulty; it is strongly alkaline, and absorbs carbonic acid from the air, but it is not poisonous unless taken in large quantity.

It forms salts with acids in the same way as ammonium hydrate, the hydroxyl group attached to nitrogen being displaced by the acid radicle. The most characteristic salt is the *platinochloride* $(C_5H_{14}NO)_2PtCl_6$, which crystallises from water in plates. When a strong aqueous solution of choline is boiled, glycol and trimethylamine are formed,

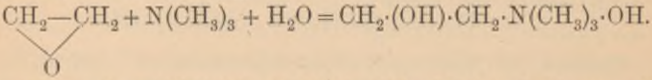
---

* Compare the constitution of the fats (part i. p. 168).

$$CH_2(OH)\cdot CH_2\cdot N(CH_3)_3\cdot OH = CH_2(OH)\cdot CH_2\cdot OH + N(CH_3)_3\,;$$

a decomposition which clearly shows the constitution of the substance.

Choline was first synthesised by Würtz, who obtained it by mixing aqueous solutions of ethylene oxide and trimethylamine, and evaporating,



$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} + N(CH_3)_3 + H_2O = CH_2\cdot(OH)\cdot CH_2\cdot N(CH_3)_3\cdot OH.$$

Muscarine, $CHO\cdot CH_2\cdot N(CH_3)_3\cdot OH + H_2O$, was discovered by Schmiedeberg and Koppe in the poisonous mushroom (*Agaricus muscarius*); it has also been found in putrid fish. It is a deliquescent, crystalline, strongly alkaline substance which forms crystalline salts; it is a powerful poison, acting especially on the heart. Its constitution is proved by the fact that it is formed when choline is oxidised by nitric acid.

Betaïne, *oxyneurine* or *lycine*, $COOH\cdot CH_2\cdot N(CH_3)_3\cdot OH$ or $CO<\substack{CH_2\\O}>N(CH_3)_3$, occurs in beetroot (in which it was discovered by Scheibler), and is obtained in large quantities as a by-product in the manufacture of sugar from beetroot; it is also found in some seeds, especially in those of the cotton-plant.

Preparation.—The mother-liquor, after the extraction of the beetroot sugar, is boiled with baryta for twelve hours; the barium is then precipitated by carbonic anhydride and the filtrate evaporated to dryness. The residue is extracted with alcohol, and the alcoholic solution precipitated with zinc chloride. The crystalline precipitate, $C_5H_{11}NO_2ZnCl_2$, is then collected, decomposed with baryta, the filtrate freed from barium by means of sulphuric acid, and evaporated to a small bulk, when betaïne chloride crystallises out.

Betaïne separates from water in large crystals, which have the composition expressed by the first of the formulæ given above; at 100° it loses 1 mol. H_2O, yielding the anhydride represented by the second formula. It is very soluble in water, and gives well-characterised salts, such as the chloride $COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl$, with one equivalent of an acid; when betaïne is heated in the dry state trimethylamine* distils over, and a carbonaceous residue is left.

Choline and betaïne stand in the relation of alcohol to acid, as is indicated by the fact that the latter is produced from the former by oxidation. Betaïne chloride has been synthetically prepared by heating together monochloracetic acid and trimethylamine in aqueous solution,

$$COOH{\cdot}CH_2Cl + N(CH_3)_3 = COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl.$$

Neurine, $CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH$, is one of the most important of the ptomaines, and is exceedingly poisonous; it is a decomposition product of lecithine, from which it is doubtless formed by bacterial action after death. It has also been shown that some proteïds (p. 594), when decomposed by bacterial growths, yield small quantities of neurine.

Neurine is a strongly alkaline syrup, which is very soluble in water, and combines energetically with acids forming crystalline salts.

It has been prepared synthetically as follows:—When choline is heated with hydrobromic acid the two hydroxyl groups are displaced by two atoms of bromine, and a substance of the formula $CH_2Br{\cdot}CH_2{\cdot}N(CH_3)_3Br$ is formed; this, when treated with silver hydroxide, yields neurine,

$$CH_2Br{\cdot}CH_2{\cdot}N(CH_3)_3Br + 2AgOH$$
$$= CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH + 2AgBr + H_2O.$$

Putrescine, or *tetramethylene diamine*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, as its name implies, is a product of the putrefactive decomposition of animal matter; it is a crystalline substance melting at 23° and boiling at 160°, and it has a most un-

---

* The trimethylamine, which is used in the manufacture of potassium carbonate, is obtained by distilling the crude betaïne contained in the residual mother-liquors after the extraction of the sugar from beetroot juice.

pleasant and penetrating smell. It is soluble in water in all proportions, is strongly basic, and forms salts with two equivalents of an acid.

Putrescine has been obtained synthetically from ethylene dibromide by converting this into the dicyanide (part i. p. 235), and then reducing with sodium in alcoholic solution,

$$CN \cdot CH_2 \cdot CH_2 \cdot CN + 8\,H = NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2.$$

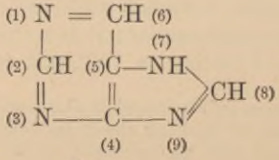
Cadaverine, or *pentamethylene diamine*, has already been mentioned, and its synthesis from trimethylene bromide has also been given (p. 478).

It is a syrup which boils at 178–179°, and, like putrescine, it is a diacid base.

The Uric Acid or Purine Derivatives.

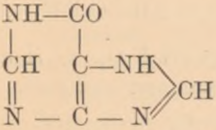
Uric acid has been briefly described in part i. (p. 291), but no attempt was there made to discuss its decomposition products or to deduce its constitutional formula. In this section the constitution of the acid is given, and also the most interesting method by which this important compound has been prepared synthetically. This section contains also a description of a number of substances of interest allied to, or derived from, uric acid; our knowledge of the constitution of these compounds is mainly due to the brilliant researches of Emil Fischer.

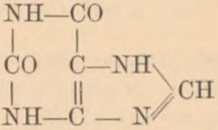
Uric acid is one of a series of very important natural products which may be regarded as derived from *purine*, a substance which has been prepared by Emil Fischer, and which has the following constitution,

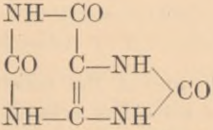


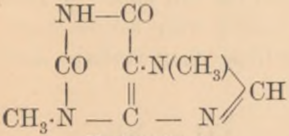
Purine.

