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ORGANIC CHEMISTRY

Part I

BY

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NEW EDITION

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PERKIN AND KIPPING'S

ORGANIC CHEMISTRY

NEW EDITION

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PREFACE TO PARTS I AND II

PERKIN and KIPPING'S *Organic Chemistry*, first published in 1894, has been widely used during more than half a century. It has been partly or completely revised at various short intervals, and for the present edition has been entirely reset.

The number of pages has been increased. This increase is due to some extent to the use of a larger and improved type-face and the *additions* to the text have been kept to a minimum consistent with dealing with all important recent advances. It would have been easy to overburden the book with new matter, but the authors feel that it is imperative to keep in mind the actual need of the student.

Very considerable revision of the text of the last edition has also been effected. Most of the structural formulae of cyclic compounds have been presented differently, so that they may be more readily understood. More attention has been paid to nomenclature and the use of different names for a given compound, in order to help students to pass from the name to the constitutional formula and *vice versa*.

The chapter on alkyl compounds of nitrogen, phosphorus, arsenic, silicon, and metals has been divided into two, and a short chapter on ethylenic and acetylenic compounds has been added, as well as many brief sections on, for example, petrol, synthetic anti-malarials, penicillin, etc. Some small portions of the text of Part III have been transferred to Part II and *vice versa*.

Perhaps the most noteworthy addition is the introduction, early in Part II, of an elementary account of the conception of resonance and of frequent references to this subject thereafter.

In spite of the changes which have been made, the general plan of the book, and any distinctive features which it may have, are unaltered and remain as in the original and later editions.

It is intended as a text-book, as an introduction to the study of Organic Chemistry, and the subject matter (of Parts I and II) corresponds approximately with that which is usually covered during a two-years' course of lectures.

With the aid of the explanatory notes and two sizes of type the text is so arranged that the course of the beginner is clearly indicated ;

he will not, therefore, be hampered by the premature study of matters beyond his needs. Having made sufficient progress, he begins the study of the summaries and other more advanced matter (in smaller type) which he has previously passed over. He will then have covered the ground usually necessary for (at least) a pass degree.

If that is his only object the greater part of Chapters 39-41 may perhaps be omitted, as these parts of the book are intended more particularly for pharmaceutical and medical students, or those reading for an honours degree. The last chapter, on dyes and their applications, is also probably beyond the needs of pass degree requirements.

One of the principal objects throughout has been to treat the subject from a practical point of view, for without a good grounding in laboratory work sound foundations cannot be laid. For this reason the preparation of many typical compounds is described in sufficient detail to enable even a beginner to carry out the operations with little supervision. A list of such preparations is given just before the Index.

Another important branch of practical work has been borne in mind, namely the identification of organic compounds. A few general directions are given, with various examples, and also sufficient data, chemical and physical, for the identification or reference to their types of most if not all of the compounds which are usually considered suitable for such exercises.

Very particular attention has been directed to the evidence on which a given structural formula is based, even in very simple cases, so that the student may be gradually trained to correlate the properties and the constitution of a compound. When he can do so, and the general reactions of the principal radicals have been mastered, structural formulae should be easily interpreted, all that they imply should be realised, and thus the study of organic chemistry should be very greatly simplified.

Many references have been made to the commercial preparation and uses of organic compounds, especially to those which are now manufactured from petroleum.

F. STANLEY KIPPING.
F. BARRY KIPPING.

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ORGANIC CHEMISTRY

Part I

CHAPTER 1

COMPOSITION, PURIFICATION, AND ANALYSIS OF ORGANIC COMPOUNDS

Origin and Present Meaning of the Word Organic. Although spirit of wine, sugar, fats, and many other substances, obtained directly or indirectly from animals or plants, have been known from the earliest times, their investigation made but little progress until towards the close of the eighteenth century, when the compositions of many of these natural products were established by Lavoisier (1743–94). He it was who first showed that, in spite of their great number, nearly all vegetable substances are composed of *carbon*, *hydrogen*, and *oxygen*, whereas animal substances, although also consisting for the most part of the same three elements, usually contain *nitrogen*, and sometimes *phosphorus* and *sulphur*.

This similarity in composition, and probably also the fact that these natural products behaved differently from mineral compounds in being *combustible*, led to the belief that all animal and vegetable substances were produced under the influence of a particular *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** compounds, 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 cyanogen and ammonium hydroxide solution, substances which were considered to be inorganic or mineral, because they could be produced in the laboratory; this synthesis showed that the influence of a living organism was not necessary for the production of the 'organic' substance urea.

In the course of time it was found that many other 'organic substances could be prepared in the laboratory from materials which were classed as 'inorganic', and ultimately it came to be generally recognised that although many processes which occur in animals and plants cannot yet be carried out in a laboratory, because of lack of knowledge, the formation of an organic compound is no more dependent on the help of a vital force than is that of an inorganic compound.

The supposed difference between the two classes of compounds having thus been disproved, the terms 'organic' and 'inorganic' lost, of course, their original meanings; they are, nevertheless, still employed in the classification of chemical compounds for the following reasons:

(1) The compounds of carbon, which are already known (more than 200,000), are far more numerous than the known compounds of any other element. (2) These carbon compounds are related to one another, but differ widely in general behaviour from those of all other elements; they form, in fact, a distinct group.

It is convenient, therefore, to class them separately, and to distinguish them by the term *organic*, which recalls the fact that carbon compounds are the most important components of all animals and plants; *organic chemistry*, therefore, is *the chemistry of the carbon compounds*.

Some of the simpler compounds of carbon, such as carbon monoxide, carbon dioxide, and the carbonates, being of general importance, are described in works on inorganic chemistry for the sake of convenience; they are, nevertheless, organic compounds, because they contain carbon.[1]

The reasons why so many carbon compounds are known are not far to seek. All the chief components of animals and plants are derivatives of carbon, and many of them occur in great abundance;

[1] It may seem to be unreasonable to class calcium carbonate as an organic compound, since limestone, chalk, marble, etc., although of animal origin, occur in the earth's crust and are called 'minerals' in daily life; unless, however, *all* carbon compounds are called 'organic', this term can hardly be defined.

each of these naturally occurring compounds has formed a starting-point from which many others have been easily obtained in the laboratory ; these, in their turn, have served as materials for further investigation. Thus many compounds, not existing in plants or animals, have been prepared and the number of both natural and synthetic products increases from day to day, as chemists all over the world pursue their research work.

Composition of Organic Compounds. In spite of their great number, most organic compounds are made up of only from two to four or five elements; many of them consist of carbon and hydrogen only, and are called *hydrocarbons*.

The most striking difference between carbon and all other elements is, in fact, that carbon, combined with hydrogen, forms a very large number of hydrocarbons, such as CH_4, C_6H_6, $C_{10}H_8$, $C_{60}H_{122}$, etc., in the molecules of which the carbon atoms are directly united; other elements rarely combine with hydrogen to form more than a few compounds, and their atoms seem to possess only to a very limited extent the power of combining with one another.

Those organic compounds—such as sugar, starch, and tartaric acid—which occur in the vegetable kingdom, generally 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: some vegetable and animal substances also contain *sulphur*, *phosphorus*, or other elements.

In addition to two or more of the elements mentioned above, organic compounds prepared in the laboratory often contain a halogen or a metal; organic derivatives of all the non-metals and of many metals are known, and doubtless it would be possible to prepare a carbon compound containing any element, except one of those of the argon family.

Purification of Organic Compounds. It need hardly be pointed out that every organic substance must be submitted to a quantitative analysis in order that a formula may be assigned to it; the preparation of the compound in a state of purity is, however, a step which must precede its analysis. Now, the purification of an organic compound, its *isolation* from a mixture of any kind, is often a matter of considerable difficulty, and it is usually necessary to employ various methods for this purpose. The main physical

processes are: (1) Those depending on the use of solvents. (2) Distillation.[1]

The separation of an organic, from an inorganic, substance can usually be accomplished by shaking or warming the mixture with some solvent, such as alcohol, ether, benzene, chloroform, petrol, etc. Most organic compounds are soluble in one or other of these liquids, whereas inorganic compounds, as a rule, are insoluble, or nearly so. Water (or a dilute acid) may often be employed for the like purpose, since many inorganic substances are soluble, many organic substances insoluble, in it. In order to ascertain whether mineral matter is present or not, a small portion of the substance is first ignited on platinum foil; if it leaves a non-combustible residue, it may contain inorganic matter as impurity, or it may be a salt of some organic acid; in the latter case, the substance may often be purified by crystallisation, or the acid contained in it may be liberated and purified in some suitable manner.

The separation of two or more organic substances may frequently 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 may then be separated from most of the sugar by extraction with alcohol, in which it is much more readily soluble than is sugar.

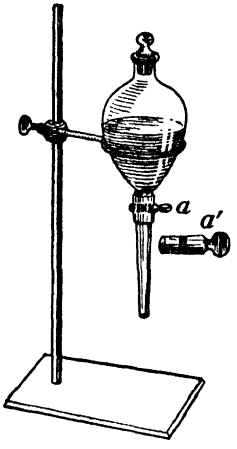


Fig. 1

Solid or liquid organic substances, suspended or dissolved in water, or in aqueous solutions of salts, etc., may often be isolated by shaking the mixture or solution with some solvent, such as ether, benzene, chloroform, etc., which is not too soluble in water. This is done in a **separating funnel** (Fig. 1), and after the operation the two solutions are separated by turning the tap (*a*, *a'*) and running off that which is underneath; the extraction is then repeated, if necessary, with a fresh quantity of the organic solvent. The combined extracts are dried (p. 8) and the

[1] It is important that the student should have some knowledge of these processes, otherwise the descriptions of the methods of preparation of various compounds will be unintelligible.

solvent is distilled, usually on a water-bath,[1] from the (filtered) solution.

In the case of compounds which are very readily soluble in water, 5–10 extractions, or more, with relatively small volumes of the organic liquid, are necessary in order to isolate most of the dissolved compound, as the process is governed by the distribution law. In extractions with ether or benzene, the organic solvent forms the upper layer, but chloroform is heavier than water.

When ether is employed the aqueous solution may be saturated with sodium chloride, calcium chloride, or some other readily soluble salt, in order to lessen the solubility of the dissolved organic substance and of the ether in the water; this process is called 'salting out'.

When this book is being studied for the first time, all the subject-matter in smaller type may be omitted, except the footnotes, examples, and the detailed descriptions of the preparation of ethylene, acetaldehyde, ether, formic acid, and other typical compounds.

The process of **crystallisation** is a very efficient method of separating and purifying solid organic substances, provided that a suitable solvent is employed.

About 0·05 g. of the substance is heated in a test-tube with about 0·5–1 c.c. of some solvent (such as water, alcohol, acetone, benzene, chloroform, ether, etc.), and when partial or complete solution has occurred, the hot liquid is cooled; if then a considerable proportion of the dissolved substance is deposited in crystals, the solvent may be regarded as suitable, but if not, another is tried. When a suitable one has been found, the substance and a little of the solvent are heated together during some minutes in a beaker or flask (on a water-bath, if an inflammable liquid is being used) and small quantities of the solvent are added, at a safe distance from the burner,[1] until solution is complete.

The crystals ultimately deposited from the cooled solution are collected on a suction-filter, washed with a small quantity of the solvent, and further purified, if necessary, by recrystallisation.

If a part of the substance is far less soluble than the rest, or

[1] In working with highly inflammable liquids great caution is necessary to avoid serious accidents. In the case of light petroleum, ether, benzene, etc., the flask should be placed *inside* the bath, so that if fracture occurs the liquid does not run on to the bench.

insoluble, it may be necessary to filter the hot solution; a hot-water or steam-jacketed funnel should then be used.

The preliminary separation of a crystalline product from small quantities of oily or tar-like matter is best accomplished by pressing the substance on a piece of an unglazed tile or plate, whereby most of the liquid is absorbed.

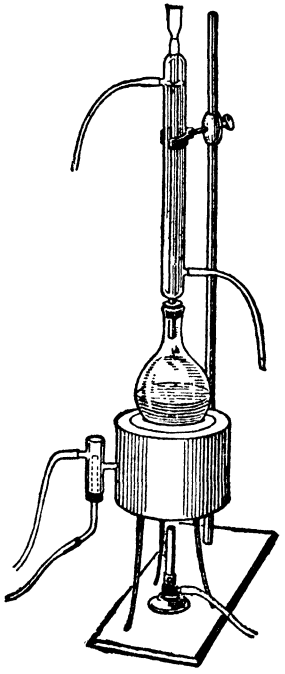


Fig. 2

If only one component of a mixture is dissolved by the liquid employed, this particular substance is obtained in a state of purity without difficulty, because the others are easily removed by filtration; when, however, two or more of the components 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. When a hot solution of two (or more) substances is cooled, one of them only is often deposited in crystals, and can then be separated by filtration; the substance remaining in the *mother-liquor* may then be obtained in crystals by concentrating the solution; the two crops of crystals are afterwards separately redissolved, and the fractionation repeated, if necessary, with the same or a different solvent, until each substance is obtained in a pure state, as shown by a determination of its melting-point (p. 12).

Animal charcoal, silica-gel, etc., are often used in purifying organic compounds, as they absorb coloured or resinous impurities from solutions. For this purpose the absorbent (about 5% of the weight of the substance) is added, and the solution is boiled for some time (with reflux condenser, Fig. 2); when the liquid is afterwards filtered, a colourless or much lighter coloured solution is usually obtained, and the dissolved substance generally crystallises more readily. Before use, bone charcoal should be repeatedly extracted with boiling hydrochloric acid to remove calcium salts and afterwards washed well, dried, and heated strongly in a crucible covered

with a lid. Various other varieties of charcoal are employed in a similar manner.

For the solution of more than, say, 5–10 g. of a substance and for a great many other operations a reflux condenser (Fig. 2) is used to prevent the loss of a volatile solvent or substance present in solution ; the vapours, which would otherwise pass away, are then condensed, and the liquid runs back into the flask. The flask may be heated over a 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 always employed.[1] In a form of apparatus similar to that shown, a liquid may be kept boiling for so long as required. When the boiling-point of the liquid is above 100–120°, a glass tube about 80 cm. long and 1 cm. in diameter is used as an air-condenser, in the place of the water-cooled tube.

Organic substances which boil without decomposition can be purified by **distillation.** The substance is placed in a distillation 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 earthenware are put in the distillation flask to prevent 'bumping' or sudden ebullition. This must always be done *before* the liquid is heated, as the addition of a solid to a superheated liquid may cause a violent ebullition. The flask may be heated on a water-bath, sand-bath, gauze, or metal-bath, or with the free flame in the case of substances of high boiling-point. In the case of liquids which boil at temperatures above 130° or so, the water in the condenser is run off to lessen the risk of fracture, or a long glass tube (*c*) is used as an air-condenser. When the compound to be purified contains only *non-volatile* impurities, the thermometer rises very rapidly as soon as the liquid begins to boil, but then remains practically constant until almost the whole has distilled. Towards the end of the operation, however, it begins to rise again, owing to the superheating of the vapour, and distillation is then stopped. If the distillate is now transferred to a clean flask, and redistilled, it should boil at a constant temperature, which is the observed **boiling-point** of the substance (p. 12).

All pure substances, which boil without decomposition, have a definite boiling-point (b.p.), which is dependent on the pressure.

[1] Footnote, p. 5.

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 decompose under atmospheric pressure.

The boiling-point is one of the more 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 (Fig. 3), and a sample of the liquid

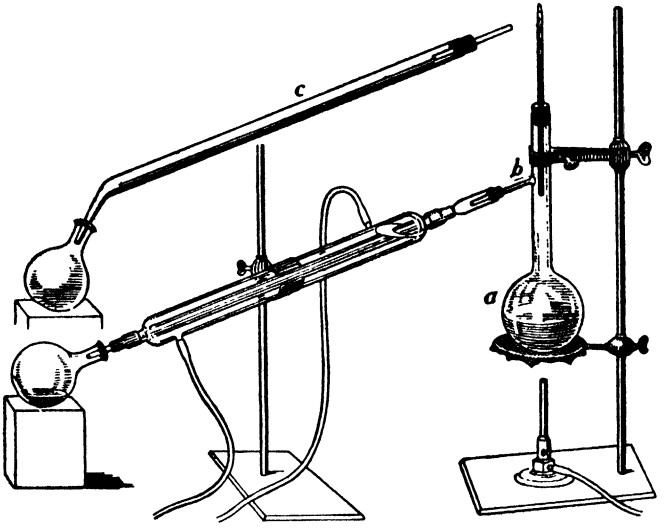


Fig. 3

should be distilled completely, in order to make sure that it has a constant boiling-point ; if not, it is impure, or it is decomposing.

Before a substance is distilled, it should be carefully freed from any water it may contain ; for this purpose liquids are well shaken with a *small* proportion of a dehydrated salt, such as anhydrous calcium chloride, magnesium sulphate, calcium sulphate, potassium carbonate, etc., or with potash, according to the nature of the liquid, and are then decanted or filtered.[1]

[1] The drying operation may be carried out in a separating funnel so that (in most cases) the aqueous solution may be run off ; the addition of the dehydrating agent is continued from time to time until no further action is observed.

When a mixture of two (or more) *volatile* substances is distilled in the manner described above, the liquid usually begins to boil at some temperature lying between the boiling-points of its components. As distillation proceeds the boiling-point rises, and towards the end of the operation 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°) and water (b.p. 100°), for example, the thermometer at first registers some temperature between 78 and 100°, according to the proportion of the two substances, and the earlier portions of the distillate contain a larger proportion of alcohol than does the original mixture. During distillation the thermometer rises slowly but continuously, and at last registers 99–100°, the liquid passing over at this temperature consisting of very nearly pure water. The change in boiling-point is due to a change in the composition of the mixture ; the alcohol, being the more volatile, passes off more quickly than the water. It is possible, therefore, to separate the liquids to some extent by collecting the distillate in portions or **fractions** at intervals of 5 or 10° ; this operation is termed **fractional distillation** and the larger fractions will generally be those collected near the boiling-points of the main components of the mixture. By redistilling each of these fractions, a further separation is effected, and, after a sufficient number of operations, each component of the mixture *may* be obtained in a practically pure condition, boiling at a constant temperature.

The process of fractional distillation is greatly facilitated when a flask with a long neck is used, or when the mixed vapours are passed through a *fractionating column*, of which there are many forms, before they enter the condenser. By these means the vapour of the liquid of higher boiling-point is much more efficiently condensed, and runs back into the distillation flask, instead of passing over with the more volatile component. It is then often possible to effect a separation when the boiling-points of the two liquids differ by a few degrees only, whereas without a fractionating column, a difference of at least 20–30° is necessary ; in many cases, even when there is a greater difference than this, a separation cannot be effected as many liquids form mixtures of constant boiling-points (*azeotropic mixtures*).

Fractional distillation is frequently carried out under reduced pressure for the reasons already stated in the case of ordinary dis-

tillation. The apparatus commonly used consists of a two-necked (*Claisen*) flask (A, Fig. 4) with its side tube inserted into the neck of a second flask (B), which is connected with a water (or other) pump and a pressure gauge. A thermometer is fixed in one neck of A and through the other passes a tube drawn out to a fine capillary, reaching nearly to the bottom of the flask. When the pump is started air bubbles are drawn through the capillary and regular

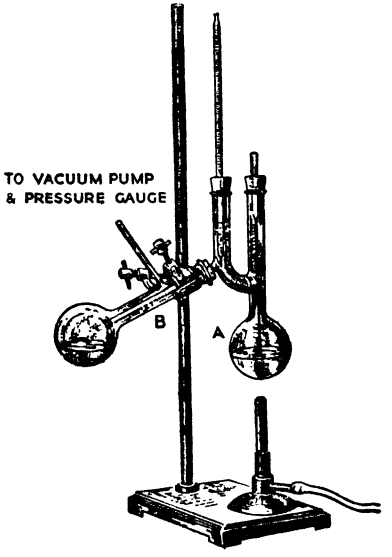


Fig. 4

ebullition is assisted. The liquid to be distilled is placed in A ; the pump is then started, and, as soon as the pressure is sufficiently low, distillation is carried out in the usual manner, the process being interrupted when the receiver is being changed.

In many cases, especially when the pressure is very low, the liquid froths badly ; this may often be overcome by heating the flask very cautiously just above and below the level of the liquid with a constantly moving, almost luminous flame.

Another method frequently used in the isolation 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. 5) which is connected with a condenser, and heated on a gauze 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 those substances which are **volatile in steam**, and are not decomposed by boiling water. Some compounds, which cannot be dis-

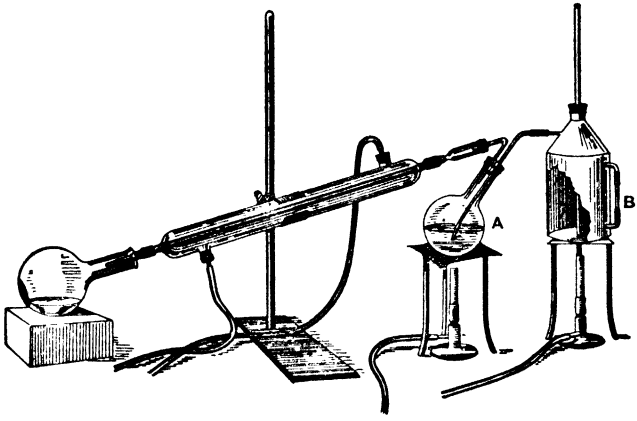


Fig. 5

tilled in the ordinary way, because they undergo decomposition, are volatile in steam, and pass over unchanged, even when their boiling-points are very much higher than that of water. Steam distillation, in fact, is equivalent to distillation under reduced pressure, as the vapour pressure of the water takes up most of the atmospheric pressure.

When a substance volatilises very slowly, *superheated* steam is often employed; in such cases the steam from B is passed through a strongly heated coil of copper tubing before being led into A.

Tests of Purity. It is very important to know whether or not a given compound is *pure*. If the substance is a solid, its purity or otherwise may often be ascertained by an examination under the microscope. A pure substance looks homogeneous, and if crys-

talline, the crystals are all of the same kind. Much more trustworthy evidence, however, is obtained by an observation of the melting-point.

Pure substances, which melt or liquefy without decomposition, have a definite **melting-point**; when, however, a substance is impure, its melting-point is usually not only lowered, but is also rendered indefinite. An impure substance becomes soft and pasty (sinters) at a certain temperature, and does not melt completely until heated considerably above this point. The determination of the melting-point, therefore, affords a valuable test of *purity*, and also serves as a means of *identifying* a compound.

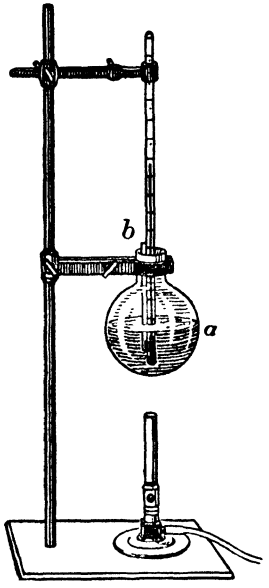


Fig. 6

An apparatus suitable for determining the melting-point consists of a small very short-necked flask (*a*, Fig. 6), or beaker, of about 50 c.c. capacity, containing concentrated sulphuric acid, glycerol, or liquid paraffin. A minute quantity of the substance is placed in a capillary tube [1] (*b*), closed below, which is caused to adhere to a thermometer by capillary attraction. The liquid is slowly heated,[2] and the temperature at which the substance liquefies—that is to say, its melting-point (m.p.)—is noted.

For solids melting below, say, 90°, the thermometer is suspended in a beaker of water. A bent glass rod as a stirrer improves the beaker apparatus.

In the case of a compound which distils without undergoing decomposition, a determination of its **boiling-point,** or rather an examination of its behaviour on distillation, will usually show whether it is pure or not (p. 7).

[1] A test-tube is held, one end in each hand, and is rotated in a blow-pipe flame until the middle portion has softened; it is then removed from the flame, suddenly drawn out to a length of 3 or 4 ft., and the capillary tube cut into pieces about 3 in. long with a pair of scissors. One end of each piece is then sealed.

[2] On a sand-bath or wire-gauze if sulphuric acid is used, to prevent the risk of splashing if the vessel breaks.

The *observed* melting- or boiling-point of a substance is usually 1–3° lower than the true value, because, as a rule, a portion of the column of mercury is not immersed in the heating liquid or vapour.

Qualitative Elementary Analysis

The methods used in the qualitative analysis of organic compounds are relatively simple and differ entirely from those employed in the case of inorganic substances. Not only are most organic compounds insoluble in water and in acids, but even those which are soluble do not, except in rare cases, show a behaviour sufficiently characteristic to allow of their recognition by the ordinary ' wet methods ' of analysis. Moreover, whereas a mixture of inorganic compounds may be directly submitted first to qualitative and then to quantitative examination, a mixture of organic compounds must almost invariably be separated into its components before the further qualitative and quantitative examination of these components can be undertaken. The term qualitative analysis, therefore, as used in reference to organic compounds, usually means the detection of the *elements* of which a *pure* compound is composed; for this reason the process is often known as *qualitative elementary analysis*. This process is a necessary step in the determination of the formula of every organic compound.

When the object of the examination of an organic compound is to identify the substance—that is to say, to prove that it is identical with some substance of known composition—the process is generally called *identification*.

The suspected identity of two solids is best tested by taking the melting-point of an intimate mixture of approximately equal quantities of the known and the unknown compounds ; if this is the same as that of the separate components, their identity may be taken as established. Before this final proof of identity can be applied a compound is generally examined by noting its appearance, smell, crystalline form, solubilities, and chemical properties, and by determining its melting- or boiling-point ; when, however, such methods are insufficient, or when the nature of the compound is quite unknown, a qualitative elementary analysis, and often even a quantitative analysis, must also be made.

Unless the substance under examination is known to be organic it will be necessary to test it for **carbon** : this element may be detected by the following methods :

The substance is heated on platinum foil. If it inflames and burns away, or swells up, giving a black mass, which on being strongly heated entirely disappears, the substance is in all probability organic. The metallic salts of organic acids usually char when treated in this way, and when further heated, 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, leaves sodium carbonate, but copper acetate gives the oxide of the metal, and silver acetate gives the metal. If a halogen, sulphur, or phosphorus is present in the salt, it is generally found in the residue in combination with the metal.

The behaviour of a substance when it is 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 gives a decisive result, the compound (0·1–0·5 g.) is mixed with 40–50 times its weight of pure copper oxide, and the mixture is heated to redness in a tube of hard glass, sealed at one end, the escaping gases being led into lime-water; under these conditions all organic substances (except the stable carbonates and cyanides of the alkalis and alkaline earths) are decomposed, yielding carbon dioxide.

It is rarely necessary to test for **hydrogen** in organic compounds, and the only reliable method is to mix the *dry* substance (0·3–0·5 g.) with *dry* copper oxide and heat the mixture in a stream of *dry* air or oxygen (p. 17); if hydrogen is present, it will be oxidised to water, which may be collected in a calcium chloride tube (weighed before and after the experiment).

In the case of very volatile compounds the tests for carbon and hydrogen are made in a combustion apparatus (p. 19).

The presence of **nitrogen** in an organic substance may often be detected when 0·1–0·2 g. of the substance is strongly heated with soda-lime [1] in a hard glass tube; if ammonia is evolved, the presence of nitrogen is proved. As, however, many organic compounds containing nitrogen do not yield ammonia when they are heated with soda-lime, the following test must be applied before the absence of nitrogen may be considered to be proved.

[1] An intimate mixture of slaked lime and caustic soda, which has been strongly heated until it is quite dry.

About 0·1–0·2 g. of the substance is placed in a small test-tube, together with a bright piece of sodium about the size of a pea, and gently heated, care being taken that the molten metal is brought into contact with the substance and thoroughly chars it; if the compound does not carbonise, it is dropped directly on to the molten sodium. The mixture is then heated more and more strongly *until all action ceases*, and when the tube has cooled a little, the hot end is plunged into about 5 c.c. of water contained in an evaporating basin or mortar, whereby the tube is broken and the soluble product is dissolved. This should be done in such a way that the eyes are not endangered.

The alkaline solution is filtered from carbonaceous matter, and a few drops of a solution of ferrous sulphate are added to the filtrate; the mixture is then boiled for a few moments, cooled, and acidified with pure hydrochloric acid, when, if nitrogen was present in the original substance, a bluish colouration, or a precipitate, is produced, either immediately or on the addition of a drop of a ferric chloride solution.

This (*Lassaigne's*) 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 hydroxide is precipitated and sodium ferrocyanide is formed:

$$6NaCN+Fe(OH)_2 = Na_4Fe(CN)_6+2NaOH.$$

On the addition of an acid the ferric salt and the ferrocyanide give Prussian blue. During the experiment some of the ferrous hydroxide generally becomes oxidised to ferric hydroxide; a blue colour or precipitate is then produced without the addition of a ferric salt.

The presence of **chlorine, bromine,** or **iodine** in organic compounds cannot be detected, as a rule, by the methods employed in the examination of inorganic substances, as, for example, by means of silver nitrate, or manganese dioxide and sulphuric acid; chloroform, for instance, contains a very large proportion of chlorine, but when pure it does not give a precipitate with an aqueous solution of silver nitrate, and just boils away when it is heated with manganese dioxide and sulphuric acid.

A simple test for the halogens is the following: A piece of copper wire is heated in the oxidising zone of the Bunsen flame until that

portion within about three inches from the end ceases to colour the flame green and is coated with oxide.[1] The end of the hot wire is then dipped into the substance and heated again in the flame, when, if a halogen is present, a green colouration is usually observed, due to the formation of a volatile halogen compound of copper. This test sometimes fails and is occasionally given by compounds free from halogen ; as, moreover, it does not give any information as to which of the halogens is present, the following method is generally adopted :

The substance is carefully heated with a bright piece of sodium and the product is treated with water exactly as described in the test for nitrogen (p. 15). A portion of the filtered alkaline solution, acidified with nitric acid, is then tested with silver nitrate ; if a precipitate is formed, the presence of halogen (or of *nitrogen*, see below) in the original substance is proved, and its nature may be determined by examining the rest of the solution, or the precipitate, by the usual methods. This test depends on the fact that when any organic substance containing chlorine, bromine, or iodine is thus heated with sodium, the halogen combines with the metal to form chloride, bromide, or iodide of sodium.

When nitrogen is present this last test for halogens is not conclusive, as the precipitate may be silver *cyanide* ; under these circumstances, the solution is boiled with dilute nitric acid for a few minutes until all the hydrogen cyanide is expelled, before adding silver nitrate ; if a precipitate is then formed the presence of halogen is proved.

Sulphur may be detected by heating the substance with sodium in the usual manner and then testing the solution of the product for an alkaline sulphide by one (or more) of the following methods : (*a*) To a portion add a few drops of sodium nitroprusside solution (p. 360) ; a violet colouration indicates sulphide. (*b*) Boil a portion with nitric acid for a few minutes ; the sulphide is oxidised to sulphate and may be detected with barium chloride as usual. (*c*) Place a few drops on a bright silver coin ; a black stain (Ag_2S) indicates sulphide.

Sulphur, *phosphorus*, and *arsenic* may be detected by adding the substance, *in very small quantities at a time*, to strongly heated potassium carbonate previously mixed with about 5% of sodium

[1] The colouration, if any, is caused by *volatile* compounds, such as copper chloride.

nitrate or peroxide; these elements are thus oxidised to sulphate, phosphate, and arsenate respectively. The residue is dissolved in water, and the solution of alkali salts is 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 (p. 25).

There is no satisfactory test for **oxygen** in organic compounds and its presence is deduced from the results of quantitative analysis (p. 20).

Metals contained in organic salts may often be detected by the ordinary methods of analysis, but as a rule it is better to ignite the compound and then test for the metal in the residue (compare pp. 14, 285).

Quantitative Elementary Analysis

Estimation of Carbon, Hydrogen, and Oxygen. Just as the qualitative analysis generally consists of a few tests to determine the nature of the elements present in the substance, so the quantitative analysis of an organic compound usually comprises one or more processes by means of which these elements are *estimated.* For this reason, and because the presence of certain elements necessitates slight changes in the methods to be employed, the qualitative examination must be completed before the quantitative analysis is commenced.

It is essential, of course, that before any quantitative analysis is undertaken, the substance under examination should have been very carefully purified. If a solid, it should be dried until constant in weight in a desiccator or at 100°, and its melting-point should then be observed; if it does not melt, or decomposes when it is heated, it should be examined under the microscope (compare p. 11). When the compound to be analysed is a liquid, its boiling-point should be constant.

The following account of the methods 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.

All organic compounds, with the exceptions already mentioned, are oxidised when they or their decomposition products are brought into contact with red-hot copper oxide, 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 of hydrogen may be readily determined (Liebig). The apparatus generally used for this purpose is shown in the accompanying figures.

The **calcium chloride** or **water tube** (Fig. 7) is filled with granulated anhydrous calcium chloride, or with fragments of pumice moistened with concentrated sulphuric acid, and serves to absorb the water; the **potash bulbs** (Fig. 8) are partly filled with

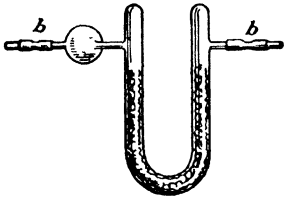


Fig. 7

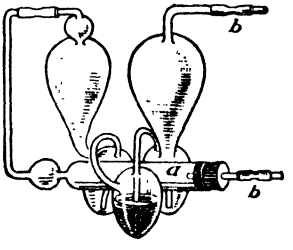


Fig. 8

potassium hydroxide solution (sp. gr. about 1·28),[1] the small tube (*a*), which contains anhydrous calcium chloride (or other dehydrating agent), serving to retain the aqueous vapour, which is taken up by the gases in their passage 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 on both occasions; the gain in weight of the former corresponds with the amount of water produced, and that of the latter with the amount of carbon dioxide formed.

The combustion is carried out in a piece of hard glass combustion tubing (*a*, *b*, Fig. 9), which is usually about 90 cm. long, and 12–15 mm. in diameter; part of the tube (*f* to *f*) is filled with a layer of coarse copper oxide, kept in its place by loose asbestos plugs (*e*, *e*). Before the analysis is started the tube is heated in a combustion furnace (*k*) at a dull-red heat, and a current of air, carefully freed

[1] The specific gravity of the potassium hydroxide solution is a matter of importance, because the narrow tubes of the potash bulbs may get blocked with crystals of potassium hydrogen carbonate if the solution is too concentrated. A U-tube containing soda-lime may be used instead of the potash bulbs.

from carbon dioxide and moisture—by being passed first through potash contained in the wash-bottle (*g*) and then through the two towers (*h*, *j*)[1] containing dry soda-lime—is led through it, in order that any moisture or traces of organic matter in the tube may be removed; the *empty* section *only* of the tube is then allowed to cool.

The water tube (*l*) having been fitted into the end (*b*) through a rubber stopper, and the potash bulbs (*m*) attached by means of a short piece of rubber tubing, 0·15–0·2 g. of the substance, accurately weighed in a narrow porcelain or platinum *boat* (*d*), is introduced into the tube; a freshly ignited roll of copper gauze (*c*) is then placed behind the boat in order to prevent so far as possible any backward diffusion of the products of combustion. When a very volatile liquid is to be analysed, it is weighed in a thin glass bulb (shown on a larger scale at *n*), which is afterwards placed in the boat (at *d*). *The whole apparatus must of course be air-tight.*

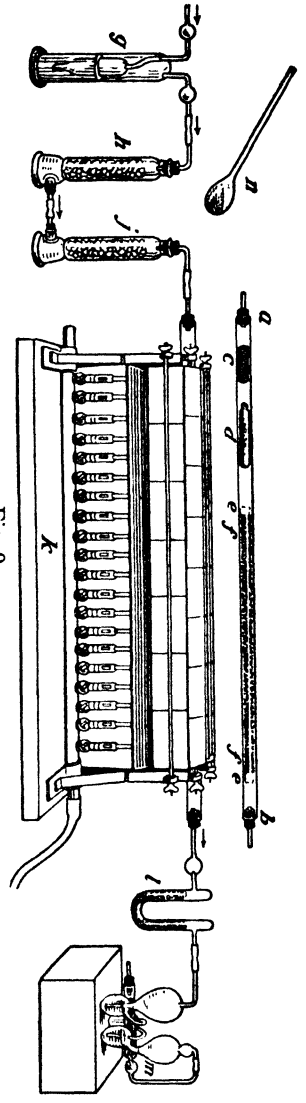


Fig. 9

A slow stream of air (about one bubble per second), carefully purified, as before, is now passed through the tube, and the combustion of the substance is *cautiously* started by lighting the gas burners (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

[1] Two such sets of drying apparatus are usually employed, one for the air, the other for the oxygen. The towers (*h*, *j*) may contain pumice and sulphuric acid.

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 $1\frac{1}{2}$ to 3 hours, according to the nature of the substance. The water tube and the potash bulbs are then disconnected, and their ends are closed with the rubber caps; after they have been left for at least two hours to cool thoroughly, 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, $\frac{1}{4}\frac{2}{4}$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 water 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.[1] The percentage of carbon and hydrogen may therefore be calculated.

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

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

C	62·4%
H	4·3%
O	33·3% (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: When the substance contains *nitrogen*, it is necessary to insert a roll of bright copper gauze, about 4 inches long, into the front part (*b*) of the tube, in the

[1] The rounded atomic weights H = 1, C = 12, O = 16, N = 14 are used here and in other calculations.

place of some of the copper oxide ;[1] this roll is kept red-hot during the combustion, and serves to decompose any oxides of nitrogen which may be produced during the operation, and which would otherwise be absorbed by the water in the calcium chloride tube and by the potash. When the substance contains a *halogen*, silver, instead of copper, gauze must be used 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. 9) is filled with lumps of fused lead chromate, instead of copper oxide. Lead chromate, like copper oxide, is an oxidising agent at high temperatures. Any sulphur dioxide, halogen, or phosphorus pentoxide produced during the combustion is completely retained by the lead, as lead sulphate, lead chloride, etc., and thus its passage into the absorption apparatus is prevented.

Estimation of Nitrogen. Nitrogen may be estimated in several ways, the more common being as nitrogen by Dumas' method, or as ammonia by Kjeldahl's method.

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 (or its oxides). If the gaseous products of combustion are passed over heated copper, to decompose the oxides of nitrogen, and then collected over potash, the carbon dioxide is absorbed, and the residual gas consists of nitrogen ; by measuring the volume of the gas obtained from a known weight of substance (0·15–0·4 g.), the percentage of nitrogen can be determined. The analysis is carried out in a combustion tube similar to that used in the estimation of carbon and hydrogen (Fig. 9), but containing in the front end (*b*) a roll of copper gauze.[1]

The weighed quantity of substance is not placed in a boat, but is intimately mixed with 10–20 g. of finely divided copper oxide on a piece of glazed paper (or in a mortar) and the *whole* of the mixture is tipped into the tube so that it occupies the space *d* to *e*.

[1] In order to render the roll of gauze as efficient as possible, it is heated in a blow-pipe flame until thoroughly oxidised, and, while red-hot, dropped into a little (1 c.c.) 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 heated at 160–180° for a few minutes, just before it is placed in the combustion tube, in order to make sure that it is free from water and methyl alcohol.

The tube is now connected to a Schiff's nitrometer (Fig. 10). This apparatus consists of a graduated tube (*a*, *c*), provided with a stop-cock (*a*) and a reservoir (*d*), by raising which the tube may be filled with potash solution (sp. gr. 1·3), and which, when lowered, serves for reducing the pressure in the apparatus during the combustion ; the lower part of the tube (*c*, *b*) contains mercury, which forms a seal and prevents the passage of the potash solution into the combustion tube (*e*).

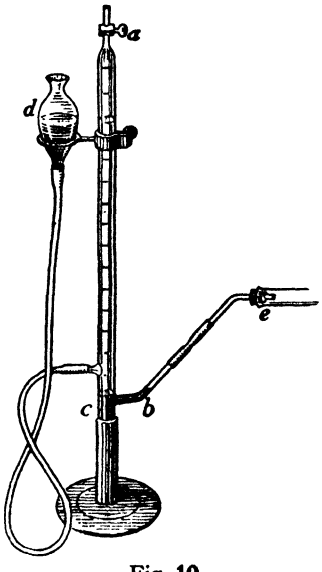


Fig. 10

Before the substance is heated, the reservoir *d* is lowered, *a* is opened, and a stream of carbon dioxide, generated in a Kipp's apparatus or by heating native magnesite or sodium bicarbonate, is passed through the tube ; when it seems probable that all the air has been expelled the nitrometer is completely filled by raising *d*, and *a* is then closed. If now the ascending bubbles are absorbed almost entirely by the potash[1] the stream of gas is stopped ; if not, it is continued until the test is satisfactory.

In the meantime the burners under the roll of gauze and the front part of the tube have been lighted, and when all this region has acquired a bright-red heat, and the stream of carbon dioxide has been stopped, the mixture of substance and copper oxide is cautiously raised to and kept at a cherry-red heat until gases cease to be evolved. Finally, carbon dioxide is again passed through the combustion tube until the rest of the nitrogen has been expelled, as shown by the disappearance of the escaping bubbles.[1]

The apparatus is now placed aside for some hours to cool ; the reservoir (*d*) is then raised until the potash is at the same level in it and in the tube (*a*, *c*), and the volume of nitrogen (*v*), the temperature ($t°$), and the barometric pressure (*B*) are noted.

[1] The bubbles are seldom absorbed completely, but the volume of gas which is collected in the course of 2–3 minutes should be barely measurable.

The weight of nitrogen in the quantity of substance taken is readily ascertained when its volume has been determined. Since the volume v is measured at $t°$ under a pressure $B-T$, where T = the tension of aqueous vapour in mm. of mercury,[1] at the temperature $t°$, the volume V at 0° and 760 mm. would be $v \times \frac{B-T}{760} \times \frac{273}{273+t°}$. As 22400 c.c. of nitrogen weigh 28 g. at N.T.P., the weight of V c.c. is $\frac{V \times 28}{22400}$ g.

Example. 0·2248 g. of substance gave 7·1 c.c. of nitrogen measured at 16° ; B = 747 mm., T = 7 mm.[1]

The weight of the gas is $7{\cdot}1 \times \frac{740}{760} \times \frac{273}{289} \times \frac{28}{22400}$ = 0·00817 g., and the percentage of nitrogen $\frac{0{\cdot}00817 \times 100}{0{\cdot}2248}$ = 3·6.

Kjeldahl's Method, used more particularly in agricultural laboratories for the analysis of foods, fertilisers, etc., depends on the fact that when many nitrogenous organic compounds are completely decomposed with hot, concentrated sulphuric acid, their nitrogen is obtained in the form of ammonium sulphate.