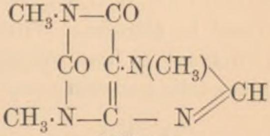
The derivatives of purine are produced by substituting various atoms or groups for hydrogen atoms, or by direct addition, or by a combination of these two processes; the positions of the new atoms or groups are shown by appending to the names the numbers in the order represented above. The names and formulæ of the more important members of the group are as follows,

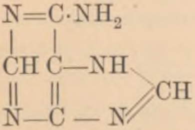

Hypoxanthine or 6-Oxypurine.

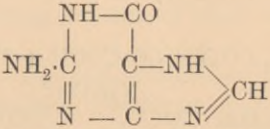

Xanthine or 2,6-Dioxypurine.


Uric Acid or 2,6,8-Trioxypurine.


Theobromine or
3,7-Dimethylxanthine.


Caffeïne or
1,3,7-Trimethylxanthine.


Adenine or 6-Amidopurine.

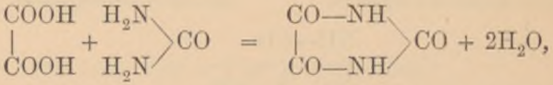

Guanine or 2-Amido-6-oxypurine.

In studying this group it will be convenient to take *uric acid* first, and to supplement the facts already recorded (part i. p. 291) by giving the proofs of the constitution and the synthesis of this acid.

Constitution of Uric Acid.—When uric acid is oxidised by means of nitric acid it yields *parabanic acid*, *alloxan*, and *urea*. The first two of these substances belong to the class known as *ureïds*, a term applied to compounds similarly constituted to the amides, but derived from an acid and urea instead of from an acid and ammonia. *Acetylurea*, the ureïd of acetic acid, for example, is obtained by treating urea with acetyl chloride,

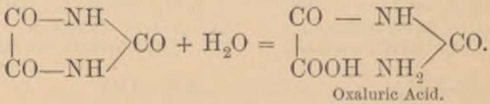
$$CH_3{\cdot}COCl + NH_2{\cdot}CO{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + HCl.$$

Oxalylurea, or *parabanic acid*,* $C_3H_2N_2O_3$, is similarly obtained by treating a mixture of urea and oxalic acid with phosphorus oxychloride,



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + \begin{array}{l} H_2N \\ \\ H_2N \end{array}\!\!>CO = \begin{array}{l} CO-NH \\ | \\ CO-NH \end{array}\!\!>CO + 2H_2O,$$

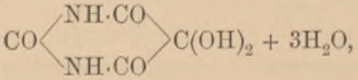
a synthesis which proves the constitution of this ureïd. Parabanic acid is a colourless crystalline substance, insoluble in ether, but soluble in water and alcohol; it yields a silver derivative, $C_3N_2O_3Ag_2$, in which the two atoms of silver are united to nitrogen. When treated with baryta water it is hydrolysed in two stages, yielding first *oxaluric acid* and then oxalic acid and urea,



$$\begin{array}{l} CO-NH \\ | \\ CO-NH \end{array}\!\!>CO + H_2O = \begin{array}{l} CO - NH \\ | \\ COOH\ NH_2 \end{array}\!\!>CO.$$

Oxaluric Acid.

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}COOH + H_2O = C_2H_2O_4 + CO(NH_2)_2.$$

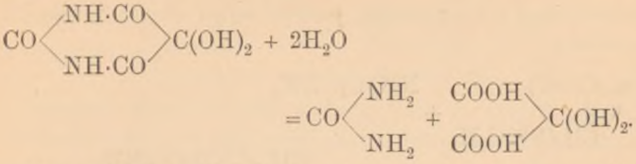


Alloxan, $CO\!\!<\!\begin{array}{l} NH{\cdot}CO \\ \\ NH{\cdot}CO \end{array}\!\!>C(OH)_2 + 3H_2O$, is mesoxalyl-

---

* It will be noticed that parabanic acid does not contain a carboxyl group, and is therefore not a true organic acid. Substances, however, which contain the >NH group between two >CO groups exhibit acid properties, the hydrogen of the >NH group being displaceable by metals (compare part i. p. 238); as this grouping occurs twice in parabanic acid, this substance behaves like a dibasic acid.

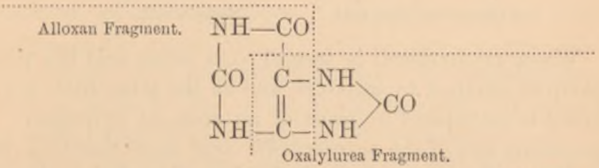
urea, since on hydrolysis it yields *mesoxalic acid** and urea,



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}\right\rangle\mathrm{C(OH)_2} + 2\mathrm{H_2O} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\\mathrm{NH_2}\end{matrix}\right. + \left.\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}\right\rangle\mathrm{C(OH)_2}.$$

It crystallises from water in colourless prisms which effloresce in the air owing to the loss of the three molecules of water of crystallisation. In contact with the skin its aqueous solution produces, after a time, a purple stain; ferrous salts colour the aqueous solution indigo-blue.

The constitutional formula for uric acid given above (p. 577) was first suggested by Medicus in 1875, and it will be seen from the following scheme that this formula can be partly deduced from the formation of the three oxidation products, oxalylurea, alloxan, and urea,



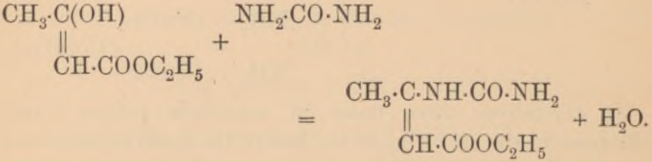
The important work of Emil Fischer and the synthesis of the acid by Behrend and Roosen (see below) prove that this formula is correct.

Syntheses of Uric Acid.—The first synthesis of this acid was carried out by Horbaczewski in 1892, who obtained small quantities of uric acid by heating together glycine and urea; but owing to the high temperature which was employed, and the complicated nature of the reaction, this synthesis is not of much value in deciding the constitution of uric acid.

---

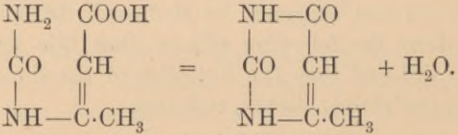
* *Mesoxalic acid*, or *dihydroxymalonic acid*, is formed when dibromomalonic acid, $\mathrm{CBr_2(COOH)_2}$, is boiled with baryta water; it crystallises in deliquescent prisms and melts at 108°.