The substance (0·5–5 g.) is placed in a round-bottomed flask of hard glass, and covered with about 20 c.c. of concentrated sulphuric acid. The flask is then heated directly over a burner, very gently at first, afterwards sufficiently to boil the acid ; the process is continued until the liquid (which is usually very dark in colour owing to the separation of carbonaceous matter) has become almost colourless. As a rule this operation is hastened by adding potassium sulphate (5–10 g.) after the first 15–30 minutes' heating, in order to raise the temperature. The ammonia which has been produced is separated by distillation with an excess of caustic soda in a current of steam (with the use of a splash bulb), collected in standard sulphuric acid, and estimated by titration.

Estimation of Chlorine, Bromine, and Iodine. The halogens in an organic compound are generally estimated by the method

[1] Some of the values of T which are often required are the following:

$t°$	10°	12°	14°	16°	18°	20°
T	9·1	10·4	11·9	13·5	15·3	17·4

When, however, as here, the nitrogen is collected over concentrated potash solution, which has a lower vapour tension than that of water, it is usual to deduct from B half the tension of aqueous vapour at the temperature $t°$.

devised by *Carius*, which consists in oxidising the substance with nitric acid at a high temperature in the presence of silver nitrate. Under these conditions the carbon is completely oxidised to carbon dioxide, and the hydrogen to water, while the halogen combines 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 (*a*, *b*, Fig. 11) about 40 cm. long and 20 mm. in diameter, sealed at one end (*a*), in which is placed about 0·2 g. of silver nitrate, and then with the aid of a thistle funnel, fuming nitric acid (2–4 c.c.); the substance (0·15–0·2 g.) is weighed in a small ignition tube, which is carefully

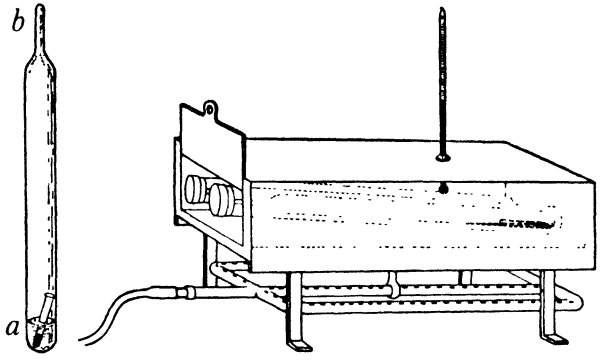


Fig. 11

lowered into the larger one, and the open end of the latter is then drawn out and sealed, as shown at *b*. The tube is then placed in an iron case, and heated in a furnace (Fig. 11) at a temperature necessary to ensure complete decomposition, usually about 200°, during four hours; in the case of very stable substances, a much higher temperature and prolonged heating are required. When *quite cold* the tube should *not be removed from its iron case*, but should be cautiously pulled or tipped forwards until the capillary just projects, using a cloth to protect the hand; a Bunsen flame is then played cautiously on the tip of the capillary until the glass softens and blows out. After the pressure has been released, and a careful examination has shown that the capillary is not choked by any solid matter, the top of the tube is cut off; all the acid and halide are then transferred to a beaker with the aid of distilled water, and boiled together gently during about 30 minutes; the halogen silver salt is further treated as usual.

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 10 times its weight of quicklime, the remainder of the tube being nearly filled with quicklime. The tube is tapped gently to form a clear channel for the passage of the gases,[1] and is then heated in a combustion furnace, the front part being raised to a bright-red heat before proceeding with the decomposition of the substance. When quite cold, the contents of the tube are cautiously shaken into an excess of dilute nitric acid, the acid solution is filtered from carbonaceous matter, and the halogen is precipitated with silver nitrate.

Estimation of Sulphur and Phosphorus. These elements 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.

Another method for determining sulphur and phosphorus, and also halogens (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 potassium nitrate or sodium peroxide, until the product is colourless.[2] Here, again, the substance is completely oxidised, and the sulphate or phosphate produced may be estimated in the residue.

Micro-analysis. Processes have been devised by *Pregl* whereby quantitative analyses can be carried out with quantities of less than 0·01 g. of an organic compound. The principles of these methods are, on the whole, similar to those described above, but special apparatus, including a very sensitive balance, is required. This form of analysis presents the additional advantage of being very rapid (owing to the small quantities of substance employed) without any sacrifice of accuracy.

[1] Should this precaution be neglected, the tube may get choked and a serious explosion may result.

[2] A sufficiently large proportion of potassium carbonate must be used, otherwise an *explosion* may occur.

CHAPTER 2

DEDUCTION OF A FORMULA FROM THE RESULTS OF ANALYSES AND DETERMINATION OF MOLECULAR WEIGHT

THE quantitative analysis of a pure organic compound is usually made with one of two objects : (*a*) to prove that a particular compound is what it is supposed to be ; (*b*) to ascertain the percentage composition of some substance in order to determine its formula.

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, this 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 was suspected to be succinic acid, $C_4H_6O_4$, and, on analysis, it gave the following results : C = 40·6, H = 5·1, O = 54·3 (by difference) %. Since the percentage composition of succinic acid, calculated from its formula, is C = 40·7, H = 5·1, O = 54·2 %, the results of the analysis afford strong confirmatory evidence as to the nature of the substance under examination.[1]

In the second case, where the object of the analysis is to deduce a formula for the substance, the process is just the same as that applied to the results of the analysis of inorganic compounds—that is to say, the percentage 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 lowest value or by some simple fraction of this value.

Example. The percentage composition of a substance is found to be C = 84·0, H = 16·0 ; deduce the 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 84/12 : 16/1 or 7 : 16 ; the formula, therefore, is C_7H_{16}.

[1] The results of combustions and of nitrogen determinations are usually given to one decimal place only, as the second place has little significance.

Example. The percentage composition of a substance is C = 39·9 H = 6·7, O = 53·4 ; deduce the formula.

Here the ratio between the number of atoms is found to be 3·33 : 6·7 : 3·33,

$$C = \frac{39{\cdot}9}{12} = 3{\cdot}33,\ H = \frac{6{\cdot}7}{1} = 6{\cdot}7.\ O = \frac{53{\cdot}4}{16} = 3{\cdot}33\ ;$$

and when each term is divided by 3·33, and experimental errors are allowed for, the ratio of the atoms C : H : O = 1 : 2 : 1 ; the formula of the substance, therefore, is CH_2O.

Example. The percentage composition of a substance as determined by analysis is C = 19·9, H = 6·9, N = 46·9, O = 26·3 ; deduce the formula.

Here the ratio is found to be :

$$C = 1{\cdot}66,\ H = 6{\cdot}9,\ N = 3{\cdot}35,\ O = 1{\cdot}65\ ;$$

and when these values are all divided by 1·65, the formula, CH_4N_2O, is obtained.

The ratio of the atoms determined experimentally is hardly ever expressed *exactly* by whole numbers, owing to unavoidable errors, and it is sometimes difficult to be sure that the formula obtained from the simplified ratio is the correct one. In such cases the percentage composition is calculated from that formula and the values so obtained are compared respectively with those found experimentally ; the difference between the calculated and experimental percentage values for any element should not be more than about 0·2–0·4.

The formula deduced from the results of analysis is merely the *simplest* expression of the *ratio* of the atoms in the molecule, and is termed the **empirical formula** ; such a formula may, or may not, show how many atoms of each element the molecule of the substance contains : formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, for example, have the same percentage composition, and consequently, on analysis, they would all be found to have the same empirical formula, CH_2O.

In order to determine the **molecular formula,** by which is meant a formula expressing not only the ratio, but also the actual numbers of the atoms in the molecule, 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, its molecular formula must be $C_2H_4O_2$, and not CH_2O or $C_3H_6O_3$.

The determination of the molecular weight of a substance, therefore, is of great importance, and for this purpose certain physical methods, based on the application of Avogadro's hypothesis, are adopted; molecular weights can rarely be established by quantitative analysis alone, although the results of such analyses often afford valuable indications of the *minimum* value of the molecular weight, as will be seen from the following examples.

Analysis of Organic Salts for the Determination of Equivalent Weights

In the case of organic acids, the analysis of a salt of the acid is often carried out; the silver salt is generally used for this purpose, and a weighed quantity of the pure substance is ignited *slowly* 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 = 39·9, H = 6·7, O = 53·4; its empirical formula is, therefore, CH_2O. Its silver salt was prepared; 0·2955 g. of the pure salt gave on ignition 0·1620 g. of silver, so that the percentage of silver in the salt is 54·82.

Now, since 54·82 parts of silver are contained in 100 parts of the salt, 1 gram atom or 107·9 parts of silver are contained in 196·83 parts of salt. The minimum molecular weight of the salt (its equivalent weight), therefore, is 196·83; and as, in the formation of the salt from the acid, 1 part of hydrogen is displaced by 107·9 parts of silver, the equivalent weight of the acid is 196·83−107·9+1 = 89·93. Since, however, the acid is composed of carbon, hydrogen, and oxygen, the atomic weights of which are all taken as whole numbers, and as the analytical results are not free from experimental errors, the minimum molecular weight of the acid may also be taken to be a whole number—that is to say, 90. The minimum molecular weight of the acid being 90, its *molecular formula* is not CH_2O (= 30) or $C_2H_4O_2$ (= 60), but may be $C_3H_6O_3$ (= 90), in which case that of the silver salt would be $C_3H_5O_3Ag$ (= 196·9).

It is clear, however, that 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 afford the same percentage of silver as before, and the minimum molecular weight, calculated as above, would again be 90. But if the acid were dibasic, it might be possible to displace only one atom of hydrogen, and obtain a hydrogen salt, $C_6H_{11}O_6M'$, the analysis of which would give the minimum molecular formula, $C_6H_{12}O_6$. Should the preparation of such a hydrogen salt be found impossible, the fact might be taken as evidence against the molecular formula, $C_6H_{12}O_6$, but the matter would not be definitely settled.

Instead of an analysis of a salt, a *titration* of the acid with standard alkali is often carried out in order to obtain the equivalent weight or the minimum molecular weight of the compound.

Most organic bases combine with hydrochloric acid to form salts which, like ammonium chloride, unite with platinic chloride and with auric chloride, giving complex salts. These complex salts usually have the compositions, B'_2,H_2PtCl_6 and $B',HAuCl_4$, respectively, where B′ represents one molecule of a monoacidic base, such as methylamine, CH_5N, ethylamine, C_2H_7N, etc. 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. The equivalent or minimum molecular weight of the base can then be calculated.

Example. The complex platinum salt (*platinichloride*) of an organic base gave on ignition 36·9% of platinum; what is its minimum molecular weight? Since 36·9 parts of platinum are contained in 100 parts of the salt, 195·2 parts of the metal are contained in 529 parts of salt; as 195·2 is the atomic weight of platinum, the minimum molecular weight of the salt is 529. The equivalent weight or the minimum molecular weight of the base (C_3H_9N), therefore, is

$$\frac{B'_2,H_2PtCl_6 - H_2PtCl_6}{2}$$

$$\text{or} \quad \frac{529-(2+195{\cdot}2+213)}{2} = \frac{529-410{\cdot}2}{2} = 59{\cdot}4 \text{ or } 59.$$

As in the case of acids, so in that of bases, the minimum value calculated from the analytical results may not be the real molecular weight of the compound. Some bases are diacidic, and form platinichlorides of the composition, B'',H_2PtCl_6, so that a diacidic base of the molecular weight 118 would yield a platinichloride con-

taining the same percentage of platinum as the salt of a monoacidic base of the molecular weight 59.

Other Methods of Examination. It will be seen from the above examples that, if there are any grounds for assuming that there is only *one atom* of any particular element in the molecule of the compound, the probable molecular weight of that compound may be calculated from the results of any analysis which gives the percentage of that particular element.

This being the case, the probable molecular formula of a compound, other than an acid or a base, may often be determined by preparing and analysing one of its simple derivatives.

Example. A liquid hydrocarbon has the percentage composition C = 92·3, H = 7·7 ; its empirical formula, therefore, is CH. On being treated with bromine, this hydrocarbon yields hydrogen bromide and a bromo-derivative consisting of C = 45·8, H = 3·2, Br = 51·0 %. The ratio of these elements being C = 3·82, H = 3·2, Br = 0·637, the empirical formula of this derivative is found to be C_6H_5Br. Now, since it is known from experience that, as a rule, the number of atoms of carbon in a molecule is not changed when a hydrocarbon is treated 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 suggested with confidence if the boiling-point and the percentage composition of the compound are known. When, for example, acetone (p. 145) is distilled with diluted sulphuric acid (p. 418), 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 it is known that other hydrocarbons, which contain only three or six atoms of carbon in the molecule, boil at temperatures much below 163°, and in the case of comparable compounds an increase in molecular weight is generally accompanied by a rise in boiling-point.

The *molecular* formula of a gaseous compound may often be determined directly from the results of an explosion with an excess of oxygen in a eudiometer tube, a method which is partly chemical and partly physical.

Example. 10 c.c. of a gaseous hydrocarbon were mixed with 100 c.c. of oxygen and the mixture exploded. The volume after explosion

(measured at the same temperature as before) was 90 c.c., and this was reduced to 70 c.c. (of oxygen) by treatment with potash solution. The volume of carbon dioxide produced was therefore 20 c.c., and of oxygen used 100−70 = 30 c.c. Now, since 10 c.c. (1 vol.) of gas gave 20 c.c. (2 vol.) of CO_2, the molecule of the gas must contain 2 atoms of carbon, and since 20 c.c. of CO_2 require 20 c.c. of O_2 and 30 c.c. of O_2 have taken part in the reaction, 10 c.c. of O_2 have combined with hydrogen to give 20 c.c. (2 vol.) of H_2O, which condensed. These results show that the molecular formula is C_2H_4 :

C_2H_4	+	$3O_2$	=	$2CO_2$	+	$2H_2O$.
1 vol.		3 vol.		2 vol.		2 vol. (condensed).
10 c.c.		30 c.c.		20 c.c.		

The Determination of Molecular Weight

The principles on which the determination of molecular weight are based are of course the same for organic as for inorganic substances, and the methods used are also the same. As a knowledge of the *molecular* formula is, however, generally speaking, much more important in the case of organic than in that of inorganic substances, the chief methods for the determination of molecular weight, although described in many text-books of inorganic chemistry, are given here.

One of the more important physical methods by which the molecular weight can be ascertained is by a determination of the vapour density since

$$\text{Vapour density} = \frac{\text{Molecular weight}}{2} \quad \text{or} \quad \text{M.W.} = \text{V.D.} \times 2.$$

Also, as one gram molecule of any gas or vapour occupies 22·4 litres at N.T.P., the weight in grams of 22·4 litres of the gas or vapour represents the molecular weight.

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.[1] 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

[1] This method, (*b*), is used mainly in the case of inorganic compounds.

vapour divided by that of the hydrogen gives the vapour density, from which the molecular weight is then deduced. A simpler method is to calculate the weight in grams of 22·4 litres of the vapour ; the result is numerically equal to the molecular weight.

The molecular weight determined experimentally 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.

Example. An organic liquid has the empirical formula, C_4H_8O ; 0·062 g. of the liquid gave 23·2 c.c. of vapour at 50° and 720 mm. What is its molecular formula ?

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

therefore 18·57 c.c. of vapour at N.T.P. weigh 0·062 g. Hence 22·4 litres weigh $\frac{{\cdot}062 \times 22400}{18{\cdot}57} = 74{\cdot}8$ g., the (approximate) molecular weight is 75, and the molecular formula is C_4H_8O.

The determination of the vapour density is only possible, of course, when a substance can be converted into vapour without decomposition under the conditions of the experiment. In many cases, however, a non-volatile compound 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 two of the methods employed in determining vapour density :

Gay-Lussac's or Hofmann's Method. A graduated barometer tube (*a*, *b*, Fig. 12), about 85 cm. long and 20 mm. wide, filled with and then inverted in mercury, is surrounded by a wider tube (*c*), through which is passed the vapour of some liquid boiling at a known and constant temperature.[1] For this purpose the upper end of the outer tube (*c*) is connected with a vessel (A), usually made of copper, in which the heating liquid is kept in rapid ebullition. 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 g.) of the substance, contained in a small stoppered vessel (*d*), *which it fills completely*, is placed under

[1] The liquids most commonly employed are water (b.p. 100°), xylene (b.p. 140°), aniline (b.p. 184°), and ethyl benzoate (b.p. 213°).

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 depressed ; as soon as the level becomes stationary, the *volume* of the vapour is noted. The *temperature* of the vapour is the boiling-point of the liquid employed

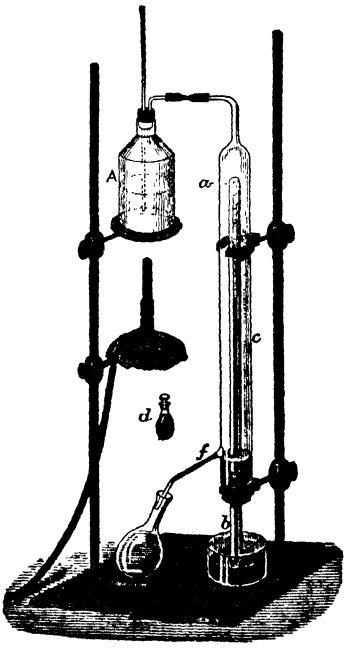


Fig. 12

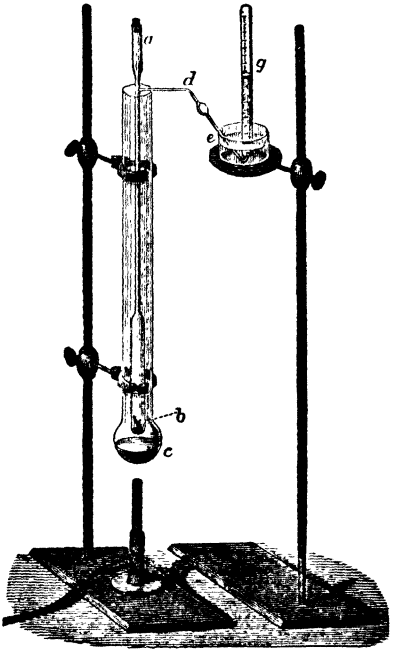


Fig. 13

to heat the barometer tube. The *pressure* is determined by subtracting the height of the column of mercury in the inner tube (*a*, *b*), above the level in the trough, from the height of the barometer, both readings having been first reduced to 0°.[1] 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 densities of substances under greatly reduced pressures, and therefore at temperatures very much

[1] By correcting for the expansion of the mercury.

below their ordinary boiling-points, so that it can often be employed with success in the case of substances which would decompose if they were heated under atmospheric pressure.

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. 13. The bulb tube (*a*, *b*) is closed (at *a*) by means of a rubber stopper, and is heated by the vapour of some liquid of constant boiling-point [1] 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 temperature of the bulb tube (*a*, *b*) 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) filled with a weighed quantity (about 0·05 g.) of the liquid is dropped into the apparatus,[2] the stopper (*a*) being replaced as quickly as possible. The substance immediately vaporises, and the vapour forces some of 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 being drawn into the apparatus.

The *volume* of the vapour is ascertained by measuring the volume (*v*) of the air in the graduated tube (*g*), its *temperature* ($t°$) and the barometric *pressure* (*B*) being noted. The volume of the air (in *g*) is not the same as that actually occupied by the hot vapour (in *a*, *b*), because the displaced air has been cooled, and is measured under a different pressure. Its volume now is (approximately) *equal to that which the given weight of vapour would 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 *B*, the volume at N.T.P. would be $v \times \frac{273}{273+t} \times \frac{B}{760}$, neglecting the tension of the aqueous vapour.[3] The weight of this

[1] Footnote, p. 32; in determining the vapour density of a substance of high boiling-point, diphenylamine (b.p. 302°) or sulphur (b.p. 444°) may be used, or the bulb tube (*a*, *b*) may be heated at a constant temperature in a metal-bath.

[2] In order to prevent fracture, a little dry asbestos, glass-wool, or sand is placed in *b*.

[3] Since only the approximate molecular weight is required (p. 32), it is unnecessary to correct for the tension of aqueous vapour in measuring *v*.

volume of vapour being known, that of 22·4 litres is calculated and the result gives the *approximate* molecular weight.

The liquid in (*c*) should have a boiling-point at least 25° higher than that of the substance of which the vapour density is required in order that the latter may be *rapidly* vaporised—otherwise its vapour may condense higher up the tube. If, as is generally the case, the temperature of the air in the tube (*a*, *b*) is lower at the top than at the bottom, this is of no consequence ; nor does it matter if the displaced air is colder than the vapour, or if the vapour is cooled a *little* while it is displacing the air. This is because any diminution in the volume of the air displaced from the tube (*a*, *b*) arising from these causes is exactly compensated during the subsequent cooling to $t°$; the lower the original temperature, the smaller the subsequent contraction. If, for example, the hot vapour measured 25 c.c. at 250°, but only displaced 24·04 c.c. of air owing to the latter being of the average temperature of 230°, the 24·04 c.c. of air at 230° would occupy the same volume as 25 c.c. at 250° if both were cooled to $t°$.

Determination of Molecular Weight by the Cryoscopic Method. When sugar is dissolved in water, the solution has a lower freezing-point than that of 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 compounds in other solvents, such as acetic acid, benzene, etc., 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 are dissolved separately in a given (and sufficiently large) quantity of the same solvent, the depression of the freezing-point is *the same* (approximately) in all the solutions, but different with different solvents. From actual experiments with dilute solutions, the depression of the freezing-point, which should be produced by dissolving the molecular weight in grams of any substance in 100 g. of a given solvent, can be calculated; the constant value, K,

which is thus found, is termed the *molecular depression* of that solvent.

If, for example, 1 g. of cane-sugar dissolved in 100 g. of water depresses the freezing-point by 0·058°, 342 g. (i.e. the molecular weight in grams) would theoretically cause a depression of 19·8° = K.

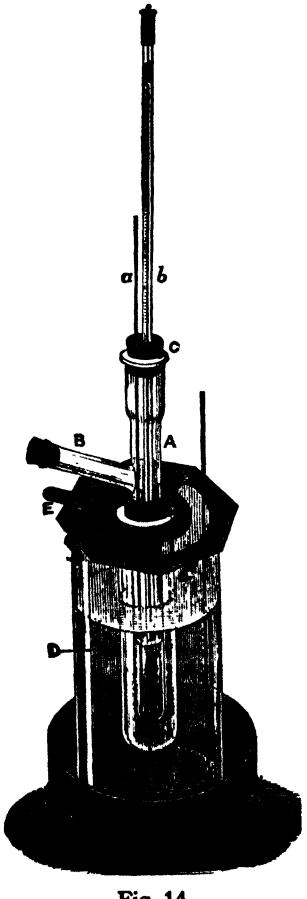


Fig. 14

This constant having been determined for any solvent, the molecular weight, M, of a substance can then be ascertained by observing the depression of the freezing-point of a sufficiently dilute solution, containing a known quantity of that substance. If 1 g. of the substance were dissolved in 100 g. 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 g.—and the depression varies directly with the weight of dissolved substance. If, again, P g. of the substance were dissolved in 100 g. of the solvent, the depression, $D = K \times \frac{P}{M}$, hence the molecular weight $M = \frac{K \times P}{D}$; K and P being known, if the depression, D, is ascertained experimentally, the molecular weight, M, can be calculated.

This method of determining the molecular weights of organic compounds was first applied by ***Raoult***, and is usually known as Raoult's or the *cryoscopic method*. The observation is made with the aid of the apparatus devised by Beckmann (Fig. 14), in the following manner: A large tube (A), about 3 cm. 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 15 g.) of the solvent is placed in the tube, which is then fitted into a wider tube (D); the latter serves as an air-jacket and protects the solvent from 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, whereupon 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 the solvent has been allowed 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.

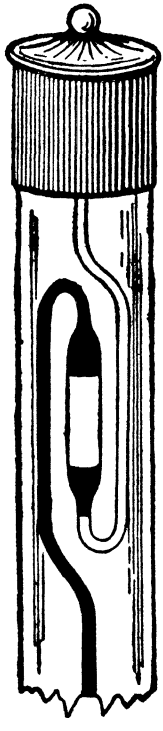


Fig. 15

Example. 1·24 g. of cane-sugar ($C_{12}H_{22}O_{11}$), dissolved in 24·2 g. of water, caused a depression, D, of 0·295° in the freezing-point. Since 24·2 g. of the solvent contain 1·24 g. of substance, P, the quantity in 100 g. is 5·12 g. The constant, K, for water is 19; hence the molecular weight, M, of cane-sugar is found to be $\frac{19 \times 5 \cdot 12}{0 \cdot 295} = 329$, the true value being 342.

As in the determination of molecular weight from the vapour density, the experimental and theoretical values may differ by 10% or more; but this is of little importance, for the reasons already stated.

The cryoscopic constants, K, for the solvents most frequently used are: acetic acid, 39; benzene, 49; phenol, 75; water, 19; camphor, about 400 (p. 38).

The *thermometer* used in such experiments has a very large bulb, and the total range shown on the scale is only about 6°, the smallest divisions corresponding with hundredths of a degree. The capillary tube connected with the bulb terminates above in a reservoir, as shown in Fig. 15, and by warming the bulb very cautiously some

of the mercury may be driven into this reservoir, and detached from the main quantity by gently tapping the thermometer. It is thus possible to diminish the quantity of mercury in the bulb (and to increase it again when required), so that the top of the column in the capillary thread stands at some suitable point on the scale, when the thermometer is at the temperature which is to be registered in the experiment. All that is required is that the thermometer shall show *differences* in temperature with a high degree of accuracy.

It was found by Jouniaux that the molecular depression, K, for camphor was exceptionally large, and on this fact Rast based a method for molecular weight determination, which can be rapidly carried out with very small quantities of substance. Further, as the melting-point of camphor is 180° and the depressions to be observed are so large (due to the large value of K), the latter can be determined with sufficient accuracy with an ordinary melting-point apparatus and an ordinary thermometer. The melting- (or freezing-) point of the camphor alone is first taken, and then that of the prepared solution ; the difference gives the depression, D.

A known weight (about 0·01 g.) of the substance whose molecular weight is to be determined is mixed with a known weight (about 0·1 g.) of camphor and the mixture is quickly melted and then immediately cooled. The melting-point of some of this mixture is then determined, but only slowly and with the aid of a lens ; the temperature at which the last trace of crystalline structure disappears is taken as the melting-point. The capillary tube should have an inside diameter of 2–3 mm. ; with the aid of a microbalance, a determination can be made with less than 0·0003 g. of the compound. The value of K for camphor differs for different samples, and it is advisable to determine it by using a compound of known molecular weight.

Determination of Molecular Weight by the Ebullioscopic Method. When molecular proportions of different substances are dissolved in fixed and sufficiently large quantities of a given solvent, the boiling-point of the solution is *raised* by the *same* amount in each case ; experiments with dilute solutions give the actual rise in boiling-point, and then by calculation, the *molecular elevation*—that is, the rise which should be produced by the molecular weight in grams of the substance in 100 g. of the solvent—may be deduced.

The value thus determined is (approximately) a constant, K', but is different for different solvents ; if now the value of K' is

known, the molecular weight of a substance soluble in that solvent can be determined experimentally by finding the elevation of the boiling-point, E, produced by dissolving a known weight of the substance in a known weight of the solvent, the formula $M = \frac{K' \times P}{E}$ being employed. (Compare p. 36.)

An apparatus, devised by Beckmann, is shown in Fig. 16. A known weight of the solvent is put into the tube (a), the thermometer is placed in position, and some glass beads are poured through the side-tube (b) until the bulb of the thermometer is nearly covered; the object of these beads is to ensure a regular boiling of the liquid. The tube (a) is surrounded by the outer jacket (c), which also contains some of the solvent; the object of this jacket is to prevent superheating. The apparatus is then placed, as shown, on an asbestos frame (d), and the condensers (e, e') are fitted. The asbestos frame, which is provided with chimneys, (f, f), is then very gradually heated below, and when the solvent has been boiling *constantly* for some time (at least five minutes) the position of the mercury thread is noted. The condenser (e) is now removed, and a weighed quantity of the substance (in tabloid form, if a solid) is introduced through the side-tube, the condenser being immediately replaced. The temperature falls at first, but rapidly rises again, and in two or three minutes the position of the mercury thread becomes constant. The difference between the readings with the solvent and the solution respectively gives the elevation, E.

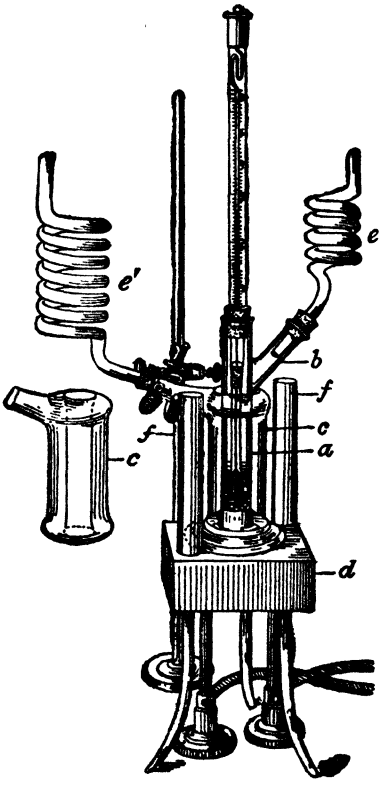


Fig. 16

A simpler apparatus is that devised by Landsberger (Fig. 17). A suitable quantity of the solvent is placed in the tube (*a*), which is about 16 cm. in height and 3 cm. in diameter, and which has a small opening (*b*) for the escape of the vapour ; this tube (*a*) is fitted by means of a cork into a larger one (*c*) which serves as an air-jacket, and the outlet (*d*) of which is connected with an ordinary

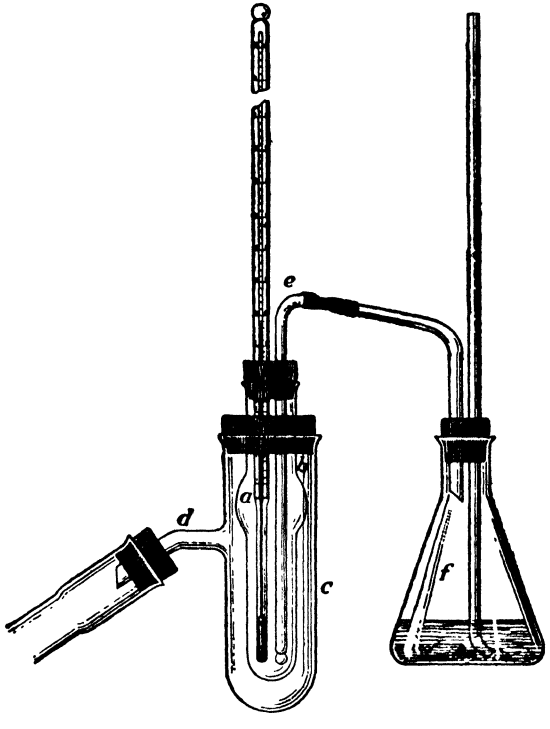


Fig. 17

Liebig's condenser. The inner tube (*a*) is closed with a cork through which pass a thermometer, graduated to $\frac{1}{20}°$, and a tube (*e*), the end of which has been cut off in a slanting direction, or perforated with a number of holes. The solvent in the tube (*a*) is not heated directly, but only by the vapour of the *same* solvent, which is generated in the flask (*f*) ; in this way superheating is avoided.

The boiling-point of the solvent alone is first determined by heating the solvent in the flask (*f*) and passing its vapour through

the solvent in (*a*) until the thermometer shows a constant temperature ; the solvent in (*a*) is then *mixed* with that in the flask (*f*), about the same quantity as originally used being poured back into the tube (*a*). A weighed quantity of the substance is now placed in (*a*), and vapour from (*f*) is again passed until the temperature is again constant. The *difference* between the two readings gives the *elevation*, *E*. The weight of the solvent in (*a*) at the time of the second reading has now to be found, and the molecular weight of the substance can then be calculated.

If the tube (*a*) is graduated, the weight of the solvent may be ascertained with sufficient accuracy by multiplying its volume by its specific gravity (approximate). The quantity of solvent originally placed in (*a*) should be so chosen that by the time the solvent is boiling constantly the total quantity amounts to about 10 g.

Example. 0·562 g. of naphthalene dissolved in carbon disulphide raised the boiling-point by 0·784° ; the solvent alone weighed 12·7 g., hence 100 g. of the solvent would have contained 4·42 g. of substance. The constant, *K'*, for carbon disulphide is 23·7 ; the calculated molecular weight, therefore, is $\frac{23{\cdot}7 \times 4{\cdot}42}{0{\cdot}784} = 134$, the true value being 128.

The ebullioscopic constants for the solvents generally used are : acetic acid, 25·3 ; benzene, 26·7 ; water, 5·2 ; ether, 21·1 ; ethyl alcohol, 11·5 ; acetone, 16·7 ; chloroform, 36·6 (per 100 g.).

In the case of electrolytes the results of cryoscopic and ebullioscopic determinations with solvents, such as water, acetic acid, and alcohol, show that the molecules of the dissolved substances are *dissociated* into simpler portions (ions). On the other hand, *some* non-electrolytes, with solvents, such as ether, benzene, and carbon disulphide, give values indicating that the chemical molecules of the dissolved substance are *associated* and form more or less complex aggregates.

In the case of very complex substances the ordinary methods for the determination of molecular weight are useless because such compounds are non-volatile, and also because they give a depression of the freezing-point or elevation of the boiling-point so small that accurate measurements are impossible. This latter difficulty does not arise to quite the same extent in measurements of osmotic pressure since larger readings are obtained ; a compound of M.W. 100,000, for example, would theoretically give an osmotic pressure of about 8 mm. in 5% aqueous solution at 0°, but a freezing-point depression of only 0·00095°. Methods have therefore been de-

veloped for determining molecular weights by this method, but great experimental difficulties are still encountered ; the substance under examination is usually very difficult to purify and even small traces of impurities of low M.W. invalidate the results. It is also rarely that a flawless membrane can be obtained.

Another method depends on measurements of the rate of sedimentation of the particles when a colloidal solution is centrifuged. It is found that the larger the particles, the faster they move to the outside of the container, and, by studying their rate of motion, the molecular weight can be calculated (Svedberg). This method also gives an indication of the homogeneity of the sample.

Staudinger has shown that determinations of the viscosity of a solution can be used for determining molecular weights, as the viscosity bears a known relationship to the M.W. of the solute.

CHAPTER 3

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.

A great many cases are known of the existence of two or more compounds which have the *same molecular formula*, and yet differ in chemical and physical properties, not only in the solid, but also in the liquid and gaseous states ; there are, for example, two compounds of the molecular formula, C_4H_{10}, three of the molecular formula, C_5H_{12}, at least six of the molecular formula, $C_3H_6O_2$, and so on.

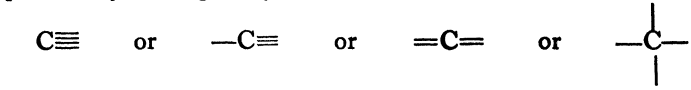
Now, if the properties of a compound depended simply on the nature and number of the atoms of which its molecule is composed, facts such as these could not be explained. It must be concluded, therefore, (*a*) that the atoms of which molecules are composed are arranged in a definite manner ; and (*b*) that when two or more compounds of the same molecular formula are known, the molecules of the one differ in arrangement, **constitution,** or **structure** from those of the other or others.

Although the actual arrangement of the atoms in a molecule cannot be directly observed, it is possible to obtain information as to the structure or constitution of a compound from a consideration of (*a*) the valencies of the elements of which the compound consists, and (*b*) the chemical and physical properties of the compound.[1]

The *valency* or atom-fixing power of an element is deduced from the molecular formulae of those compounds which contain *one* atom of the element in question, united with other elements of known valency. Thus, in the case of carbon, the molecular formulae of compounds such as (*a*) CH_4 and $CHCl_3$; (*b*) CO_2 and COS ; (*c*) $COCl_2$; and (*d*) HOCN, which contain only one atom of carbon

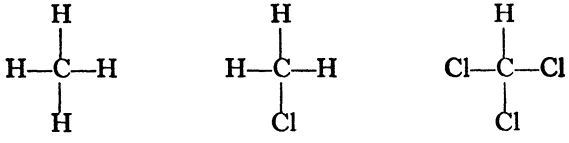
[1] The relation between the structure and the physical properties of a compound (except that of optical activity) are not discussed until later (Part III), but it may be noted here that X-ray analysis often affords very important information as to the arrangement of the atoms in a molecule.

in the molecule, are considered. In all these compounds the atom of carbon is combined with (*a*) 4 univalent atoms, (*b*) 2 bivalent atoms, (*c*) 1 bivalent and 2 univalent atoms, or (*d*) 1 tervalent atom and 1 univalent HO— group : that is to say, with four univalent atoms or their valency equivalent. With the exception of carbon monoxide, CO, no stable compound containing only *one* carbon atom is known, in which the carbon atom is combined with *more* or *less* than four univalent elements or their valency equivalent ; carbon, therefore, is *quadrivalent*, and this deduction may be expressed by writing its symbol,



In a similar manner the univalent hydrogen atom may be represented by H—, bivalent oxygen by O= or —O—, tervalent nitrogen by N≡ or >N—, and so on ; the number of lines drawn from the symbol then shows 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 univalent atoms, the symbol of each of the latter is placed at the extremity of *one* of the four lines which represents a carbon valency, the following formulae are obtained :



Similarly in the case of substances such as CO_2, $COCl_2$, COS, the symbol of each of the bivalent atoms is given *two* lines, and in that of cyanic acid, HOCN (p. 362), the nitrogen atom is given *three* :

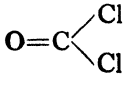
Formulae of this kind are termed **graphic formulae,** and the elements whose symbols are joined by one or more lines are said to be *directly united.* Thus in the case of the compound, $COCl_2$, the oxygen atom is directly united to the carbon atom ; so also are the two chlorine atoms ; but the oxygen and chlorine atoms are *not* directly united. The idea is that the carbon atom is holding or

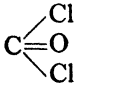
fixing the oxygen atom *and* the two atoms of chlorine, the whole forming a molecule of definite structure. A graphic formula, therefore, expresses the structure or constitution of the compound —that is to say, it shows not only the valency of each of the atoms in the molecule, but also indicates the *disposition* of the atoms. In all such formulae, obviously, the number of lines running to or from any given symbol must correspond with the valency of the element represented by that symbol. The formula of cyanic acid, for example, should not be written H—O—C—N, or that of carbon dioxide O—C—O, because the valencies of the elements are not correctly indicated by the lines drawn from their symbols.

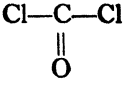
These lines, which represent units of valency, are called **bonds, links,** or **bindings**; in the compound, $\begin{matrix}Cl\\Cl\end{matrix}\!>\!C\!=\!O$, the chlorine atoms are said to be combined with carbon by one bond or binding, the oxygen atom by two. The chlorine and oxygen atoms are not directly combined, but are both united with carbon.

It is obvious that such lines or bonds may be shortened or lengthened at will without their significance being altered: as a rule, they are shortened, as in the formulae, H·O·C·N and O:C:S, which are then called **structural** or **constitutional,** instead of graphic formulae, but these terms do not differ essentially.

It may next be pointed out that although in a structural, constitutional, or graphic formula, all the atoms in the molecule are necessarily represented as lying in one plane (the plane of the paper), it is known that the atoms in a molecule are actually arranged in space of *three* dimensions (p. 296). In spite of this difficulty, the use of plane structural formulae, instead of mere molecular formulae, is a prime necessity in the case of organic compounds, for reasons which will be obvious later. Consequently it is essential that the meaning of a structural formula, and its *limitations*, should be clearly understood. Since the formula is not intended to show how the atoms are arranged *in space*, but merely which atoms are directly united to one another, it makes no difference how the formula is shown, provided that it fulfils this condition and represents correctly the valencies of the elements in the molecule. Thus, the formulae,



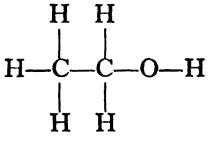




are equally good expressions of the structure of carbonyl chloride; but *no formula shows that the strength or stability of a bond depends on the elements united by that bond and on the structure of the molecule as a whole.*

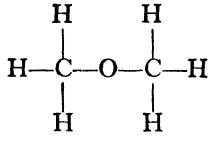
In all the cases considered above, the structural formula was based on considerations of valency alone. An example may now be given in which the chemical behaviour of the compound must also be studied, before the structure of the molecule can be represented by a formula.

The compound ethyl alcohol has the molecular formula C_2H_6O. On the assumption that hydrogen is univalent, oxygen bivalent, and carbon quadrivalent, the molecule of ethyl alcohol might be represented by one of two graphic formulae (I) and (II), which correspond respectively with the structural formulae:



$CH_3—CH_2—OH$

I



$CH_3—O—CH_3$

II

Now, ethyl alcohol is readily acted on by sodium, yielding a compound of the composition, C_2H_5NaO, which is formed by the displacement of one hydrogen atom (*a*) by one atom of the metal; the other five hydrogen atoms in the molecule of ethyl alcohol cannot be displaced, no matter how large a quantity of sodium is employed. Again, when ethyl alcohol is treated with hydrogen chloride, one atom of hydrogen *and* one atom of oxygen are displaced by one atom of chlorine, a compound of the composition, C_2H_5Cl, being formed:

$$C_2H_6O+HCl = C_2H_5Cl+H_2O.$$

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

From these and other experiments it is concluded that ethyl alcohol contains one atom of hydrogen (*a*), combined differently from the other five. Also, that one atom of hydrogen is closely

associated with the oxygen atom, forming a univalent group —OH ; if this were not the case, it would be difficult to understand how one atom of univalent chlorine could displace, or be displaced by, one atom of univalent hydrogen *and* one atom of bivalent oxygen.

Hence a study of the chemical behaviour of ethyl alcohol shows that the structure of its molecule is expressed by formula (I) given above ; a compound of the structure represented by formula (II) would show a totally different behaviour, as is proved later (p. 128). Further, since the compound, C_2H_5Cl, does not contain a hydrogen atom which can be displaced by sodium, it is concluded that the particular hydrogen atom (*a*) in ethyl alcohol, which is displaceable by sodium, is that which is closely associated with the oxygen atom ; hence the structure of the sodium derivative is written $C_2H_5 \cdot ONa$ or $CH_3 \cdot CH_2 \cdot ONa$.