Of far greater importance is the synthesis of Behrend and Roosen, who first combined ethylic acetoacetate * with urea, and obtained a condensation product called *ethylic β-uramido crotonate*,



$$\begin{array}{l}CH_3\cdot C(OH)\\ \quad\|\\ CH\cdot COOC_2H_5\end{array} + NH_2\cdot CO\cdot NH_2 = \begin{array}{l}CH_3\cdot C\cdot NH\cdot CO\cdot NH_2\\ \quad\|\\ CH\cdot COOC_2H_5\end{array} + H_2O.$$

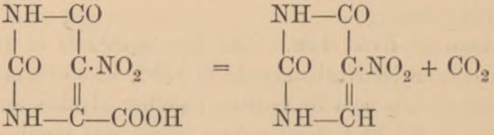
This on hydrolysis yields the corresponding acid, *β-uramido-crotonic acid*, which readily loses water and forms *methyl-uracil*,



$$\begin{array}{ll}NH_2 & COOH\\ | & |\\ CO & CH\\ | & \|\\ NH- & C\cdot CH_3\end{array} = \begin{array}{ll}NH- & CO\\ | & |\\ CO & CH\\ | & \|\\ NH- & C\cdot CH_3\end{array} + H_2O.$$

β-Uramidocrotonic Acid. Methyluracil.

When methyluracil is treated with nitric acid the methyl group is oxidised to carboxyl, and at the same time a nitro-group is introduced in place of an atom of hydrogen. The potassium salt of the *nitrouracilic acid* thus obtained, when boiled with water, loses carbonic anhydride and yields *nitrouracil*,



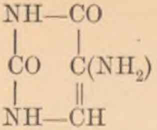
$$\begin{array}{ll}NH- & CO\\ | & |\\ CO & C\cdot NO_2\\ | & \|\\ NH- & C-COOH\end{array} = \begin{array}{ll}NH- & CO\\ | & |\\ CO & C\cdot NO_2\\ | & \|\\ NH- & CH\end{array} + CO_2$$

Nitrouracilic Acid. Nitrouracil.

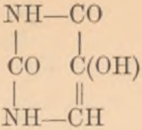
This on treatment with tin and hydrochloric acid gives a mixture of amidouracil and hydroxyuracil,

---

* Ethylic acetoacetate, $CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5$, sometimes behaves as if it had the constitution $CH_3\cdot C(OH):CH\cdot COOC_2H_5$ (part i. p. 195).

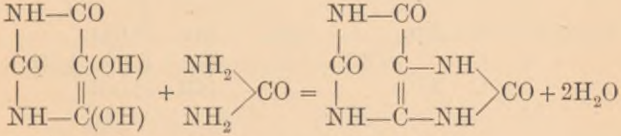


Amidouracil.



Hydroxyuracil.

Bromine water oxidises hydroxyuracil to dihydroxyuracil (*dialuric acid*), and this when heated with urea and sulphuric acid yields uric acid,



Dialuric Acid. Uric Acid.

Since this synthesis was discovered, uric acid has been synthesised in other ways, notably from *pseudouric acid;* but it is not possible to give these methods here.

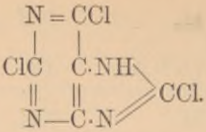
Xanthine, or 2,6-*dioxypurine*, $C_5H_4N_4O_2$, occurs in small quantities in the blood, also in the liver and in urine and urinary calculi; it is also present in tea. It is formed from guanine (p. 582) by the action of nitrous acid, the amido-group being replaced by hydroxyl in the usual way.*

Xanthine is a white amorphous powder, sparingly soluble in water, but readily soluble in aqueous potash; it gives a lead derivative, which when heated with methyl iodide yields theobromine (p. 498). When oxidised with potassium chlorate and hydrochloric acid it is resolved into urea and alloxan. Synthetically it has been obtained by Emil Fischer in the following way:

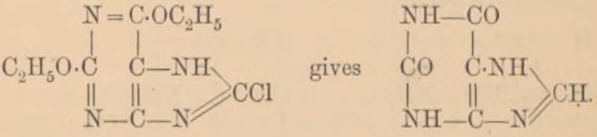
Uric acid on treatment with phosphorus oxychloride at 160° yields 2,6,8-trichloropurine,*

---

* In this and in many other cases it will be noticed that the group NH·CO– sometimes reacts as if it were N=C(OH), and *vice versâ;* these two forms are distinguished as lactam NH·CO– and lactim N=C(OH). Compare the somewhat similar case of ethylic acetoacetate (part i. p. 195).



Sodium ethylate converts this into 2,6-diethoxy-8-chloropurine, and this on reduction with hydriodic acid gives xanthine.



Adenine, or 6-*amidopurine*, $C_5H_5N_5$, can be prepared from the nuclei of cells, and is thus often found in the extracts of animal tissues. It crystallises from water (with $3H_2O$) in pearly plates, which become anhydrous at 54°. Nitrous acid converts it into hypoxanthine, the amido-group being replaced by hydroxyl. It has been obtained synthetically from trichloropurine (p. 581), which when treated with aqueous ammonia gives 6-amido-2,8-dichloropurine; this on reduction with hydriodic acid gives adenine.

Hypoxanthine, *sarkine*, or 6-*oxypurine*, $C_5H_4N_4O$, has been found, usually accompanying xanthine, in blood and urine, and in the muscles, spleen, liver, pancreas, and marrow. It is sparingly soluble in water, but dissolves readily in both acids and alkalis. Its formation from adenine has just been mentioned.

Guanine, $C_5H_5N_5O$, or 2-*amido*-6-*oxypurine*, has been found in guano, the liver, pancreas, and in animal tissues. It is an amorphous powder, which combines with acids to form salts. When treated with nitrous acid it yields xanthine, and when oxidised with potassium chlorate and hydrochloric acid it gives parabanic acid (p. 578) and guanidine (p. 584).

Caffeïne, *methyltheobromine*, or 1,3,7-*trimethylxanthine*,

$C_8H_{10}N_4O_2$, and *theobromine*, or 3,7-*dimethylxanthine*, $C_7H_8N_4O_2$, have already been described, and the relationship between these compounds and uric acid has also been pointed out (pp. 497–498); theobromine can be obtained from xanthine by the method given above (p. 581), and can be converted into caffeïne in the manner previously described (p. 498).

Purine, $C_5H_4N_4$, which may be regarded as the parent substance of all the members of the uric acid group, has been prepared by Emil Fischer, by treating trichloropurine (p. 581) with hydriodic acid at 0°, when partial reduction takes place with formation of 2,6-diiodopurine,

$$C_5HN_4Cl_3 + 4HJ = C_5H_2N_4J_2 + 3HCl + 2J.$$

This when boiled in aqueous solution with zinc dust is reduced to purine.

Purine melts at 217°, and is characterised by being very readily soluble in water; it possesses both basic and acid properties.

At the close of this section a short account is given of *thiourea* and *guanidine*. These substances, the latter especially, are related to guanine and other members of the uric acid group.