Now, any compound, such as propyl alcohol, C_3H_8O (p. 118), which behaves in the above-mentioned respects like ethyl alcohol, under the same conditions, must be supposed to contain one atom of hydrogen and one atom of oxygen in the same state of combination as in ethyl alcohol, and may be represented by a formula such as $C_3H_7(OH)$, which expresses this conclusion.

The constitution of a compound, therefore, may be ascertained by carefully studying its chemical behaviour under various conditions, and also, if possible, by comparing its behaviour with that of other compounds of *known* constitution. Compounds which are found to show a similar behaviour are considered to contain atoms or groups of atoms in a similar state of combination.

It is thus possible, with the added help of valency considerations, to determine the state of combination of all the atoms of which the molecule is composed, and to express the results in a *structural formula* ; **this formula then shows not only the constitution or structure of the compound, but also summarises in a concise and simple manner the more important chemical properties of the compound.** The physical properties, such as solubility, boiling-point, etc., are also determined by the structure, as well as by the composition, of the compound.

In structural formulae in general, each of the *uni*valent atoms is to be considered as directly united to that atom, the symbol of which it immediately follows or precedes without the interposition of a line (or dot, or bracket). Thus in the formula $CH_3—CH_2—OH$, $CH_3 \cdot CH_2 \cdot OH$, or $CH_3 \cdot CH_2(OH)$, the three hydrogen atoms of

the CH_3— group are directly combined to the carbon atom of this group; the two hydrogen atoms, and also the hydroxyl group (—OH) which follow the second carbon atom are directly united to it. In order to avoid any misapprehension on this point, the graphic and structural formulae already given for ethyl alcohol should be carefully compared.

CHAPTER 4

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 trivial name implies, in marshes and other places in which the decomposition or decay of vegetable matter is taking place under water; when a marshy pond or swamp is stirred, bubbles, consisting mainly of methane and carbon dioxide, frequently rise. It is one of the principal components of the gas which streams out of the earth in the petroleum districts of America, Russia, etc.; 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% of methane, to the presence of which, mixed with air, explosions in coal-mines are often due. Ordinary coal-gas usually contains about 24–36% of methane.

Methane is formed [1] by the direct union of carbon and hydrogen at a temperature of about 1200°. It is also obtained when hydrogen sulphide (or steam), together with the vapour of carbon disulphide, is passed over heated copper (Berthelot),

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

and when a mixture of carbon monoxide and hydrogen is passed over finely divided nickel which is heated at 220°. These reactions are all examples of a *complete synthesis* of the gas, because all the reagents involved can be obtained from their elements.

Methane is also formed when chloroform (p. 76) or carbon

[1] The words *formed, obtained,* or *produced* are used when the method is of general theoretical importance but is not a convenient one for the actual *preparation* of the compound.

tetrachloride (p. 79)[1] is reduced with sodium amalgam and water,[2]

$$CHCl_3+6H = CH_4+3HCl,$$
$$CCl_4+8H = CH_4+4HCl,$$

and when methyl magnesium iodide (p. 236) is decomposed by water, an alcohol, or an amine (primary or secondary, p. 213),

$$CH_3\cdot MgI+H_2O = CH_4+MgI\cdot OH,$$
$$CH_3\cdot MgI+C_2H_5\cdot NH_2 = CH_4+C_2H_5\cdot NH\cdot MgI.$$

Methane is *prepared*[3] by heating anhydrous sodium or potassium acetate (1 part) with soda-lime[4] (4 parts) in a hard glass tube, retort, or copper flask,

$$CH_3\cdot COONa+NaOH = CH_4+Na_2CO_3.$$

The gas obtained in this way and collected over water contains a small proportion of hydrogen, ethylene (p. 85), and other impurities; if, however, anhydrous barium hydroxide is used instead of soda-lime, the methane is nearly pure.

Pure methane is prepared by dropping a solution of methyl iodide[5] in about an equal volume of 95% alcohol, from a stoppered funnel, into a flask containing a large quantity of a zinc-copper couple.[6] The methyl iodide is reduced by the nascent hydrogen, formed by the action of the aqueous alcohol on the zinc-copper couple, and a slow but continuous evolution of methane takes place without the application of heat,

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

the gas is passed through a tube containing some damp zinc-copper

[1] Many compounds are often unavoidably mentioned long before their properties are described; in such cases references are often given.

[2] The common *reducing agents* used in organic chemistry are listed before the Index.

[3] The word '*prepared*' is used when the given method can be carried out in the laboratory with apparatus and chemicals, which are commonly available, and does not involve expert manipulation; when also the weight of the product (the *yield*) is a satisfactory percentage of that theoretically obtainable. On the large scale, the cost of the product and the risk of danger from fumes, fires, and explosions are the main considerations.

[4] Soda-lime (footnote, p. 14) may be represented in equations as NaOH.

[5] The univalent groups of atoms, CH_3—, C_2H_5—, C_3H_7—, and C_4H_9—, are termed *methyl*, *ethyl*, *propyl*, and *butyl* respectively (p. 80).

[6] The zinc-copper couple is prepared by heating copper powder (obtained by reducing the oxide in hydrogen) with small pieces of clean zinc foil, or with zinc filings, in an atmosphere of coal-gas, until the mixture has caked together.

couple, in order to free it from methyl iodide, and collected over water.

In a similar manner, all halogen derivatives of methane (p. 70) may be converted into the hydrocarbon by reduction in a suitable manner.

Methane is an almost odourless, colourless gas,[1] boiling at $-161{\cdot}5°$ [2] or at $-11°$ under a pressure of 180 atmospheres; it is almost insoluble in water but rather more soluble in alcohol. It burns with a pale-blue, non-luminous flame, and forms an explosive mixture with certain proportions of air or oxygen,

$$CH_4+2O_2 = CO_2+2H_2O \mid 211{,}900 \text{ cal.}$$
$$1 \text{ vol.}+2 \text{ vol.} = 1 \text{ vol.}+2 \text{ vol.}$$

Methane reacts with steam at 800–900° in the presence of nickel and alumina, $CH_4+H_2O = CO+3H_2$,

and when the resulting gaseous mixture is passed over ferric oxide at about 500° with more steam, carbon dioxide and hydrogen are produced; four volumes of hydrogen are thus obtained from one of methane. This is an important commercial method.

Methane is very stable; when passed through bromine, potash, nitric acid, sulphuric acid, or a solution of potassium permanganate or chromic acid, it is not absorbed or changed in any way. When mixed with chlorine in the dark it is not attacked; but if a mixture of about 1 volume of methane and 2 volumes of chlorine is exposed to direct sunlight an 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 hydrogen chloride and four other compounds is produced, the proportion of each depending on that of the reagents, 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 dichloride

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

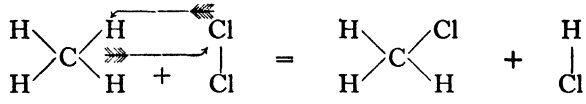
$CH_4+4Cl_2 = CCl_4+4HCl$ — Carbon tetrachloride

All these compounds are formed by the displacement of one or more hydrogen atoms by an equivalent quantity of chlorine. The

[1] Unless otherwise stated, every compound described in Part I is colourless.
[2] Except when otherwise stated, all boiling-points refer to standard pressure (760 mm.).

carbon atom cannot combine with more than four univalent atoms, so that hydrogen must be displaced if any action at all takes place.

Now, it may be supposed that in the formation of methyl chloride, CH_3Cl, for example, one of the hydrogen atoms is displaced by one atom of chlorine without the other atoms in the molecule being disturbed or their state of combination altered ; this view may be represented diagrammatically as follows :



In the formation of methylene dichloride, CH_2Cl_2, it may be supposed that a repetition of this process occurs, and so also in the cases 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 methane 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 reactions as these, in which certain atoms are merely displaced by an equivalent quantity of other atoms, without the state of combination of the rest of the atoms 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 *di*chloride, CH_2Cl_2, a *di*-substitution product of methane, and so on ; chloroform, $CHCl_3$, is a *tri*-substitution product of methane, and also a *di*-substitution product of methyl chloride.

Similarly, when by treatment with nascent hydrogen in the manner described above, any of these substitution products is converted into methane, the change is a process of substitution.

The only way in which it is possible for a chemical change to occur in the case of methane and its chloro-substitution products is by a process of substitution. The atom of carbon already holds in combination its maximum number of atoms, some of which must be displaced if any other atom enters the molecule. Compounds such as these, which can only yield derivatives by substitution, and in which the maximum combining capacity of all the carbon atoms is exerted, are termed **saturated compounds.**

Ethane, 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, more conveniently, methyl iodide is heated with sodium [1] in *dry* ethereal solution (Wurtz reaction),

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

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

Ethane is produced when ethyl magnesium bromide (p. 235) is decomposed with water or with an alcohol, reactions analogous to those which occur in the case of methyl magnesium iodide (p. 50).

It is also formed when ethylene (p. 85) is treated with hydrogen in the presence of platinum black, even at ordinary temperatures,

$$C_2H_4+H_2 = C_2H_6.$$

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

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

Also, by the electrolysis of aqueous 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 anode, hydrogen at the cathode,

$$\begin{matrix} CH_3COOH \\ CH_3COOH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} +2CO_2+H_2 ;$$

when potassium acetate is employed the same gases are evolved as before.

Ethane is an odourless, tasteless gas, which boils at $-89°$ and liquefies at 4° under a pressure of 46 atmospheres; it is practically insoluble in water, slightly soluble in alcohol. Its chemical properties are very similar to those of methane. It is inflammable,

[1] The sodium is best used in the form of wire, which is obtained with the aid of a sodium press.

burns with a feebly luminous flame, and can be exploded with air or oxygen :

$$2C_2H_6+7O_2 = 4CO_2+6H_2O$$
$$2 \text{ vol.}+7 \text{ vol.} = 4 \text{ vol.}+6 \text{ vol.}$$

It is very stable, and is not acted on by alkalis, 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 :

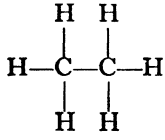
$CH_3 \cdot CH_2Cl$	$CH_3 \cdot CHCl_2$
Ethyl chloride or chloroethane	Ethylidene dichloride or dichloroethane

The *final* product is hexachloroethane,

$$C_2H_6+6Cl_2 = C_2Cl_6+6HCl.$$

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

The *constitution* or *structure* of ethane is expressed by the formula,



or $CH_3 \cdot CH_3$,

which is securely founded on considerations of valency. The two atoms of carbon must be directly united, because a univalent hydrogen atom could not link the two carbon atoms together ; as, moreover, carbon is quadrivalent, each of the carbon atoms must also be directly united with three atoms of hydrogen.

Propane, C_3H_8, occurs in petroleum, and can be obtained by reducing propyl iodide or *iso*propyl iodide (p. 75) with zinc and an acid, or with the zinc-copper couple and water,

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

It is also obtained (together with ethane and butane) by heating a mixture of ethyl and methyl iodides with sodium,

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

and by decomposing propyl magnesium bromide with water, alcohol, or an amine (p. 50).

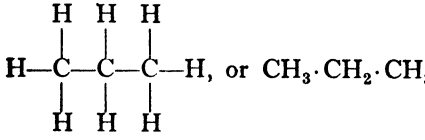
Propane is a gas, and closely resembles methane and ethane in chemical properties, but it burns with a flame more luminous than

that of ethane. It is sold in cylinders for use as a fuel and is also employed as a solvent and refrigerant in the petroleum industry.

When treated with chlorine in diffused sunlight propane yields propyl chloride and other substitution products, one or more hydrogen atoms being displaced by an equivalent quantity of chlorine,

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

The *constitution* of propane is represented by the formula,



which is based, of course, on considerations of valency, but which is fully confirmed by a study of the derivatives of the hydrocarbon (p. 119). Propane may be regarded as derived from ethane, just as ethane may be considered as derived from methane, by the substitution of the univalent 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, **normal butane,** can be obtained by heating ethyl iodide with sodium,

$$2CH_3\cdot CH_2I+2Na = CH_3\cdot CH_2\cdot CH_2\cdot CH_3+2NaI.$$

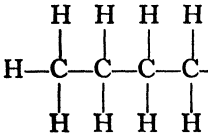
The other, *iso***butane,** or trimethylmethane, is formed when tertiary butyl iodide (p. 117) is reduced with sodium amalgam and water,

$$(CH_3)_3CI+2H = (CH_3)_3CH+HI.$$

These two hydrocarbons, which have been proved to have the same molecular formula, are yet different in properties. Although they are both gases under ordinary conditions, normal butane liquefies at about 0°, *iso*butane not until about −12°, under atmospheric pressure. In chemical properties they closely resemble propane and one another. They give substitution products with chlorine, but every compound obtained from normal butane is different from the substance of the same molecular formula, which is produced from *iso*butane.

Constitutions of the two butanes. The production of normal butane from ethyl iodide in the above-mentioned manner indicates

that this hydrocarbon is formed by the union of two $CH_3 \cdot CH_2$— groups. It is, therefore, represented by the formula,



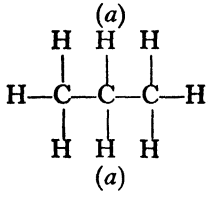
or $C_2H_5—C_2H_5$, or $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

Normal butane

I

Normal butane, in fact, may be regarded as propane in which one atom of hydrogen has been displaced by the univalent CH_3— group.

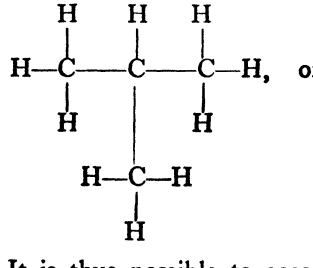
When, however, the graphic formula of propane is carefully considered, it will be seen that the eight atoms of hydrogen are not all in the same state of combination relatively to the rest of the molecule, but that two of them (*a*),



or $CH_3—CH_2—CH_3$, or $CH_2(CH_3)_2$,

(*a*) (*a*)

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. In order to derive from propane a hydrocarbon having the structure of normal butane, one of the *six* similarly situated hydrogen atoms must be displaced by a CH_3— group. If, on the other hand, one of the (*a*) hydrogen atoms were displaced by a CH_3— group, the constitution of the product would be represented by the formula,



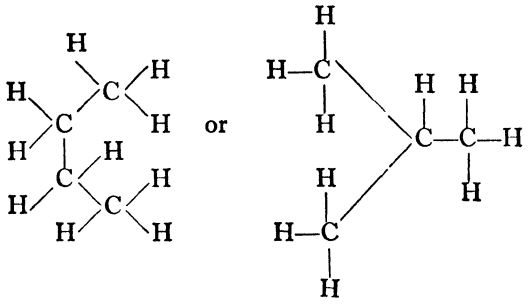
or $CH_3—CH(CH_3)—CH_3$, or $CH(CH_3)_3$.

*Iso*butane

II

It is thus possible to account for the existence of two hydrocarbons of the molecular formula, C_4H_{10}; the molecules of the two compounds differ in *structure* and consequently also in properties.

It is next important to note that the above two are the *only* formulae which can be constructed with four atoms of carbon and ten atoms of hydrogen, on the assumption that carbon is quadrivalent and hydrogen univalent. Graphic formulae, such as



which at first sight might seem to express constitutions different from either of those given above, will, on examination, be found to be identical with one of the latter. Furthermore, it must be concluded that formula (I) represents the constitution of normal butane, which is formed from ethyl iodide, and formula (II) that of *iso*-butane (or trimethylmethane), which is produced by reducing tertiary butyl iodide (p. 82), a compound known to have the structure,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_3 \\ I \end{matrix}$$

These conclusions are confirmed by a study of (*a*) other methods of formation, (*b*) derivatives of the two hydrocarbons.

Pentanes. Three hydrocarbons of the molecular formula, C_5H_{12}, are known ; two of them—namely, **normal pentane** (b.p. 36°) and ***iso*pentane** (b.p. 28°)—occur in petroleum, and are colourless mobile liquids ; the third, **tetramethylmethane** (b.p. 9·5°), is obtained synthetically (p. 64).

The constitutions of the three pentanes are respectively represented by the following formulae :

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3 \qquad CH_3\cdot CH_2\cdot CH\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

Pentane — *Iso*pentane

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

Tetramethylmethane

These are based on considerations of valency, as well as on a study of the methods of formation of the compounds and of the properties of their derivatives. All three hydrocarbons may be regarded as derived from the butanes (pentane and *iso*pentane from *normal* butane, tetramethylmethane from *iso*butane) by the substitution of a CH_3— group for one atom of hydrogen.

Isomerism. Compounds, such as the two hydrocarbons, C_4H_{10}, or the three hydrocarbons, C_5H_{12}, which have the *same molecular formula, but different constitutions or structures*, are said to be **isomeric.** The phenomenon is spoken of as **isomerism,** and the compounds themselves are called **isomers** or **isomerides** (Gr. *isomerēs*, composed of equal parts). Isomerism, as already explained, is due to a difference in the disposition or state of combination of the atoms in the molecules, and isomeric substances always differ more or less both in physical and in chemical properties.

If one hydrogen atom in each of the three pentanes were 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, other hydrocarbons, 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 obtained, either from petroleum (p. 65) or in other ways.

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 366,319 of the formula, $C_{20}H_{42}$ could, theoretically, be formed.

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

Homologous Series. When the paraffins are arranged in the order of their (increasing) molecular weights they form a series, the

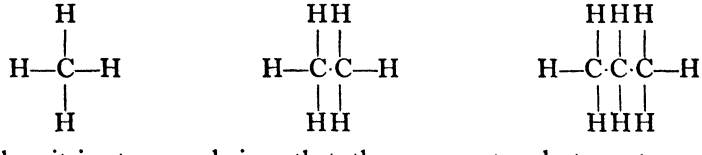
molecular formula of each member of which contains one atom of carbon and two atoms of hydrogen more than the molecular formula of the preceding member :

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

Such a series, the members of which are *similar in constitution, and therefore, also, in chemical properties*, is termed a **homologous series,** and the several members are spoken of as **homologues** of one another; there are many such series of organic compounds, *successive members of which always differ in molecular formula by* CH_2, and indeed any organic compound containing a $\geqslant CH$ group is, theoretically, a member of a homologous series.

Although the members of a homologous series always resemble one another in chemical behaviour, *because* they are similar in structure, both the chemical and the physical properties undergo a gradual and regular *variation* as the molecular weight increases.

General Formulae. 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 formulae of some of the paraffins in the following manner :



when it is at once obvious that there are not only two atoms of hydrogen for every atom of carbon but also two extra ones.

The molecular formula of a gaseous paraffin may be found by the explosion method already described (p. 30), but in the case of liquids and solids a quantitative elementary analysis and molecular weight determination are necessary. The higher members, and isomeric paraffins in general, may often be distinguished and

identified by their boiling-point, melting-point, specific gravity and absorption spectrum.

Nomenclature. In olden times organic compounds were named in a haphazard manner, very often according to their origin, as, for example, marsh-gas, wood-spirit, spirit of wine, and so on; or on a relationship, real or assumed, to some known substance, the structure of which, however, might not have been determined. Many such *trivial* names, often translated into Latin, Greek, etc., are still in common use. Nowadays, as soon as its structure is known a compound may be given a name from which this structure can be deduced provided that the relevant system of nomenclature has been studied.

For this purpose all the members of the homologous series of paraffins are now distinguished by names ending in **ane**, a termination which, by convention, is used only to denote *saturated hydrocarbons*. And except in the case of the first four members (named before the system was adopted), each name has a Greek prefix, which shows the number of carbon atoms in the molecule, as, for example, pentane, C_5H_{12}, and hexane, C_6H_{14}.

When isomerides became known, and had to be distinguished, this was done with the help of additional conventions and the following are now in general use: All those paraffins in the molecules of which no carbon atom is united to more than two others are classed as *normal* (or *n*) hydrocarbons, e.g. normal pentane, normal hexane, and so on,

$$\underset{n\text{-Pentane}}{CH_3—CH_2—CH_2—CH_2—CH_3},$$

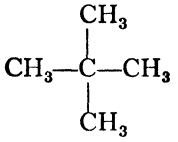
$$\underset{n\text{-Hexane}}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_3}.$$[1]

Solely from the look of their formulae, as written or printed, the normal hydrocarbons then became known as *straight chain* or *unbranched chain* compounds.

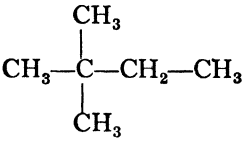
The isomerides of the normal paraffins, showing chains in which a carbon atom is united to more than *two* others, were then called *branched chain* compounds, among which those containing the group $(CH_3)_2CH—$ were distinguished as **iso**-paraffins, e.g. *iso*pentane, *iso*hexane; for convenience the hydrogen atom of a $>CH—$ group is known as a *tertiary* hydrogen atom.

[1] These two formulae may also be expressed by $CH_3{\cdot}[CH_2]_3{\cdot}CH_3$ and $CH_3{\cdot}[CH_2]_4{\cdot}CH_3$ respectively.

Finally, when the molecule contains a carbon atom, directly united to four others, as shown below, the paraffin is termed a *quaternary* hydrocarbon,



Tetramethylmethane

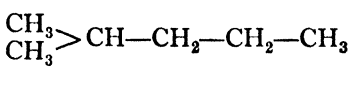


Trimethylethylmethane

As the number of known isomerides gradually increased it became necessary to devise some further method by which the structures of the compounds could be expressed in their names. This was done by regarding each paraffin except the normal (and possibly the *iso*) compound as a derivative of methane, and naming it accordingly, as in the examples just given.