Thiourea, $NH_2{\cdot}CS{\cdot}NH_2$, is obtained by a reaction which is analogous to the formation of urea from ammonium cyanate (part i. p. 289), namely, by heating ammonium thiocyanate (part i. p. 288), when this salt undergoes intramolecular change,

$$NH_4{\cdot}S{\cdot}CN = NH_2{\cdot}CS{\cdot}NH_2.$$

The only difference in the two reactions is, that in the latter case it is necessary to heat the dry salt at 170–180°, whereas the formation of urea from ammonium cyanate takes place on simply evaporating the aqueous solution of the salt. Thiourea crystallises in silky needles, and melts at 172°; it is very soluble in water, and when heated with water at 140° it is reconverted into ammonium thiocyanate.

Guanidine, or *imidourea*, $NH_2 \cdot C(NH) \cdot NH_2$, was first prepared by Strecker in 1861 by oxidising guanine (p. 582) with potassium chlorate and hydrochloric acid. It may be synthesised by treating cyanogen iodide * with ammonia, cyanamide being formed as an intermediate product,

$$CNJ + NH_3 = \underset{\text{Cyanamide.}}{NH_2 \cdot C \vdots N} + HJ,$$

$$NH_2 \cdot C \vdots N + H \cdot NH_2 = NH_2 \cdot C(NH) \cdot NH_2.$$

Guanidine is most conveniently prepared by heating ammonium thiocyanate at 170–200°, when the thiourea which is first produced (see above) reacts with a further quantity of the ammonium thiocyanate, yielding guanidine thiocyanate,

$$NH_2 \cdot CS \cdot NH_2 + NH_3,HCNS$$
$$= NH_2 \cdot C(NH) \cdot NH_2,HCNS + SH_2.$$

Guanidine is a colourless crystalline substance, and is readily soluble in water; it is a strong base, forming salts with one equivalent of an acid, and of these salts the nitrate, $NH_2 \cdot C(NH) \cdot NH_2,HNO_3$, like the nitrate of urea, is characterised by being sparingly soluble in water.

When guanidine is treated with a mixture of nitric and sulphuric acids it yields *nitroguanidine*, $NH_2 \cdot C(NH) \cdot NH \cdot NO_2$, which on reduction with zinc dust and acetic acid is converted into *amidoguanidine*, $NH_2 \cdot C(NH) \cdot NH \cdot NH_2$. When the latter is digested with acids it yields in the first place *semicarbazide*,

$$NH_2 \cdot C(NH) \cdot NH \cdot NH_2 + H_2O = NH_2 \cdot CO \cdot NH \cdot NH_2 + NH_3,$$

and this on further treatment is decomposed into ammonia, carbonic anhydride, and hydrazine,

$$NH_2 \cdot CO \cdot NH \cdot NH_2 + H_2O = NH_3 + CO_2 + NH_2 \cdot NH_2.$$

Semicarbazide, like phenylhydrazine (p. 377), interacts with alde-

---

* Cyanogen iodide sublimes in colourless needles on heating a mixture of iodine and mercuric cyanide; it is very poisonous.

hydes and ketones to form crystalline compounds (semicarbazones), and is now much used in the isolation of such substances. *Benzaldehyde semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N:CH \cdot C_6H_5$ (m.p. 214°), for example, separates at once in crystals, when benzaldehyde is shaken with an aqueous solution of semicarbazide hydrochloride and sodium acetate. Like the hydrazones, the semicarbazones are decomposed by treatment with acids, yielding the aldehyde or ketone and a salt of semicarbazide.

The Amido-acids and their Derivatives.

The compounds considered in this section are comparatively simple, and most of them are decomposition products of the more complex constituents of animals (and plants); but instead of being formed during putrefaction, as are the ptomaines or toxines, they are usually produced as the result of purely chemical processes—as, for example, by decomposing the proteïds (p. 594) with acids or alkalis.

Most of the compounds of this group are either amido-acids, such as glycine (part i. p. 292), or derivatives of an amido-acid, such as hippuric acid (p. 418); the two compounds just named should be considered together with those described below.

Sarcosine, or *methylglycine*, $CH_3 \cdot NH \cdot CH_2 \cdot COOH$, was first obtained by Liebig in 1847, by boiling creatine with baryta water (p. 587); it is also formed when caffeïne is subjected to the same treatment. It was prepared synthetically in 1862 by Volhard from chloracetic acid and methylamine,

$$CH_3 \cdot NH_2 + CH_2Cl \cdot COOH = CH_3 \cdot NH \cdot CH_2 \cdot COOH + HCl.$$

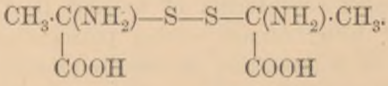
Sarcosine is very readily soluble in water, sparingly soluble in alcohol, and crystallises in prisms which melt and decompose at 210–220°, giving dimethylamine and carbonic anhydride,

$$CH_3 \cdot NH \cdot CH_2 \cdot COOH = CH_3 \cdot NH \cdot CH_3 + CO_2.$$

Like glycine, it has both basic and acid properties, and forms well-characterised salts, such as the nitrate $C_3H_7NO_2,HNO_3$, and the copper salt $Cu(C_3H_6NO_2)_2+2H_2O$; the latter crystallises in blue, rhombic prisms.

Alanine, or *a-amidopropionic acid*, $CH_3\cdot CH(NH_2)\cdot COOH$, and the corresponding β-amidopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot COOH$, have been prepared from the corresponding bromopropionic acids (part i. pp. 226–227) by treatment with ammonia. They have properties very similar to those of glycine.

Cystine, $C_6H_{12}N_2O_4S_2$, a substance which sometimes separates from urine as a sediment, appears to be a derivative of alanine, and to have the constitution,



$$\begin{array}{lcl} CH_3\cdot C(NH_2) & -S-S- & C(NH_2)\cdot CH_3. \\ \quad | & & \quad | \\ \quad COOH & & \quad COOH \end{array}$$

The amido-derivatives of butyric and valeric acids may be prepared by the general methods, but they are not of special physiological interest.

Leucine, or *a-amidocaproïc acid*, $CH_3\cdot[CH_2]_3\cdot CH(NH_2)\cdot COOH$, is very widely distributed in the animal kingdom, and is a substance of great physiological importance. It is found in small quantities in many organs, and especially in the pancreas; in typhus and some other diseases it is found in considerable quantity in the liver. It is produced during the putrefaction of proteïds, and when proteïds are treated with strong alkalis; and, in such cases, is nearly always accompanied by tyrosine (p. 589).