A more general system, by which not only the paraffins but also all their substitution products are given names, which, with numerical additions or Greek letters, express their structures, is that elaborated by a convention held in Geneva in 1892:

(1) The name is based on that of the *longest* normal or straight chain in the molecule, and any hydrocarbon groups which do not form links in this chain are regarded as substituents of the normal chain. Thus, as the longest *normal* chain in *iso*hexane, (I), contains five carbon atoms only, this hydrocarbon is a CH_3— or methyl derivative of *pentane*, whereas the compound (II), the longest normal chain of which contains only four carbon atoms, is a dimethyl*butane*,



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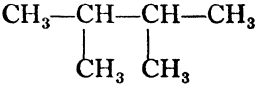
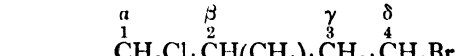


II

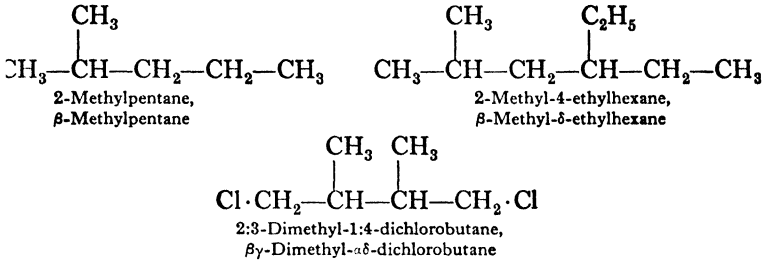
(2) The carbon atoms of the normal or straight chain are then numbered, or lettered in order, starting from either end,[1] so that the position in the molecule of any substituent can be shown:



1-Chloro-4-bromo-2-methylbutane,
α-Chloro-δ-bromo-β-methylbutane

[1] The numbering or lettering usually begins from that end which is nearer to the principal substituent(s), so that the numbers (or letters) are as low as possible.

(3) The name of the paraffin or its derivative is then that of the longest normal chain, preceded by the name or names of its substituents (in an agreed order) with the appropriate numbers or letters. The following formulae with their names will further illustrate this system :



It will be evident that when this system is adopted the structure of the compound can be deduced from its name, but it must again be emphasised that except in the case of the normal compounds, the name does not express directly the number of carbon atoms in the molecule.

Since the members of a homologous series, as a rule, can be obtained by similar or *general methods*, if these are given it is then only necessary to describe, in addition, any *special* method for the preparation of a particular compound. In view, also, of their great similarity in chemical properties, a detailed account of each compound may be omitted, if the *general properties* of the members of the series are described ; the physical properties may also be dealt with in a general manner, since they undergo a regular and gradual variation as the molecular weights of the members increase.

The following is a summary of the principal facts relating to the paraffins, treated in this way ; *it will be found advantageous to omit the study of this and all other summaries until the main text of Part I, at least, has been read.*

SUMMARY AND EXTENSION

The Paraffin or Methane Series. *Saturated* hydrocarbons of the general formula, C_nH_{2n+2}. Some of the simpler members of the series are the following: The number of possible isomerides is

indicated by the figures in brackets, and the boiling-points of the *normal* hydrocarbons are given :

		b.p.			b.p.
Methane	CH_4	−161·5°	Hexane (5)	C_6H_{14}	69°
Ethane	C_2H_6	−89°	Heptane (9)	C_7H_{16}	98·5°
Propane	C_3H_8	−42°	Octane (18)	C_8H_{18}	125·5°
Butane (2)	C_4H_{10}	−0·55°	Nonane (35)	C_9H_{20}	150·7°
Pentane (3)	C_5H_{12}	36°	Decane (75)	$C_{10}H_{22}$	174°

Nomenclature. The names of all the hydrocarbons of this series (also called the **alkanes**) end in **ane** and have a Greek prefix showing, except in the first four, the number of carbon atoms in the molecule; the chain is numbered or lettered as already described (p. 61).

Occurrence. The paraffins are found in nature in enormous quantities as petroleum or mineral naphtha, in small quantities in natural gas, and as earth-wax or ozokerite (p. 66). They are formed in the low temperature carbonisation of coal and by the catalytic hydrogenation of the products of cracked petroleum.

Methods of Formation or Preparation. (1) The alkali salt of a fatty acid (p. 160) is heated 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) The halogen substitution products of the paraffins are reduced with nascent hydrogen,

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

(3) The alkyl halogen compounds, in ethereal solution, are heated with sodium or zinc (Wurtz),

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

(4) The zinc alkyl compounds (p. 233) are decomposed with water (Frankland), or the alkyl magnesium halides (p. 235) are decomposed with water, an alcohol, or a primary or secondary base (p. 213),

$$Zn(CH_3)_2+2H_2O = 2CH_4+Zn(OH)_2,$$
$$C_3H_7\cdot MgI+H_2O = C_3H_8+MgI\cdot OH.$$

(5) The alkyl halogen compounds are treated with the zinc alkyl derivatives, or with the alkyl magnesium halides,

$$2CH_3I+Zn(C_2H_5)_2 = 2CH_3\cdot C_2H_5+ZnI_2,$$
$$C_2H_5I+C_2H_5\cdot MgI = C_4H_{10}+MgI_2.$$

Tertiary or quaternary paraffins are often obtained in this way,

$$(CH_3)_2CHBr+CH_3MgI = (CH_3)_3CH+MgBrI,$$
$$(CH_3)_3CCl+CH_3MgCl = C(CH_3)_4+MgCl_2.$$

(6) Aqueous solutions of the sodium or potassium salts of certain fatty acids are submitted to electrolysis (Kolbe),

$$2CH_3\cdot COOK+2H_2O = CH_3\cdot CH_3+2CO_2+2KOH+H_2.$$

This reaction is of limited application (propionates, for example, give ethylene and a little butane), but it has been used for the preparation of very high members of the series.

(7) Olefines and acetylenes are reduced with hydrogen in the presence of nickel; this method is of great value as many olefines are readily obtained from alcohols of known structure, synthesised by means of the Grignard reagents (p. 235).

(8) Hydroxy-derivatives of the paraffins are reduced with hydriodic acid at high temperatures,

$$C_2H_5\cdot OH+2HI = C_2H_6+H_2O+I_2.$$

Physical Properties. The first four members of the series are gases, while those containing from 5 to about 16 atoms of carbon are liquids under ordinary conditions; the boiling-point rises regularly as the series is ascended, but the difference between the boiling-points of consecutive *normal* hydrocarbons gradually diminishes (see table). The higher members of the series, from about $C_{16}H_{34}$ (m.p. 18°), are solids. The specific gravity gradually increases from butane (sp. gr. 0·6) until the higher members are reached, when it becomes almost constant at 0·775–0·780, this value being determined at the melting-point of the compound in the case of solids.

The paraffins are insoluble, or nearly so, in water, but they are miscible with alcohol, ether, and many other organic liquids.

Chemical Properties. The paraffins are characterised by great stability. At ordinary temperatures the lower normal compounds are not acted on by nitric acid, fuming sulphuric acid, sodium, alkalis, or such powerful oxidising agents as chromic acid and potassium permanganate, and even at higher temperatures they are only very slowly attacked; they are, therefore, easily distinguished from unsaturated hydrocarbons (p. 94), which combine with bromine and with sulphuric acid and are readily oxidised. They react, however, with chlorine and, but far less readily, with bromine in diffused sunlight with the formation of substitution products, the halogen displacing hydrogen of a $-CH_2-$ more readily than that of a $-CH_3$ group, and most readily that of a $>CH$ group (a *tertiary* hydrogen atom). Iodine has no action on the hydrocarbons. Some paraffins are attacked by ozone

at ordinary temperatures ; methane, for example, gives formaldehyde. The higher paraffins, especially those containing a tertiary hydrogen atom, are more reactive than the lower members of the series and this atom may often be displaced directly by $—NO_2$,$—SO_3H$,—OH, etc.

Natural Petroleum

In various districts of North America, in Baku, south-east Russia, Iran, and in other parts of the world, a gas escapes from the earth under considerable pressure, either from a natural fissure or a drilled hole. 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 and for the manufacture of methyl alcohol (p. 106) and other compounds (p. 367). Some natural gas, as, for example, that of Dexter, U.S.A., contains *helium* (1·84%), which has been used in airships because of its non-inflammability.

In the localities already mentioned and in many others, enormous quantities of *petroleum* or *mineral naphtha* [1] are also obtained, either from natural springs or from artificial borings. The world production of petroleum is over 250 million tons per annum.

The origin of natural gas and petroleum is unknown, but it is possible that these mixtures of hydrocarbons have been produced by the destructive distillation, in the lower layers of the earth's crust, of the fatty remains of (sea) animals or plants, or by the action of water on carbides [2] ; the slight optical activity (p. 292) of many samples of petroleum supports the former view.

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 complex mixture of hydrocarbons, that obtained from Pennsylvania and from Iran being composed chiefly of paraffins, that from Baku contains aromatic hydrocarbons, such as toluene, and those of the naphthene or *cyclo*-paraffin series (p. 406).

Natural petroleum is not employed in a raw state, but it is the source of many substances in general use. These commercial

[1] Greek, *naphtha*, a volatile, inflammable liquid issuing from the earth.

[2] Certain carbides, such as aluminium carbide, are decomposed by water, giving paraffins,

$$Al_4C_3+6H_2O = 3CH_4+2Al_2O_3.$$

products are obtained from the crude oil by fractional distillation and the fractions are then purified, if necessary, by treatment with absorbents, such as *bauxite* (which removes coloured substances, p. 6), or by chemical processes.

Some of the more important fractions are : *Benzine* (b.p. 35–80°), *petroleum ether* or *petrol* (b.p. 40–70°), *gasoline* (b.p. 70–90°), and *ligroin* or *light petroleum* (b.p. 80–120°), colourless mobile liquids used in petrol-engines and also as solvents for fats, oils, etc. ; *cleaning oil* (b.p. 120–150°), employed for dry-cleaning purposes, and as a substitute for oil of turpentine in the preparation of varnishes ; *refined petroleum*, *kerosene*, *paraffin*, or burning oil (b.p. 150–300°), used for illuminating purposes, heating, and Diesel engines ; the portions collected above 300° are employed as lubricating oils, and also give *vaseline*, *paraffin-wax*, etc., and the residual carbonaceous mass is used for electrical purposes.

All petroleum products of low boiling-point are highly inflammable, forming explosive mixtures with air (used in petrol-engines); they should be handled with extreme caution. Petroleum for use in lamps should be free from the more volatile paraffins, as shown by a determination of its ' flash-point ', otherwise it may give rise to dangerous explosions. Although corresponding fractions of petroleum from different parts of the world may differ in their chemical composition, any two of a given range of boiling-point have much the same outward properties and are used for similar purposes.

Ordinary paraffin-wax is also obtained from the tar which is produced by the destructive distillation of cannel-coal or shale. It is a waxy substance, soluble in ether, etc., 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. 254).

When shale tar is fractionally distilled, it yields several liquid products similar to those obtained from petroleum, which are used as solvents, for illuminating purposes and as fuel ; also a mixture of solid paraffins, or paraffin-wax, which is purified by treatment with concentrated sulphuric acid and redistillation.

Ozokerite is a naturally occurring solid paraffin or *earth-wax* which is found in Galicia and Rumania ; it is purified by treatment with concentrated sulphuric acid, and when decolourised is known as *ceresine*.

The Cracking of Petroleum

The great demand for the more volatile liquid hydrocarbons (petrol) obtained from crude petroleum by fractional distillation, and the relative cheapness of some of the fractions of high boiling-point, have led to the introduction of commercial processes, known as *cracking*, by which the latter can be partially transformed into the former. In this process the mixtures of hydrocarbons of high boiling-point are passed under pressure through tubes or chambers, heated above a dull-red heat. Very complex reactions occur : gas, containing various hydrocarbons, is evolved, and a proportion of the original liquid is converted into a mixture of hydrocarbons of much lower boiling-point, which can be used in petrol engines or for the manufacture of various other compounds ; at the same time there is a separation of carbon or of hydrocarbons of very high molecular weight, decomposition and combination going on side by side.

The use of catalysts in this process renders it possible to bring about the desired changes at a much lower temperature, and thus to modify the results very materially and obtain better yields of the volatile liquids. Many different substances have been so employed ; not only metals such as iron and copper, but metallic oxides such as alumina and titanium dioxide, and salts such as aluminium chloride. As some of the unsaturated hydrocarbons in these products are readily oxidised in the air and have a nasty smell, the mixtures containing these substances may be reduced with hydrogen in the presence of nickel (p. 405), and thus converted into more suitable petrol substitutes ; alternatively, the two processes may be combined by cracking in the presence of hydrogen.

The importance of the cracking industry can be realised from the fact that at least 120 million tons per annum of petroleum are cracked.

Some of the many products of cracked petroleum are given on p. 368.

Fuels for Internal Combustion Engines

The power developed by a given petrol internal combustion engine increases as the mixture of air and gas or vapour is compressed prior to ignition ; when, however, compression reaches a certain limiting value, the mixture detonates instead of burning, and the efficiency of the engine, which then starts ***knocking***, is

diminished. By a gradual increase of the compression the *knock rating value* or *octane number* can be found for any such fuel.

The octane number depends on the composition and structure of the fuel components ; 2:2:4-*trimethylpentane* (below), miscalled *iso-octane*, is taken as the standard and given the value 100. The octane number of any other fuel is then expressed by the percentage of 2:2:4-trimethylpentane which, in admixture with *n*-heptane, has the same knock rating as that fuel.

In general the normal paraffins have low, whilst those with branched chains have much higher, octane numbers ; olefines and aromatic hydrocarbons also have higher values than normal paraffins.

During investigations on knock rating, etc., many complex hydrocarbons have been synthesised in an almost pure state ; normal heptane, for example, has been prepared by condensing butyraldehyde (butanal) with acetone and reducing the product first to a saturated ketone and then to the paraffin,

$$C_3H_7\cdot CHO + CH_3\cdot CO\cdot CH_3 \longrightarrow C_3H_7\cdot CH{:}CH\cdot CO\cdot CH_3 \longrightarrow$$
$$C_3H_7\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow C_3H_7\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3.$$

2:2:4-*trimethylpentane* is prepared from *iso*butylene (from cracked petroleum), which with sulphuric acid gives di-*iso*butylene, a mixture of 2:4:4-*trimethylpentene*-1 and 2:4:4-*trimethylpentene*-2 ; [1] this mixture is hydrogenated and thus converted into the required paraffin,

$$CH_2{:}CMe_2 \begin{cases} \nearrow CH_2{:}CMe\cdot CH_2\cdot CMe_3 \\ \searrow CH_3\cdot CMe{:}CH\cdot CMe_3 \end{cases} \searrow CH_3\cdot CHMe\cdot CH_2\cdot CMe_3.$$

(1 2 3 4)

It may also be prepared by the direct combination of *iso*butylene and *iso*butane in the presence of 20% sulphuric acid at 70°, an example of a remarkable process known as *alkanation*,

$$Me_3CH + CH_2{:}CMe_2 = Me_3C\cdot CH_2\cdot CHMe_2.$$

The knock rating of a given petrol is greatly increased by the addition of lead tetraethyl (*anti-knock*) which is now added to almost all motor and aviation fuels ; in order to prevent the deposition of lead liberated during the explosion, sufficient ethylene dibromide is also added to convert all the lead into its bromide.

Nowadays little, if any, petrol is a direct or ' straight ' fraction of natural petroleum as any such would have only a very poor knock rating value ; it is all blended from products obtained from cracked petroleum, from carbon monoxide, or from coal. When a mixture

[1] The number following the name of each of these olefines shows the carbon atom at which the double binding (indicated by the terminative *ene*, p. 93) commences ; the paraffin chain is numbered from the other end.

of carbon monoxide and hydrogen is passed over a catalyst of activated iron, cobalt, or nickel at ordinary pressures and at about 200° the chief products are at first carbon dioxide and steam. After the lapse of some hours, however, other reactions set in and oil and water are produced ; the oil consists of paraffins and olefines, from the lower members up to solid waxes, and after suitable fractionation, etc., furnishes many products similar to those obtained from natural petroleum (Fischer-Tropsch method). Petrols, Diesel oils, heating oils and lubricating oils are also obtained by the low temperature carbonisation or catalytic high pressure hydrogenation of coal (Bergius process).

CHAPTER 5

HALOGEN DERIVATIVES OF THE PARAFFINS

WHEN the paraffins are treated with chlorine, substitution occurs, and one, two, three, or more atoms of hydrogen are displaced,

$$CH_4+Cl_2 = CH_3Cl+HCl,$$
$$CH_3Cl+Cl_2 = CH_2Cl_2+HCl,$$

giving chloro-substitution products of the paraffins. Such compounds, however, are usually prepared by other methods, as the action of chlorine on paraffins is slow and incomplete and a complex mixture of products may be formed. Similar compounds of bromine and iodine (almost invariably prepared indirectly) are known, and all these substances are classed together as *halogen substitution products of the paraffins*. They may be divided into mono-, di-, etc., substitution products according to the number of halogen atoms in their molecules; thus CH_3Cl and C_2H_5Br are mono-, CH_2Br_2 and $C_2H_4Cl_2$ are di-, $CHCl_3$ and CHI_3 are tri-, and CCl_4 and $C_2H_2Br_4$ are tetra-substitution products.

Such compounds may also be regarded as halogen esters of known or hypothetical alcohols. Corresponding fluorides are also known.

Mono-halogen Derivatives

These compounds are usually obtained from the alcohols (p. 106); 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
Ethyl chloride	C_2H_5Cl	Ethyl bromide	C_2H_5Br
Propyl chloride	C_3H_7Cl	Propyl bromide	C_3H_7Br
		Methyl iodide	CH_3I
		Ethyl iodide	C_2H_5I
		Propyl iodide	C_3H_7I

Methyl chloride, or chloromethane,[1] CH_3Cl, is one of the four substitution products obtained by treating methane with chlorine in daylight, and is formed in *small* proportions when methyl alcohol is heated with *concentrated* hydrochloric acid,

$$CH_3\cdot OH+HCl = CH_3Cl+H_2O.$$

[1] This nomenclature is explained later (p. 81).

It is prepared by passing hydrogen chloride into methyl alcohol containing anhydrous zinc chloride (*Groves'* process), as described in the case of ethyl chloride (below); also by heating methyl alcohol with sodium chloride and concentrated sulphuric acid, that is to say, with hydrogen chloride and sulphuric acid.[1]

It is a gas, which liquefies at $-24°$ under ordinary atmospheric pressure. It burns with a green-edged flame, is moderately easily soluble in water, and when heated with water or aqueous alkalis under pressure, it is converted into methyl alcohol,

$$CH_3Cl+HOH = CH_3\cdot OH+HCl.$$

Methyl chloride is employed on the large scale in the preparation of various dyes, and the compressed gas is also used for the production of a low temperature; for these purposes it may be manufactured by heating crude trimethylamine hydrochloride (p. 219) with hydrochloric acid,

$$N(CH_3)_3,HCl+3HCl = 3CH_3Cl+NH_4Cl,$$

or by the methods given above.

Methyl bromide, CH_3Br (b.p. 4·5°), and **methyl iodide,** CH_3I (b.p. 43°), are prepared by methods similar to those employed in the case of the corresponding ethyl compounds, which they closely resemble in chemical properties. The former is largely used as a fire extinguisher, especially in aircraft, and methyl iodide is a very important reagent in organic chemistry (pp. 74, 82, 236).

Ethyl chloride, or chloroethane, C_2H_5Cl, is formed when ethane is treated with chlorine in daylight, and when alcohol is heated with concentrated hydrochloric acid, or treated with phosphorus pentachloride, or trichloride, at ordinary temperatures,

$$C_2H_5\cdot OH+PCl_5 = C_2H_5Cl+POCl_3+HCl.[2]$$

Ethyl chloride is prepared by Groves' process—namely, by passing dry hydrogen chloride into absolute alcohol, to which about half its weight of anhydrous zinc chloride has been added,

$$C_2H_5\cdot OH+HCl = C_2H_5Cl+H_2O.$$

[1] The action of an acid on an alcohol is reversible, and reagents such as zinc chloride and sulphuric acid are usually employed to make the reaction proceed so far as possible in the desired direction (compare p. 188). These reagents are not usually included in the equation although their presence is essential for the success of the operation.

[2] This equation represents only one of several reactions which take place (p. 108).

The flask containing the mixture is connected with a reflux condenser 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 as it passes up the condenser, and the liquid runs back into the flask. The gaseous ethyl chloride is passed through three wash-bottles containing water, dilute aqueous alkali, and concentrated sulphuric acid respectively, by which means it is freed from hydrogen chloride, alcohol, and moisture; the purified ethyl chloride is then collected in a U-tube immersed in a freezing mixture.

Ethyl chloride, like methyl chloride, may also be prepared by warming a mixture of anhydrous alcohol, concentrated sulphuric acid, and sodium chloride; it is obtained commercially by the combination of ethylene and hydrogen chloride under pressure in the presence of a catalyst such as aluminium chloride, charcoal, or bauxite.

It is a liquid, boiling at 12·5°; it burns with a greenish, smoky flame, and is only sparingly soluble in water, but it is miscible [1] with alcohol, ether, etc. When heated with water or aqueous alkalis under pressure, it yields ethyl alcohol,

$$C_2H_5Cl+HOH = C_2H_5\cdot OH+HCl;$$

on treatment with chlorine in sunlight, it gives di-, tri-, etc. substitution products of ethane. It does not give an immediate precipitate with an aqueous solution of silver nitrate, but from a warm *alcoholic* solution, silver chloride is quickly precipitated,

$$C_2H_5Cl+AgNO_3 = C_2H_5\cdot O\cdot NO_2+AgCl.$$

Ethyl chloride is used as a local anaesthetic in dentistry, etc., as a refrigerant, and for preparing lead tetraethyl (p. 235).