Preparation.—Horn shavings (2 parts) are boiled with sulphuric acid (5 parts) and water (13 parts) for 24 hours, and the hot liquid is then mixed with excess of lime; after filtering and precipitating the calcium in solution by means of oxalic acid, the filtered liquid is concentrated, and the mixture of leucine and tyrosine thus obtained is separated by crystallisation from water, the latter being the less soluble. The yield of leucine is 10 per cent.

Leucine crystallises in glistening plates, melts at 270°, and when carefully heated sublimes unchanged; when rapidly heated it decomposes into normal amylamine, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, and carbonic anhydride.

It dissolves in 48 parts of water, and is very sparingly soluble in alcohol. Its solution in hydrochloric acid is dextrorotatory; but when leucine is boiled with baryta water it becomes optically inactive. Inactive leucine has been prepared synthetically by treating α-bromocaproïc acid, $CH_3{\cdot}[CH_2]_3{\cdot}CHBr{\cdot}COOH$, with ammonia; it is more sparingly soluble in water than naturally-occurring leucine.

In contact with *penicillium glaucum*, a solution of inactive leucine becomes levorotatory owing to the destruction of the dextro modification (compare p. 544); *l*-leucine has properties identical with those of natural leucine, except, of course, that it is levorotatory.

Creatine, $NH{:}C(NH_2){\cdot}N(CH_3){\cdot}CH_2{\cdot}COOH$, is a very important substance found in the muscles, nerves, and blood, and also in considerable quantity in meat extract, from which it was isolated by Chevreul in 1834. Muscles contain about 0·3 per cent. of creatine, and it has been calculated that the total muscles of a full-grown man contain no less than 90–100 grams of this substance. The name creatine is derived from χρεας, meat.

Preparation.—Meat extract (40 grams) is dissolved in water (800 grams), and basic lead acetate added until no further precipitate is produced; the filtrate is freed from lead by passing hydrogen sulphide, and, after filtering, concentrated to about 40 cc. The crystals which separate are washed with dilute alcohol (88 per cent.) and purified by crystallisation from water.

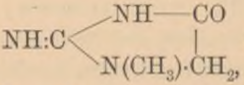
Creatine crystallises from water in colourless prisms containing one molecule of water, which is driven off at 100°; it is moderately soluble in water, but very sparingly in alcohol. It has a neutral reaction and a bitter taste, and forms salts with 1 equivalent of an acid, but it does not appear to possess acid properties. When boiled with acids it is converted into creatinine (p. 588), and when digested with baryta water it is decomposed into urea and sarcosine,

$$NH{:}C(NH_2){\cdot}N(CH_3){\cdot}CH_2{\cdot}COOH + H_2O$$
$$= NH_2{\cdot}CO{\cdot}NH_2 + NH(CH_3){\cdot}CH_2{\cdot}COOH.$$

Creatine has been prepared synthetically by heating together cyanamide and sarcosine in alcoholic solution,

$$N{\vdots}C{\cdot}NH_2 + HN(CH_3){\cdot}CH_2{\cdot}COOH$$
$$= NH{:}C(NH_2){\cdot}N(CH_3){\cdot}CH_2{\cdot}COOH.$$

Creatinine,

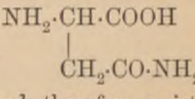


the anhydride (lactam) of creatine, is formed, as mentioned above, by the action of acids on the latter, and it is reconverted into creatine by treatment with alkalis.

It is found in considerable quantities in urine (about 0·25 per cent.), and is also present in the muscles, especially after great exertion; in both these cases it is evidently produced from creatine.

Creatinine crystallises in prisms, and is much more soluble in water than creatine; it is a strong base, and yields salts such as the hydrochloride $C_4H_7N_3O,HCl$, with 1 equivalent of an acid. When zinc chloride is added to its solution in water a highly characteristic, sparingly soluble compound, $(C_4H_7N_3O)_2,ZnCl_2$, separates in the form of fine needles, and this compound is used in the quantitative determination of creatinine. Creatinine reduces Fehling's solution (part i. p. 263), and gives, with phosphomolybdic acid (p. 488), a yellow crystalline precipitate.

Asparagine, or *amidosuccinamic acid,*



$$\begin{array}{l} NH_2{\cdot}CH{\cdot}COOH \\ \quad | \\ CH_2{\cdot}CO{\cdot}NH_2, \end{array}$$

contains an asymmetric carbon atom, and therefore exists in two active modifications, both of which have been prepared.

l-*Asparagine*, the more important modification, is formed in the decomposition of proteïds. It occurs in many plants, particularly in asparagus, and in the young shoots of beans, peas, and lupines, from which it may be obtained by extraction with water. It crystallises from water, in which it is readily soluble, in glistening prisms, and is sparingly soluble in alcohol and ether; the aqueous solution is levorotatory, but becomes dextrorotatory on the addition of hydrochloric acid. When treated with acids or alkalis, asparagine is converted into *l*-aspartic acid, $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH$ (part i. p. 240).

d-*Asparagine* occurs together with *l*-asparagine in the young shoots of lupines, and is, of course, identical with the latter in all ordinary properties. It is noteworthy that when mixed in equal quantities in aqueous solution *d*- and *l*-asparagine do not, like the tartaric acids, combine to form an inactive modification, but the solution, on evaporation, deposits crystals of the two active modifications side by side. When treated with hydrochloric acid, *d*-asparagine yields *d*-aspartic acid.

Tyrosine, or p-*hydroxyphenyl-α-amidopropionic acid*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, is formed together with leucine (p. 586) in the decomposition of proteïds; it is found in the liver in some diseases, in the spleen, pancreas, and in cheese (the name is derived from τυρος, cheese); it was first prepared by Liebig in 1846 by fusing cheese with potash. Tyrosine crystallises in silky needles, which are sparingly soluble in water and alcohol, and almost insoluble in ether; it combines with both acids and bases to form salts. When its aqueous solution is mixed with a solution of mercuric nitrate, a yellow precipitate is produced, which when boiled with dilute nitric acid acquires an intense red colour; this reaction is used as a delicate test for tyrosine.

Tyrosine decomposes at 270° into carbonic anhydride and p-*hydroxyphenylethylamine*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, and when fused with potash it yields *p*-hydroxybenzoic acid (p. 438), acetic acid, and ammonia.

The constitution of this substance is clearly indicated by these reactions, and is proved by the following synthesis which was carried out by Erlenmeyer and Lipp. Phenylacetaldehyde,* $C_6H_5{\cdot}CH_2{\cdot}CHO$, yields, with hydrocyanic acid, the nitrile of phenyllactic acid, $C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CN$. When this compound is heated with alcoholic ammonia on the water-bath, the hydroxyl is displaced by the amido-group, and the *nitrile* of *phenylamidopropionic acid*, $C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CN$, is formed; this nitrile, on hydrolysis, yields *phenylamidopropionic acid* (phenylalanine), $C_6H_5{\cdot}CH_2.CH(NH_2){\cdot}COOH$.

Nitric acid converts this amido-acid into *p-nitrophenylamidopropionic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, from which, on reduction, the corresponding *amidophenylamidopropionic acid* is obtained; the latter, on treatment with nitrous acid, yields tyrosine.

Compounds of Unknown Constitution found in Bile.

Most of the important compounds of animal origin of known constitution having been described, this section includes some rather more complex substances of unknown constitution, which are classed together merely because they occur together in bile.

The bile contains, besides lecithine (p. 572) and colouring matters, two remarkable acids called glycocholic acid and taurocholic acid, and an alcohol named cholesterine.

Glycocholic acid, $C_{24}H_{39}O_4{\cdot}NH{\cdot}CH_2{\cdot}COOH$, crystallises in colourless needles, and melts at 133°; it is soluble in water and alcohol, but very sparingly soluble in ether; its alcoholic solution is dextrorotatory. It occurs in bile in the form of its sodium salt, $C_{26}H_{42}NaNO_6$, which crystallises in stellate groups.

Preparation.—Fresh bile is mixed with a few drops of hydrochloric acid and rapidly filtered through sand. The filtrate is mixed with concentrated hydrochloric acid and ether, in the proportion of 5 vols. of the former and 30 vols. of the latter to 100 vols.

---

* *Phenylacetaldehyde*, $C_6H_5{\cdot}CH_2{\cdot}CHO$, is prepared by distilling a mixture of the calcium salts of phenylacetic and formic acids. It is a colourless oil, boiling at 206°, and has properties very similar to those of the aldehydes of the fatty series.

of bile. The crystals of glycocholic acid, which separate on standing, are washed with water containing hydrochloric acid and ether. Taurocholic acid is contained in the mother-liquors.

When boiled with alkalis, glycocholic acid yields *cholalic acid* and glycine,

$$\begin{aligned} &C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot COOH + H_2O \\ &\qquad = C_{24}H_{40}O_5 + NH_2\cdot CH_2\cdot COOH. \end{aligned}$$

Taurocholic acid, $C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H$, occurs in human bile, and generally in the bile of all carnivora. It crystallises in silky needles, is readily soluble in alcohol, and is dextrorotatory. Like glycocholic acid, it occurs in bile in the form of the sodium salt $C_{26}H_{44}NaNO_7S$. When boiled with water it is decomposed into cholalic acid and taurine,

$$\begin{aligned} &\underset{\text{Taurocholic Acid.}}{C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H} + H_2O \\ &\qquad = \underset{\text{Cholalic Acid.}}{C_{24}H_{40}O_5} + \underset{\text{Taurine.}}{NH_2\cdot CH_2\cdot CH_2\cdot SO_3H}. \end{aligned}$$

Cholalic acid, $C_{24}H_{40}O_5$, crystallises in glistening plates, which are sparingly soluble in water, readily in alcohol and ether; its solutions are dextrorotatory. The only known decomposition which throws any light on the constitution of this interesting acid is the fact that when oxidised with permanganate it yields acetic acid and *o*-phthalic acid.

Taurine, or *amidoisæthionic acid,* $NH_2\cdot CH_2\cdot CH_2\cdot SO_3H$, was discovered by Gmelin in 1824 in oxgall (hence the name from ταῦρος, an ox), in which it occurs in the form of taurocholic acid (see above). Taurine crystallises in prisms which dissolve readily in water, but are insoluble in absolute alcohol; it reacts neutral, but forms salts such as the sodium salt $NH_2\cdot CH_2\cdot CH_2\cdot SO_3Na$, with bases. Taurine has been prepared synthetically by carefully treating alcohol with sulphur trioxide, when *isæthionic acid* is produced,

$$CH_3\cdot CH_2\cdot OH + SO_3 = SO_3H\cdot CH_2\cdot CH_2\cdot OH.$$

This crystalline and very hygroscopic acid, on treatment with phosphorus pentachloride, yields *chlorethylsulphonic acid*, $CH_2Cl{\cdot}CH_2{\cdot}SO_3H$, from which, by treating with ammonia, taurine is obtained.

Cholesterine, $C_{27}H_{45}{\cdot}OH$, is an alcohol which occurs in bile and in the brain, and in considerable quantities in gall-stones and in cancerous and tubercular deposits; it is also found in the yolk of egg, in the fat obtained from wool, and in guano.*

It is readily obtained by extracting gall-stones with absolute alcohol and evaporating the extract; the residue is purified by treatment with alcoholic potash, which removes extraneous matter, and then crystallised from a mixture of ether and alcohol.

Cholesterine crystallises from water in colourless needles, melts at 145°, and distils at about 360° without decomposing appreciably.

Reactions of Cholesterine.—If a few centigrams of cholesterine are dissolved in chloroform (2 cc.) and the solution shaken with concentrated sulphuric acid (2 cc.), the chloroform solution is coloured red and then purple, and the sulphuric acid acquires a green fluorescence. If a few drops of the chloroform solution are poured into a dish the colour changes to blue, then to green, and lastly to yellow.

Concentrated sulphuric acid containing a little iodine colours cholesterine first violet, then blue, then green, and lastly red. Warmed with dilute (20 per cent.) sulphuric acid, cholesterine crystals are coloured red on the edges.

Hæmoglobins.

Hæmoglobin is the name given to the pigment of the red corpuscles of the blood. 'It exists in the blood in two conditions; in arterial blood it is loosely combined with oxygen, and is called *oxyhæmoglobin;* the other condition is the deoxygenated or reduced hæmoglobin (often simply called *hæmoglobin*), which occurs in venous blood—that is, the blood

---

* A substance very similar to cholesterine, and named paracholesterine or phytosterine, is found in the seeds of certain plants.

which is returning to the heart, after it has supplied the tissues with oxygen. Hæmoglobin is thus the oxygen-carrier of the body, and it may be called a respiratory pigment.'*

Oxyhæmoglobin can be obtained from defibrinated blood by mixing it with salt solution (1 vol. of saturated salt solution to 9 vols. of water), which precipitates the blood-corpuscles. These are washed with salt water of the same strength, mixed with a little water, and extracted with ether, which removes cholesterine, &c., all these operations being conducted as nearly as possible at 0°. The ethereal solution is decanted, the aqueous solution filtered, the filtrate mixed with one-fourth of its vol. of alcohol, and cooled to $-10°$, when crystals of oxyhæmoglobin separate. These can be purified by again dissolving in water, adding alcohol, and allowing to stand at 0°.