Ethyl bromide, or bromoethane, C_2H_5Br, is formed when alcohol is heated with concentrated hydrobromic acid, or treated with phosphorus tribromide or pentabromide, at ordinary temperatures,

$$C_2H_5\cdot OH+PBr_5 = C_2H_5Br+POBr_3+HBr.$$ [2]

It may be prepared by adding coarse hydrated sodium bromide ($NaBr,2H_2O$; 37 g.) to a cold mixture of alcohol (37 c.c.) and

[1] Two or more liquids are *miscible* when they give a homogeneous solution in *all* proportions.

[2] Compare footnote, p. 108.

concentrated sulphuric acid (37 c.c.), diluted with water (25 c.c.), and then distilling the mixture slowly.

The materials are placed in a distillation flask, which is connected with a condenser, and, in order to avoid loss of ethyl bromide by evaporation, the other end of the condenser dips under water contained in the receiver. The heavy oil is separated with the aid of a tap-funnel, and shaken with a dilute solution of sodium carbonate to free it from bromine, hydrobromic acid, and alcohol; when this is done in a tap-funnel, the funnel is grasped firmly by the stoppered end, inverted, and *gently* agitated; the tap is then opened for a moment to allow the carbon dioxide to escape, otherwise the pressure of this gas may blow out the stopper or burst the tap-funnel. These operations are repeated until no further evolution of gas occurs, and the oil is then washed with water, dried with calcium chloride, and purified by distillation.

Ethyl bromide is also prepared by combining ethylene with hydrogen bromide. It is a pleasant-smelling, heavy liquid, and boils at 38·5°; it resembles ethyl chloride in its behaviour towards water, aqueous alkalis, and silver nitrate.

Ethyl iodide, or iodoethane, C_2H_5I, is formed when alcohol is heated with concentrated hydriodic acid; it is prepared by gradually adding iodine (65 g.), in small quantities at a time, to a mixture of alcohol (25 g.) and red phosphorus (5 g.), and then distilling from a water-bath,

$$3C_2H_5 \cdot OH + P + 3I = 3C_2H_5I + H_3PO_3.$$

The product is purified exactly as described in the case of ethyl bromide.

Ethyl iodide is a pleasant-smelling, highly refractive liquid, boiling at 72°; on exposure to light it slowly turns yellow or brown, owing to the separation of iodine, a phenomenon which is observed in the case of nearly all organic compounds containing iodine. In chemical properties it closely resembles ethyl chloride and ethyl bromide.

Other halogen mono-substitution products of the paraffins, or halogen esters, such as *propyl bromide*, C_3H_7Br, *butyl iodide*, C_4H_9I, etc., may be prepared by methods similar to those given above.

All the halogen *mono*-substitution products of the paraffins are classed as **alkyl halogen compounds** or **alkyl halides** (p. 80); they are very much used in the preparation of other substances and

are constantly referred to later. They are nearly all neutral, pleasant-smelling liquids, mostly specifically heavier than water, in which they are practically insoluble; their physical properties, however, depend greatly on the halogen which they contain, as will be seen from the following data:

		d. at 0°	b.p.			*d.* at 0°	b.p.
Methyl chloride	CH_3Cl	—	−24°	Ethyl chloride	C_2H_5Cl	0·921	12·5°
Methyl bromide	CH_3Br	1·73	+4·5°	Ethyl bromide	C_2H_5Br	1·47	38·5°
Methyl iodide	CH_3I	2·33	43°	Ethyl iodide	C_2H_5I	1·975	72°

The alkyl halogen compounds resemble one another very closely in chemical properties, and the following are some of their more important reactions:

They are reduced by nascent hydrogen giving paraffins (p. 50),

$$C_2H_5Br+2H = C_2H_6+HBr.$$

They react with sodium giving paraffins (Wurtz reaction, p. 53),

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

They are slowly decomposed, or hydrolysed (p. 189), by boiling water, by **aqueous** alkalis, and by moist silver oxide (which acts as AgOH), yielding the alcohols,

$$C_2H_5Br+KOH = C_2H_5\cdot OH+KBr;$$

but when boiled with **alcoholic** potash,[1] those containing two or more carbon atoms are converted into olefines (p. 87),

$$C_3H_7I+KOH = C_3H_6+KI+H_2O.$$

They do not react readily with silver nitrate in aqueous solution, but when their alcoholic solutions are heated with this, or with other silver salts, or with salts in general, they undergo double decomposition and give *esters* (p. 185),

$$CH_3I+AgNO_3 = CH_3\cdot O\cdot NO_2+AgI,$$
$$C_2H_5Br+AgC_2H_3O_2 = C_2H_5\cdot C_2H_3O_2+AgBr.$$

They combine directly with magnesium in the presence of ether, giving a most important class of compounds (the *Grignard reagents*), of which a description is given later (p. 235).

[1] Alcoholic potash (a solution of potassium hydroxide in methyl or ethyl alcohol) often has an action on organic compounds different from that of an aqueous solution of potassium hydroxide, as in the above example; since it may contain a variable proportion of water, the results of its action may vary with the percentage of water as well as that of alkali (p. 94).

The monohalogen derivatives of propane and of 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. 102·5°) and iso*propyl iodide*, $CH_3 \cdot CHI \cdot CH_3$ (b.p. 89·5°). The monohalogen derivatives of butane also correspond with the four alcohols, $C_4H_9 \cdot OH$; two of them, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2X$ and $CH_3 \cdot CH_2 \cdot CHX \cdot CH_3$, are derived from normal butane, and 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 *iso*butane.

Di-halogen Derivatives

The halogen di-substitution products of the paraffins have the general formula, $C_nH_{2n}X_2$, and are obtained from olefines (p. 85), aldehydes (p. 133), or ketones (p. 144), and in other ways.

Methylene dichloride (dichloromethane), CH_2Cl_2, a heavy liquid, boiling at 41°, is prepared by reducing chloroform with zinc and hydrochloric acid in alcoholic solution,

$$CHCl_3 + 2H = CH_2Cl_2 + HCl.$$

Methylene di-iodide, CH_2I_2, is prepared by reducing iodoform with sodium arsenite and caustic soda; it boils at 181°, and owing to its high density (3·33 at 15°) is used, mixed with other liquids, in determining the specific gravities of minerals.

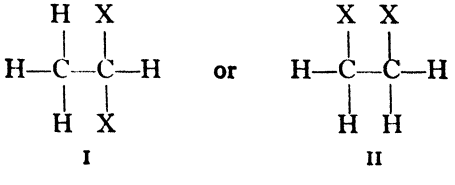
Ethylene dichloride, $C_2H_4Cl_2$, and **ethylene dibromide,** $C_2H_4Br_2$, are described later (p. 91).

Ethylidene dibromide, $C_2H_4Br_2$ (b.p. 110°), is obtained by treating acetaldehyde with phosphorus pentabromide (p. 156),

$$C_2H_4O + PBr_5 = C_2H_4Br_2 + POBr_3,$$

or acetylene with hydrogen bromide.

When the structure of ethane is considered it will be seen that, although all the hydrogen atoms are similarly situated, two isomeric di-halogen substitution products may be derived from it,



In (I), the halogen atoms are both combined with the *same* carbon atom, but in (II) with different carbon atoms. These formulae (when X = Br) represent ethylidene dibromide or unsymmetrical dibromoethane (I), and ethylene dibromide or symmetrical dibromoethane (II). The two compounds may be distinguished by boiling each with a solution of potassium carbonate when ethylene dibromide yields glycol (p. 240) and ethylidene dibromide gives acetaldehyde (p. 138).

Tri- and Tetra-halogen Derivatives

The more important members of these groups are those derived from methane, such as chloroform, bromoform, and iodoform.

Chloroform, or trichloromethane, $CHCl_3$, is formed when methane, methyl chloride, or methylene dichloride is treated with chlorine in daylight, and when many simple organic substances containing oxygen, such as ethyl alcohol, acetone, etc., 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 fresh bleaching-powder (about 275 g.) is made into a cream with about 800 c.c. of water and placed in a 2-litre flask connected with a condenser ; acetone (28 g., 35 c.c.), diluted with water (about 70 c.c.), is then gradually added, and the flask is *cautiously* heated on a water-bath ; a vigorous reaction usually sets in, and a mixture of chloroform, water, and 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 acetone is present, the chloroform must be precipitated by adding water. The oil is run off with the aid of a tap-funnel, washed with water, shaken once or twice with a little concentrated sulphuric acid, which frees it from water, acetone, etc., and redistilled from a water-bath. Yield about 24 g.

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 present in the bleaching-powder (or produced during the reaction), yielding chloroform and calcium formate:

$$CH_3\cdot CH_2\cdot OH + CaOCl_2 = CH_3\cdot CHO + CaCl_2 + H_2O,$$
$$2CH_3\cdot CHO + 6CaOCl_2 = 2CCl_3\cdot CHO + 3Ca(OH)_2 + 3CaCl_2,$$
$$2CCl_3\cdot CHO + Ca(OH)_2 = 2CHCl_3 + (H\cdot COO)_2Ca.$$

When acetone is employed, trichloroacetone 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 also prepared commercially by the reduction of carbon tetrachloride (p. 79) with iron and water.

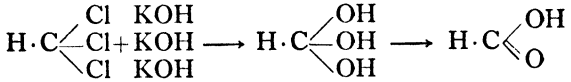
The product of these methods may be impure ; pure chloroform is best prepared by warming chloral or chloral hydrate (p. 143) with a solution of sodium hydroxide, and then isolating the product in the manner already described,

$$CCl_3\cdot CHO+NaOH = CHCl_3+H\cdot COONa.$$

Chloroform is a heavy, pleasant-smelling liquid of sp.gr. 1·5 at 15°, and boils at 61° ; when 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,

$$CHCl_3+4KOH = H\cdot COOK+3KCl+2H_2O.$$

The stages of the reaction may be indicated as follows :



When a drop of chloroform is added to a mixture of aniline (p. 443) and alcoholic potash, and the solution is gently warmed, an intensely nauseous smell is observed, owing to the formation of *phenylcarbylamine* or *phenyl* iso*cyanide*,[1]

$$CHCl_3+3KOH+C_6H_5\cdot NH_2 = C_6H_5\cdot NC+3KCl+3H_2O.$$

This reaction affords a very delicate test for chloroform (and for primary amines, p. 216), and it is known as Hofmann's **carbylamine reaction.**

Chloroform is employed in surgery, usually mixed with ether, as an anaesthetic, its vapour when inhaled causing unconsciousness (Simpson, 1848). For this purpose pure chloroform must be employed, as the impure substance is dangerous. In the presence of air, chloroform gradually undergoes decomposition, especially

[1] The experiment should be performed in a test-tube, with *one drop* only of aniline, and the contents of the test-tube should afterwards be carefully poured into the sink pipe, in a draught closet if possible.

under the influence of light, carbonyl chloride (phosgene) and hydrochloric acid being produced,

$$CHCl_3 + O = COCl_2 + HCl.$$

As carbonyl chloride is very poisonous, all chloroform required for anaesthetic purposes should be kept in the dark in a well-stoppered bottle; a little alcohol (1–2%) is generally added to convert any carbonyl chloride which might be formed into diethyl carbonate,

$$COCl_2 + 2C_2H_5 \cdot OH = 2HCl + CO(OC_2H_5)_2.$$

Pure chloroform gives no precipitate with silver nitrate, and does not darken when it is shaken with concentrated sulphuric acid or with a strong solution of potassium hydroxide. Chloroform is also used as a solvent.

Chloropicrin, or nitrochloroform, $CCl_3 \cdot NO_2$, is formed by the action of nitric acid on chloral and certain other tri-chloro-compounds. It is prepared by the action of bleaching-powder on picric acid (p. 485). It is a liquid boiling at 112° and has been used as a poison gas.

Iodoform, or tri-iodomethane, CHI_3, is formed when *ethyl alcohol* (but *not* methyl alcohol), *acetaldehyde*, *acetone*, and other methyl ketones are warmed with iodine and an aqueous solution of an alkali hydroxide or alkali carbonate; the changes which occur are due to the formation of hypoiodite, and are doubtless similar to those which take place in the preparation of chloroform (p. 76).

All alcohols and all ketones, which contain the group, $CH_3 \cdot CH(OH)$—, or $CH_3 \cdot CO$— respectively, yield iodoform under the above conditions, the —CH(OH)— or —CO— group being converted into —COOH, the CH_3— group into iodoform. When bromine or chlorine is used instead of iodine, a similar change occurs, and *bromoform*, $CHBr_3$ (b.p. 151°), or chloroform separates; this reaction is of considerable practical importance, and is often used for the conversion of a ketone into an acid containing one atom of carbon less than the original substance.

Iodoform may be prepared by gradually adding a dilute solution of sodium hypochlorite to potassium iodide (25 g.), acetone (3 g.), and sodium hydroxide (1 g.), which are dissolved together in about 750 c.c. of water, until no further precipitate is formed; the iodoform is then separated by filtration, and may be purified by recrystallisation from dilute alcohol. On the large scale it is obtained by the electrolysis of an aqueous solution of alcohol, potassium

iodide, and sodium carbonate, the iodine, liberated at the anode, giving hypoiodite, which then gives iodoform. It crystallises in lustrous, *yellow*, six-sided plates, melts at 120°, 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.

Carbon tetrachloride, or tetrachloromethane, CCl_4, the final product of the action of chlorine on CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$, may be formed by passing chlorine into boiling chloroform in sunlight, and is manufactured by passing chlorine into carbon disulphide in the presence of iodine (p. 179), or from carbon disulphide and sulphur monochloride in the presence of iron,

$$CS_2+3Cl_2 = CCl_4+S_2Cl_2,$$
$$CS_2+2S_2Cl_2 = CCl_4+6S.$$

In the former case the chloride of sulphur is removed, after a preliminary distillation, by shaking the product with caustic soda, and the carbon tetrachloride is purified by redistillation. Carbon tetrachloride is a pleasant-smelling liquid of sp. gr. 1·60 at 15°, boiling at 76·5°; on treatment with nascent hydrogen, it is successively converted into $CHCl_3$, CH_2Cl_2, CH_3Cl, and CH_4. It is decomposed by hot alcoholic potash, but the reaction is complex and the chief products are carbon monoxide and ethyl orthoformate. It is used as a solvent and in fire-extinction.

Difluorodichloromethane, CF_2Cl_2, is prepared from carbon tetrachloride and antimony trifluoride. It boils at −30° and is an important refrigerant (*Freon*) as it is non-toxic, non-inflammable, and does not corrode metals. Other fluoro-compounds are important solvents and plastics.

Radicals. A study of the constitutions or structures of organic compounds clearly shows that certain groups of atoms often remain unchanged during a whole series of reactions. Ethane, for example, may be converted into ethyl chloride, the latter may be transformed into ethyl alcohol, and this compound may be reconverted into ethyl chloride; but during all these interactions the group, C_2H_5—, remains unchanged, and behaves, in fact, as if it were a single atom.

$$C_2H_5\cdot H+Cl_2 = C_2H_5\cdot Cl+HCl,$$
$$C_2H_5\cdot Cl+H\cdot OH = C_2H_5\cdot OH+HCl,$$
$$C_2H_5\cdot OH+PCl_5 = C_2H_5\cdot Cl+HCl+POCl_3.$$

Similarly, the compounds, $CH_3\cdot H$, $CH_3\cdot Cl$, $CH_3\cdot OH$, may be transformed one into the other, and there are many other examples.

Groups of atoms, such as CH_3— and C_2H_5—, which act like *single atoms*, and which occur in a considerable number of compounds, are termed **radicals,** or sometimes compound radicals.

Radicals may be univalent, bivalent, etc., according as they act like univalent, bivalent, etc., atoms; the radicals C_2H_5— and CH_3—, for example, are univalent because they are united with one atom of hydrogen or its valency equivalent, as shown in the compounds just given.

The class name, **alkyl,** is given to all the *univalent* groups of atoms which, *theoretically*, are obtained when one atom of hydrogen is removed from the molecule of a paraffin, methane, ethane, etc.; the distinctive names of these radicals are derived from those of the hydrocarbons by changing the termination *ane* into *yl*, thus: *methyl*, CH_3—; *ethyl*, C_2H_5— or $CH_3 \cdot CH_2$—; *propyl*, C_3H_7— or $CH_3 \cdot CH_2 \cdot CH_2$—; iso*propyl*, C_3H_7— or $(CH_3)_2CH$—; normal *butyl*, C_4H_9— or $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2$—; iso*butyl*, C_4H_9— or $(CH_3)_2CH \cdot CH_2$—, etc.

The paraffins, the compounds formed by the combination of these *hypothetical* alkyl radicals with hydrogen—as, for example, $CH_3 \cdot H$, $C_2H_5 \cdot H$, $C_3H_7 \cdot H$—were formerly called the *alkyl hydrides*; 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 any alkyl radical—as, for example, in the formula $R \cdot Br$, which is that of an alkyl bromide. The symbols Me, Et, Pr, Bu, etc., are also often used instead of CH_3—, C_2H_5—, C_3H_7—, C_4H_9—, etc., and when the radical may be one of two isomeric forms—as, for example, in the case of C_3H_7—, which may be either $CH_3 \cdot CH_2 \cdot CH_2$— or $(CH_3)_2CH$—, the former is represented by Pr^{α}, the latter by Pr^{β}.

The name **alkylene** is given to the *bivalent* radicals, which may be regarded as derived from the paraffins by the removal of two hydrogen atoms; certain of these radicals are capable of existing alone, and are then called *olefines*. The compounds which the alkylenes form, with chlorine for example, such as CH_2Cl_2, $C_2H_4Cl_2$, are termed collectively the *alkylene dichlorides*, and so on.

Other radicals of great importance are: hydroxyl, —OH; carbonyl, $>CO$; carboxyl, $—CO \cdot OH$; cyanogen, —CN; acetyl, $—CO \cdot CH_3$; and the aldehyde, —CHO, amino-, $—NH_2$, and nitro-, $—NO_2$, groups.

One of the principal objects of the student should be to learn the

reactions of these and of other groups, and how the groups determine the properties of the molecules of which they form a part. Since any radical usually *behaves more or less independently of the rest of the molecule, the reactions of the compound depend on those of its constituent groups* (pp. 143, 164).

SUMMARY AND EXTENSION

Halogen Compounds of various types, $C_nH_{2n+1}X$, $C_nH_{2n}X_2$, $C_nH_{2n-1}X_3$, etc., are derived from the paraffins by the displacement of one or more hydrogen by halogen atoms.

Nomenclature. The monohalogen compounds are given names showing the hydrocarbon (radical) and halogen from which they are derived, but when the paraffin shows isomerism and the name no longer gives the *structure* of the molecule, the compound is regarded as a *substitution* product of the hydrocarbon, and is named according to the system already given (p. 61). Thus, the four isomerides, C_4H_9Cl, may be named as shown, or Greek letters may be used instead of numerals :

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl$	$CH_3 \cdot CH_2 \cdot CHCl \cdot CH_3$
1-Chlorobutane	2-Chlorobutane
$CH(CH_3)_2 \cdot CH_2Cl$	$C(CH_3)_2Cl \cdot CH_3$
1-Chloro-2-methylpropane	2-Chloro-2-methylpropane

Di-, tri-, and tetra-, etc., halogen derivatives are also named according to this latter system, except in the case of a few compounds with well-known less systematic names ; $CH_2Br \cdot CH_2 \cdot CH_2Br$, for example, is often called trimethylene dibromide instead of 1:3-dibromopropane.

General Methods of Preparation. (1) Alcohols are treated with halogen acids, or with an alkali metallic halide, or halogen acid and sulphuric acid ; the lower chlorides are often prepared by Groves' process (p. 71),

$$R \cdot OH + HX = R \cdot X + H_2O.$$

(2) Alcohols are treated with phosphorus tri- or penta-halides, or with red phosphorus and bromine or iodine (p. 108),

$$3R \cdot OH + P + 3I = 3RI + H_3PO_3.$$

(3) Hydrocarbons of the olefine (p. 85) and acetylene (p. 97) series are treated with halogens or with halogen acids,

$$C_2H_4 + Br_2 = C_2H_4Br_2,$$
$$C_2H_4 + HI = C_2H_5I.$$

(4) Aldehydes (p. 133) and ketones (p. 144) are treated with phosphorus penta-halides,

$$CH_3 \cdot CHO + PCl_5 = CH_3 \cdot CHCl_2 + POCl_3,$$
$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3.$$

(5) Iodides are often prepared by treating chlorides or bromides with a solution of sodium iodide in acetone.

The paraffins, treated with chlorine (or sometimes bromine), give substitution products, which are usually mixtures ; nevertheless the chlorination of various petroleum fractions is very important commercially (p. 120).

Special Methods of Preparation. Chloroform is prepared from alcohol or acetone and bleaching-powder, from carbon tetrachloride, and by the hydrolysis of chloral (p. 77). Iodoform is made from alcohol or acetone with an iodide and a hypochlorite, or electrolytically (p. 78). Carbon tetrachloride is prepared from carbon disulphide (p. 79).