Oxyhæmoglobin crystallises in light-red rhombic plates, which dissolve readily in water and are re-precipitated by alcohol. On analysis it gives results which agree closely with those obtained in the analysis of albumin (p. 596), except that oxyhæmoglobin always contains 0·4 per cent. of iron. If the aqueous solution of oxyhæmoglobin is placed in a vacuum, or treated with weak reducing agents, it loses oxygen and is converted into *hæmoglobin*, a substance which has also been obtained in a crystalline form; and *vice versâ*, an aqueous solution of hæmoglobin is rapidly converted into oxyhæmoglobin in contact with air. If carbonic oxide is led into a solution of oxyhæmoglobin this substance loses its oxygen and combines with the carbonic oxide to form *carbonic oxide hæmoglobin*, a compound which crystallises in large bluish crystals. This compound is not capable of absorbing and giving up oxygen like hæmoglobin — a fact which explains the poisonous action of carbonic oxide, since this gas by combining with the oxyhæmoglobin prevents the aëration of the blood. Oxyhæmoglobin, hæmoglobin, and carbonic oxide hæmoglobin all show characteristic absorption spectra,

---

* Halliburton, *Chemical Physiology*, p. 267.

which allow of their being easily identified and distinguished from one another.

Hæmin and Hæmateïn.—When oxyhæmoglobin or dried blood is warmed with a drop of acetic acid and a small crystal of common salt on a microscopic slide, a mass of reddish-brown crystals separates on cooling. These consist of *hæmin*, the chloride of hæmateïn, and have the composition $C_{32}H_{31}N_4O_3FeCl$. If these crystals are treated with alkali, brownish-red flecks of *hæmateïn*, $C_{32}H_{31}N_4O_3Fe{\cdot}OH$, separate; and this formation of hæmin and hæmateïn serves as a very delicate test for blood.

The Proteïds or Albuminoids.

The substance known as 'white of egg,' or egg-albumin, when separated from the yolk, membrane, and shell, is a colourless, transparent, thick, sticky fluid, soluble in or miscible with water; on exposure to the air it rapidly loses in weight owing to evaporation of the water contained in it, and if dried artificially it quickly shrivels up, giving a translucent amorphous solid.

When white of egg is put into boiling water it undergoes a remarkable change, and is said to have *coagulated;* it is now insoluble in water and opaque, and forms a solid mass, which, however, still contains a large percentage of water; during coagulation it is probable that chemical as well as physical changes have occurred.

When white of egg is left exposed to the air under ordinary (non-sterile) conditions it soon begins to putrefy—that is to say, it decomposes under the influence of organisms, yielding a great number of products, amongst which are the ptomaines or toxines already described. Further, when white of egg is heated with dilute mineral acids or with alkalies it again undergoes profound decomposition, giving ammonia, carbon dioxide, and a number of other compounds, such as glycine, leucine, tyrosine, &c.

This brief account of the behaviour of white of egg will suffice to show that it is an extremely unstable and complex substance, and its physical properties are so indefinite that it would be almost impossible to say whether or not it is a definite chemical compound.

Now, white of egg, or egg-albumin, may be taken as the representative of a group of substances which are classed together as the **proteïds** or **albuminoids**. These substances form not only the most important part of the contents of the cells of all animals (πρωτεῖον, pre-eminence), but they also occur in considerable quantities in all plants, especially in the seeds or grain; it is, in fact, from these vegetable proteïds that those contained in animals are formed, since the animal, unlike the plant, is incapable of building up more complex substances from simpler food material, except to a very limited extent. The vegetable proteïds, then, are assimilated by animals, and apparently they are changed very little during this process.

As practically nothing is known of the constitution of these proteïds, any attempt to define exactly what is meant by this term would meet with little success. Proteïds differ in physical properties and in behaviour towards various reagents, and these slight differences may be temporarily made use of in order to subdivide them into various groups. As regards their chemical behaviour little can be said, except that they all give a similar complex mixture of products when decomposed by organisms or by purely chemical agents. There are, however, two statements which are true of all proteïds: firstly, they are extremely complex compounds; and, secondly, they all consist of the five elements, carbon, hydrogen, oxygen, nitrogen, and sulphur.

The determination of the percentage composition of a proteïd is itself a task of considerable difficulty. As found in nature, all proteïds contain mineral matter, and consequently leave on ignition a small percentage of ash; after the removal of these mineral constituents by repeated precipitation, dialysis, &c., or allowing for their presence in calculating the result, the percentage composition of the various proteïds is found to vary within fairly wide limits, as shown by the following numbers:

Carbon	50 –55	per cent.
Hydrogen	6·9– 7·3	"
Nitrogen	15 –19	"
Oxygen	19 –24	"
Sulphur	0·3– 2·4	"

Egg-albumin has been obtained free from mineral matter and in a crystalline condition; its composition is C = 51·48, H = 6·76, N = 18·14, O = 22·66, S = 0·96 per cent.

The *empirical* formula calculated from the percentage composition of egg-albumin or from that of some other members of the group of proteïds comes out to something like $C_{146}H_{226}N_{44}SO_{50}$. This formula, which requires C = 51·2, H = 6·6, N = 18·0, S = 0·9 per cent., cannot be regarded as having much value, as a very slight difference in the analytical results would make a very great difference in the formula.

The molecular formulæ of the proteïds are unknown; attempts have been made to determine the molecular weight of some of them by the freezing-point method (part i. p. 48), and the results, which are very uncertain, seem to show that egg-albumin may have a molecular weight of 15,000—a number which will afford an idea of the great complexity of the proteïds.

The proteïds are insoluble in alcohol and ether, and mostly also in water; but many of them dissolve in salt solutions, and the presence of salts probably accounts for their remaining dissolved in the fluids of the animal body. One of the most interesting properties shown by many of the proteïds is that of undergoing *coagulation*, a change which is readily brought about by heat, different proteïds coagulating at somewhat different temperatures, varying roughly between

55° and 75°; some proteïds are also coagulated by alcohol and by mineral acids.

Those proteïds which *are coagulated* by heat are, for convenience' sake, divided into two groups:

(*a*) *Albumins*, soluble in water and in solutions of salt or magnesium sulphate.

(*b*) *Globulins*, insoluble in water, but soluble in solutions of salt or magnesium sulphate.

To the former class belong egg-albumin and serum-albumin; to the latter fibrin-globulin.

Those proteïds which *are not coagulated* by heat are divided into:

(*a*) *Albuminates*, insoluble in water and in salt solutions, but readily soluble in mineral acids and in sodium carbonate; these substances are produced by the action of alkalis on the albumins, globulins, &c.

(*b*) *Albumoses* and *Peptones*. When proteïds are subjected to the action of the gastric or pancreatic juices, they are first converted into *albumoses*,* and finally into *peptones*. Albumoses are mostly soluble in water and salt solutions; they are precipitated by alcohol, nitric acid, and ammonium sulphate solution. Peptones are soluble in water, and are precipitated by alcohol, but not by nitric acid or ammonium sulphate solution.

Besides those mentioned above, there are several other classes of proteïds, for a description of which works on Physiological Chemistry must be consulted.

When subjected to hydrolysis with mineral acids or baryta water, proteïds yield, besides ammonia and carbonic anhydride, varying quantities of amido-acids of both the fatty and aromatic series, such as *glycine* (part i. p. 292), *leucine*

---

* Also called proteoses or propeptones.

(p. 586), *tyrosine* (p. 589), *aspartic acid* (p. 589), and *β-phenyl-α-amidopropionic acid* (*phenylalanine*),

$$C_6H_5 \cdot CH_2 \cdot CH(NH_2) \cdot COOH.$$

Under the putrefying influence of certain organisms, proteïds yield, besides fatty acids, *phenylacetic acid* (p. 429) and *phenol*, substances of more complicated structure, such as *indole*, C_8H_7N, and *skatole*, C_9H_9N.

Tests for Proteïds.—All proteïds are coloured violet-red by a solution of mercuric nitrate containing traces of nitrous acid. This reagent (called *Millon's reagent*) is prepared by dissolving one part by weight of mercury in two parts of strong nitric acid and diluting the solution with twice its bulk of water; after standing some time the supernatant liquid is decanted from the precipitate. When nitric acid is added to a proteïd a yellow colour is produced, which on the addition of ammonia becomes bright orange. This reaction, called the *xanthoproteïc reaction*, is stated to be the most delicate test for proteïds. If a few drops of copper sulphate solution are added to a proteïd, and then excess of caustic potash, a red to violet colouration is produced. This reaction is called the *biuret reaction*, because it resembles the colour-reaction obtained under similar circumstances with biuret.*

Gelatin is a substance somewhat similar in composition to egg-albumin, but containing only carbon, hydrogen, nitrogen, and oxygen; it may be obtained by the action of dilute acids on the white fibres of connective tissue.

It is best prepared by digesting bones, first with dilute acids to remove inorganic matter, and then with water under pressure at 110–120°; the solution after filtering and evaporating yields commercial gelatin.

Gelatin is a hard, almost transparent, horn-like substance which is insoluble in alcohol, ether, and in cold water, but

---

* When urea is heated at about 155° ammonia is evolved and the residue contains *biuret*,

$$2NH_2 \cdot CO \cdot NH_2 = NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2 + NH_3,$$

a crystalline substance (m.p. 190°), readily soluble in alcohol and water; the formation of biuret (the presence of which can be shown with the aid of the above colour-reaction) affords a very useful test for urea.

dissolves readily in hot water, yielding a solution which, on cooling, sets to a jelly (*gelatinises*). If, however, the aqueous solution is boiled for some hours the power of gelatinising is entirely destroyed. Gelatin forms an insoluble compound with tannic acid, and the process of tanning consists partly in converting the gelatin in the hides into this hard insoluble compound by steeping them in tannic acid solution. When digested with dilute sulphuric acid gelatin breaks down much in the same way as the proteïds yielding *glycine*, *leucine*, and other fatty amido-acids.

INDEX.

[Where more than one reference is given, and one of them is in heavy type, the latter refers to the systematic description of the substance.]

INDEX TO APPENDIX.

[Where more than one reference is given, and one of them is in heavy type, the latter refers to the systematic description of the substance.]

THE END.

Edinburgh:
Printed by W. & R. Chambers, Limited.

CHAMBERS'S

NEW SCIENCE BOOKS

For South Kensington and University Requirements.

PHYSICS: An Elementary Text-book for University Classes. By C. G. KNOTT, D.Sc. (Edin.), F.R.S.E., Lecturer on Applied Mathematics and Physics (Medical) in the University of Edinburgh. 652 pages. 7s. 6d.

ELEMENTARY MECHANICS, including Hydrostatics and Pneumatics. By OLIVER J. LODGE, D.Sc., LL.D., F.R.S., Professor of Physics in University College, Liverpool. New Edition. 308 pages. 4s. 6d.

ELEMENTARY HUMAN PHYSIOLOGY. By J. G. M'KENDRICK, M.D., F.R.S., Professor of Physiology in the University of Glasgow. Illustrated with 164 woodcuts. Cloth, 2s. 6d.

PHYSIOGRAPHY, Elementary. New Edition by DAVID FORSYTH, M.A., D.Sc. With Diagrams, Questions, and Examination Papers. Elementary Course, 2s. 6d.

AGRICULTURE, Elementary Course. By R. HEDGER WALLACE, late Lecturer and Examiner in Agriculture to the Education Department of Victoria. Adapted to the *New* Syllabus. Profusely illustrated. Cloth, 3s.

ORGANIC CHEMISTRY. By W. H. PERKIN, Jun., Ph.D., F.R.S., and F. STANLEY KIPPING, Ph.D., D.Sc. (Lond.), F.R.S. With Diagrams. Part I., 3s. 6d. Part II., 3s. 6d. Appendix, 1s. In one volume, 7s. 6d.

ELECTRICITY and MAGNETISM, Elementary Course. By C. G. KNOTT, D.Sc. (Edin.), F.R.S.E., Lecturer on Applied Mathematics, University of Edinburgh. 2s. 6d.

W. & R. CHAMBERS, Limited,
47 PATERNOSTER ROW, LONDON; AND EDINBURGH.

Price 4s. 6d.

ARITHMETIC.

THEORETICAL AND PRACTICAL.

By JOHN STURGEON MACKAY, M.A., LL.D., Fellow of the Royal Society of Edinburgh; Head Mathematical Master in the Edinburgh Academy.

Price 4s. 6d.

CHAMBERS'S ALGEBRA FOR SCHOOLS.

By WILLIAM THOMSON, M.A., B.Sc.,
Registrar, University of the Cape of Good Hope.

Price 3s. 6d.

THE ELEMENTS OF EUCLID.

BOOKS I. TO VI., AND PARTS OF BOOKS XI., XII.

With numerous Deductions, Appendices, and Historical Notes by J. S. MACKAY, LL.D.

412 pages, 392 diagrams. Key, 3s. 6d.

QD P447o 1890

60740170R

NLM 05028982 8

NATIONAL LIBRARY OF MEDICINE