Physical Properties. Halides are mostly neutral, pleasant-smelling liquids, practically insoluble in, and heavier than, water, but methyl chloride and the lower alkyl fluorides are gases at ordinary temperatures and the lower alkyl chlorides are lighter than water. The density and the boiling-point increase in every series, RF<RCl<RBr<RI (p. 80), and it will be seen from the table that the boiling-points of isomerides fall as the branching of the chain increases.

		Fluoride b.p.	Chloride b.p.	Bromide b.p.	Iodide b.p.
Methyl CH_3X		−78°	−24°	4·5°	43°
Ethyl C_2H_5X		−32°	12·5°	38·5°	72°
Propyl	C_3H_7X	−3°	46·5°	71°	102·5°
*Iso*propyl		−11°	35°	59°	89·5°
n-Butyl	C_4H_9X	32° (746 mm.)	78·5°	101°	131°
Sec. butyl		25°	68°	91°	120°
*Iso*butyl		16°	69°	91°	120°
Tert. butyl [1]			52°	72°	100°

Chemical Properties. The reactions of these halides depend almost entirely on the presence of the halogen atom or atoms, all of which, as a rule, behave similarly, but iodides are more reactive than bromides, and the latter are more reactive than chlorides.

The *alkyl halides*, RX, show the following reactions :

(1) They are reduced by nascent hydrogen giving paraffins,

$$RX + 2H = R \cdot H + HX.$$

[1] Derived from secondary, *iso* and tertiary butyl alcohols respectively.

(2) With sodium they give paraffins,

$$RX+2Na+R'X = R\cdot R'+2NaX.$$

(3) They are acted on by *aqueous alkali*, or moist silver oxide, with the displacement of the halogen by a hydroxyl group,

$$R\cdot X+NaOH = R\cdot OH+NaX.$$

(4) When they are boiled with *alcoholic potash* the halogen is removed together with a hydrogen atom from the neighbouring carbon atom and an olefine is formed (p. 85), or it is displaced by $-OEt$,

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

(5) With the sodium derivatives of alcohols they give ethers (p. 125),

$$RX+NaOR' = R\cdot O\cdot R'+NaX.$$

(6) When they are heated with potassium cyanide, nitriles or cyanides (p. 360) are produced,

$$RX+KCN = R\cdot CN+KX.$$

Silver cyanide, however, gives *iso*nitriles (also called *iso*cyanides or carbylamines, p. 361),

$$RX+AgCN = R\cdot NC+AgX.$$

(7) In alcoholic solution with silver or other salts of many acids they give esters (p. 185),

$$RX+AgOOC\cdot CH_3 = ROOC\cdot CH_3+AgX,$$
$$RX+AgO\cdot NO_2 = R\cdot O\cdot NO_2+AgX.$$

Silver nitrite, however, yields a nitro-compound (p. 192) as well as an ester.

(8) They react with ammonia in alcoholic solution producing mixtures of amines (p. 214). Primary amines are best prepared from them with the aid of phthalimide (p. 226).

(9) They react with magnesium in the presence of ether, giving the Grignard reagents (p. 235),

$$RX+Mg = R\cdot Mg\cdot X.$$

(10) They react with the sodium derivative of diethyl malonate (p. 207) and of ethyl acetoacetate (p. 200).

The following are some of the compounds into which ethyl iodide may be converted ; the numbers refer to the reactions given above :

(1) C_2H_6, (2) C_4H_{10}, (3) $C_2H_5\cdot OH$, (4) C_2H_4,
(5) $(C_2H_5)_2O$, (6) $C_2H_5\cdot CN$, $C_2H_5\cdot NC$, (7) $C_2H_5\cdot OOC\cdot CH_3$,
(8) $C_2H_5\cdot NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $(C_2H_5)_4NI$,
(9) $C_2H_5\cdot MgI$.

Di-halogen derivatives in which the two halogen atoms are combined with *different* carbon atoms show, as a rule, reactions corresponding with those of the alkyl halides, but both the halogen atoms take part in the change. Ethylene dibromide, for example, gives a dihydroxy-derivative (p. 241), a dicyanide (p. 277), and an acetylenic hydrocarbon,

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2KOH = \begin{matrix} CH \\ \| \\ CH \end{matrix} + 2KBr + 2H_2O.$$

Ethylene dibromide, trimethylene dibromide and a few other compounds of a similar type are much used in syntheses.

Di- and *tri*-halogen derivatives, in which the halogen atoms are united to the *same* carbon atom, behave in the same way as the alkyl halides towards aqueous alkalis, but water is eliminated from the primary product, with the formation of an aldehyde, ketone, or acid (as a salt),

$$CH_3 \cdot CHBr_2 \xrightarrow{2H_2O} CH_3 \cdot CH(OH)_2 \longrightarrow CH_3 \cdot CHO,$$

$$(CH_3)_2CCl_2 \xrightarrow{2H_2O} (CH_3)_2C(OH)_2 \longrightarrow (CH_3)_2C{:}O,$$

$$CHCl_3 \xrightarrow{3H_2O} CH(OH)_3 \longrightarrow H \cdot CO \cdot OH.$$

Tri-halogen compounds which contain only one carbon atom are attacked by alcoholic potash in the same way as by aqueous alkali; thus chloroform yields potassium formate and potassium chloride.

Many secondary and tertiary halides, containing the group $>$ CHX or $\rightarrow$ CX respectively, especially the latter, do not show the reactions 6, 8 and 10 (see above), but give olefines (4), with the loss of HX.

CHAPTER 6

THE OLEFINES, OR HYDROCARBONS OF THE ETHYLENE SERIES

WHEN the halogen mono-substitution products of the paraffins (the *alkyl halides*), such as ethyl bromide, propyl chloride, etc. (p. 70), are heated with an alcoholic solution of potash, they may be converted into hydrocarbons,

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

The molecules of the compounds obtained in this way, and by other methods, contain two atoms of hydrogen less than those of the corresponding paraffins, and may be regarded as alkylene radicals (p. 80); as, moreover, the new hydrocarbons are formed by similar processes from compounds which resemble one another in structure, they themselves are similar in constitution, 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* or *ene*,[1]

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 this series is *ethylene*; a hydrocarbon, CH_2, which would correspond with methane, is *unknown*, and all attempts to prepare it from a halogen mono-substitution product of methane, or in other ways, have been unsuccessful; this seems to show that a compound in which carbon would be *bivalent* is incapable of existence.

The word **olefine** is derived from that of *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 term 'olefine' is now applied as a *class name* to all the hydrocarbons of this series.

Ethylene, C_2H_4, is formed during the destructive distillation of many organic substances, and occurs in coal-gas, of which it

[1] As the termination *ene* shows that the compound is an olefine the letters *yl* in *ylene* are frequently omitted, ethylene becoming *ethene*, and so on.

forms about 3% by volume ; the luminosity of a coal-gas flame is partly due to ethylene.

Ethylene is obtained when acetylene (p. 97), in the form of copper acetylide, is reduced with zinc dust and ammonia,

$$C_2H_2+2H = C_2H_4.$$

It is also formed when a solution of potassium succinate (p. 276) is submitted to electrolysis (Kekulé),

$$\begin{matrix}CH_2\cdot COOK\\ |\\ CH_2\cdot COOK\end{matrix} +2H_2O = \overbrace{C_2H_4}+\overbrace{2CO_2}+2KOH+H_2.$$

A mixture of ethylene and carbon dioxide rises from the anode, while hydrogen and potassium hydroxide are produced at the cathode. This method of formation of ethylene recalls the production of ethane by the electrolysis of potassium acetate (p. 53).

Ethylene may be prepared in the laboratory by heating ethyl alcohol with concentrated sulphuric acid or with phosphoric acid ; the *final results* may be expressed by the equation,

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

but the reaction really takes place in two stages (p. 195).

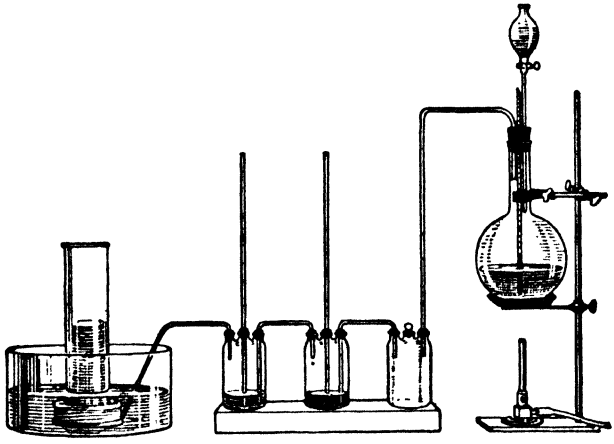


Fig. 18

A mixture of ethyl alcohol (60 c.c.) and concentrated sulphuric acid (160 c.c.) is placed in a large flask (Fig. 18), and heated to

about 165° (the bulb of the thermometer is immersed in the *liquid*)[1]; the gas thus produced is passed first through water and then through dilute potash, in order to free it from sulphur dioxide and carbon dioxide, and is finally collected over water. When the evolution of gas slackens, a further supply may be obtained by dropping a mixture of equal volumes of alcohol and sulphuric acid through the funnel, at the same temperature as before. The liquid in the flask generally darkens considerably, owing to the oxidising action of the acid, and when impure alcohol is used a large quantity of carbonaceous matter is often formed. For this reason phosphoric acid may be advantageously employed, in which case the alcohol is dropped into syrupy phosphoric acid heated at about 220°; the yield by this method is good, and for most purposes the gas does not require purification.

Another, but less satisfactory, method is by dropping ethyl bromide from a stoppered funnel into a flask containing an excess of boiling alcoholic potash,

$$C_2H_5Br+KOH = C_2H_4+KBr+H_2O.$$[2]

The flask is heated on a water-bath, and is provided with a reflux condenser (p. 7), the end of which is connected to a delivery tube passing to the pneumatic trough; during the reaction potassium bromide separates from the solution.

Ethylene is prepared commercially from cracked petroleum and by cracking propane obtained from natural gas,

$$C_3H_8 = C_2H_4+CH_4,$$

but where petroleum is too expensive, the gas is produced by the catalytic dehydration of alcohol with heated phosphoric acid or alumina.

It is to be noted that a reversible reaction may often be carried out on a large scale in one or the other direction according to the available raw material: thus $C_2H_5\cdot OH \longrightarrow C_2H_4$ in the U.K., but $C_2H_4 \longrightarrow C_2H_5\cdot OH$ in the U.S.A.

Ethylene is a gas with a sweet and rather pleasant smell; it liquefies at 10° under a pressure of 60 atmospheres and boils at −105° under 1 atmosphere; it is very sparingly soluble in water,

[1] In the presence of about 5% of anhydrous aluminium sulphate the reaction takes place more rapidly, and the mixture need not be heated so strongly.

[2] Compare footnote, p. 74.

more readily in alcohol and ether. It burns with a luminous flame, and forms a highly explosive mixture with air or oxygen,

$$C_2H_4+3O_2 = 2CO_2+2H_2O.$$

Its chemical behaviour is totally different from that of the paraffins. It combines *directly* with hydrogen, in the presence of nickel, at temperatures from about 75–120° and, in the presence of platinum black, at ordinary temperatures, forming ethane,

$$C_2H_4+H_2 = C_2H_6.$$

Although it is not readily acted on by hydrochloric acid (p. 72), it combines *directly* with hydrogen bromide and iodide in concentrated aqueous solution at 100°, forming ethyl bromide and iodide respectively,

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

It combines *directly* with chlorine and bromine (p. 91), and also with iodine in alcoholic solution,

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

It is absorbed by, and combines *directly* with warm sulphuric acid and with cold anhydro-sulphuric acid, yielding ethyl hydrogen sulphate (p. 194),[1]

$$C_2H_4+H_2SO_4 = C_2H_5\cdot HSO_4.$$

It is readily oxidised by a cold solution of potassium permanganate forming glycol (p. 240), and it combines directly with ozone, forming a liquid explosive *ozonide*, $C_2H_4O_3$ (p. 96).

Ethylene polymerises (p. 136) under high pressure, forming open chain molecules which may contain up to 1000 carbon atoms.

Some of the important uses of ethylene are given in the table (p. 368).

Constitution of Ethylene. It can be proved by analysis and by vapour density determinations that the molecular formula of ethylene is C_2H_4. The two carbon atoms in this molecule are known to be directly united, because hydrogen is a univalent element; further, a study of all the methods of formation of ethylene leads to this conclusion, because the carbon atoms in the molecules of ethyl bromide and of ethyl alcohol are known to be directly united, and there is no reason to suppose that they become separated

[1] The absorption of ethylene by anhydro-sulphuric acid is easily shown with the aid of Hempel's gas-analysis apparatus.

when these two compounds are converted into ethylene. The four hydrogen atoms in the ethylene molecule must all be directly united to the carbon atoms, and therefore may be distributed in one of two possible ways, represented respectively by the expressions, CH_2—CH_2 and CH_3—CH.

Now, two isomeric compounds of the molecular formula, $C_2H_4Br_2$, are known. One of these, *ethylene dibromide*, is formed by the direct combination of ethylene and bromine (p. 91); the isomeride, *ethylidene dibromide*, is obtained from acetaldehyde, and is known to have the structure, CH_3—$CHBr_2$ (p. 75). As these are the only two compounds of the molecular formula, $C_2H_4Br_2$, which, theoretically, are possible, and as the isomeride of ethylidene dibromide must have the structure, CH_2Br—CH_2Br, it is concluded that this formula must represent the constitution of ethylene dibromide. Further, since ethylene dibromide is formed by the direct union of ethylene and bromine, each of the carbon atoms in the ethylene molecule must be combined with two atoms of hydrogen. This being the case, the constitution of ethylene might be expressed by the formula, CH_2—CH_2. But such a formula would not show that carbon is quadrivalent, nor would it recall the fact that ethylene combines directly with Cl_2, Br_2, HBr, etc.; for these and other reasons the constitution of ethylene is represented by,

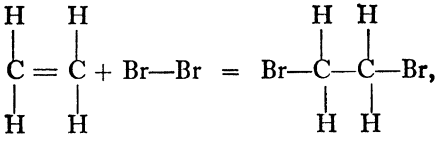
$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C{=}C\!<\!\!\begin{matrix} H \\ H \end{matrix} \quad \text{or} \quad CH_2{=}CH_2 \quad \text{or} \quad CH_2{:}CH_2,$$

and the two carbon atoms are said to be united by a **double bond,** or double binding.

The above view of the constitution of ethylene receives support from the formation of the gas by the electrolysis of succinic acid, a compound of *known constitution* (p. 276). The structure of this acid has been fully established independently of its relation to ethylene, and its conversion into that hydrocarbon (p. 86) can only be accounted for in a simple manner provided that the olefine has the symmetrical structure given above. Further independent evidence (p. 168) affords conclusive proof of this formula.

It must not be supposed that a double bond has any mechanical significance, or that it implies that the two carbon atoms attract one another more strongly than when they are singly bound. A double bond in the structural formula of any hydrocarbon is merely a convenient expression of certain facts which have been established

experimentally—namely, that *the compound is capable of combining directly with two univalent atoms or groups of particular elements, and that these atoms or groups unite with those carbon atoms which are represented as being doubly bound.* All organic compounds which, like ethylene, contain carbon atoms having the power of combining directly with certain other atoms or groups, are said to be **unsaturated.** In the graphic or structural formulae of all such substances, these particular carbon atoms are represented as being joined by a double bond; the structural formula thus summarises the more important chemical properties of the compound. When an unsaturated compound enters into direct combination, the double bond is said to be 'broken,' and in the structural formula of the product the two carbon atoms, previously represented as being doubly bound, are then shown as being united together in the same way as those in the formula of ethane (p. 54); the combination of ethylene with bromine, for example, is expressed graphically,



and the formula of ethylene dibromide shows that, like the paraffins, this substance is saturated, and cannot give derivatives 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 from substitution products.

A halogen derivative of a hydrocarbon may be regarded as an additive or as a substitution product; in the former case the name of the hydrocarbon is put first, as in the case of *ethylene dibromide*, but in the latter it follows the name of the halogen, as in *dibromoethane.* This system applies throughout organic chemistry; thus, methyl chloride or chloromethane may be regarded as an additive product of the methyl radical or as a substitution product of methane.

Unsaturated compounds may contain two, four, or more unsaturated carbon atoms, and they always combine with an *even* number of univalent atoms or groups. A single hydrogen atom cannot be removed from a paraffin, C_nH_{2n+2}, to form a stable hydrocarbon, C_nH_{2n+1}, such as CH_3— or $CH_3 \cdot CH_2$—; further,

whenever two hydrogen atoms are taken away, giving an olefine, these atoms are lost by carbon atoms which are themselves *directly* united. Thus, by the action of alcoholic potash on bromobutane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2Br$, the olefine, *butene*, $CH_3 \cdot CH_2 \cdot CH : CH_2$, is produced, and *not* a compound,

$$CH_3 \cdot \underset{|}{CH} \cdot CH_2 \cdot CH_2— \quad \text{or} \quad —CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2—$$

For these reasons the formula of ethylene is not written $—CH_2 \cdot CH_2—$; such a symbol would not give any indication that the presence or existence of one unsaturated carbon atom is dependent on the existence of another such atom directly combined with it.

Ethylene dichloride, $C_2H_4Cl_2$ or $CH_2Cl \cdot CH_2Cl$ (p. 75), 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 liquid of sp. gr. 1·28 at 0°, boiling at 84°. It is isomeric with *ethylidene dichloride*, $CH_3 \cdot CHCl_2$, b.p. 57°.

Ethylene dibromide, $C_2H_4Br_2$ or $CH_2Br \cdot CH_2Br$, is prepared by passing ethylene into bromine.

The gas (freed from sulphur dioxide, p. 87) is passed through a wash-bottle which contains bromine (2–5 c.c.), covered with water to diminish loss by evaporation. When the wash-bottle no longer contains free bromine, the heavy oily product is separated with the aid of a tap-funnel, washed with water and dried with calcium chloride.

It boils at 132° (m.p. 10°) and its sp. gr. is 2·21 at 0° ; it is isomeric with *ethylidene dibromide*, $CH_3 \cdot CHBr_2$ (p. 75).

Ethylene dibromide is used in ethyl petrol (p. 68).

Substitution products of ethylene, such as *chloroethylene*, $CH_2 : CHCl$, and *bromoethylene*, $CH_2 : CHBr$, cannot be obtained by treating ethylene with a halogen (because additive compounds are formed), but are produced by the action of alcoholic potash on the halogen additive compounds of ethylene (p. 338),

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

Propylene, C_3H_6, or $CH_3 \cdot CH : CH_2$, is formed when either propyl or *iso*propyl bromide is boiled with alcoholic potash,

Propyl bromide $CH_3 \cdot CH_2 \cdot CH_2Br$
*Iso*propyl bromide $CH_3 \cdot CHBr \cdot CH_3$ $\rightarrow CH_3 \cdot CH : CH_2 + HBr.$

It may be prepared by heating propyl or *iso*propyl alcohol (4 vol.)

with sulphuric acid (3 vol.), containing 5% of aluminium sulphate, at about 105°,

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

or by passing propyl or *iso*propyl alcohol vapour over heated alumina. It is a gas very similar to ethylene in properties, and it combines readily with bromine, forming *propylene dibromide*, $CH_3 \cdot CHBr \cdot CH_2Br$, an oily liquid boiling at 142°. Propylene is an important product of cracked petroleum.

Three isomeric **butylenes** or **butenes** of the molecular formula, C_4H_8, are known—namely,

$CH_2{:}CH \cdot CH_2 \cdot CH_3$	$CH_3 \cdot CH{:}CH \cdot CH_3$	$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{:}CH_2.$
α-Butylene or butene-1 (*Ethylethylene*)	β-Butylene or butene-2 (Symm. *dimethylethylene*)	*Iso-* or γ-butylene (Unsymm. *dimethylethylene*)[1]

The first two compounds are derived from normal butane, the third from *iso*butane, and it should be noted that the number of possible isomerides, in the case of an olefine, is greater than in that of the corresponding paraffin. The three butylenes are all gases, and combine directly with chlorine, bromine, hydrogen bromide, etc.

Five isomeric **amylenes** or **pentylenes**, C_5H_{10}, are known, the most important being *trimethylethylene* or β-iso*amylene*, $(CH_3)_2C{:}CH \cdot CH_3$, which is obtained (mixed with isomerides) by heating fusel oil (p. 115) with zinc chloride ; it boils at 38·5°.

The butylenes and amylenes are important products of cracked petroleum.

The great difference in chemical properties between the saturated hydrocarbons of the paraffin series and the unsaturated compounds of the olefine series may be conveniently demonstrated by contrasting the behaviour of ' light petroleum ' with that of ordinary amylene. When a few drops of bromine are added to, say, 5 c.c. of a good sample of light petroleum, the solution retains the colour of the halogen and little, if any, action (due to impurities) occurs. When, on the other hand, bromine is cautiously dropped into amylene, a vigorous reaction occurs and the colour of the halogen immediately disappears, but little, if any, hydrogen bromide is evolved. After sufficient bromine has been added, the liquid

[1] For nomenclature, see p. 93. The terms symmetrical and unsymmetrical (*not* asymmetric or asymmetrical, p. 293) are often used to distinguish isomerides.

product (amylene dibromide) is found to sink in water, whereas amylene floats.

Concentrated sulphuric acid does not mix with, and has no appreciable action on, light petroleum ; but an energetic reaction occurs when the acid is cautiously added to amylene, and some of the unsaturated hydrocarbon passes into solution in the form of amyl hydrogen sulphate.

Light petroleum does not decolourise a dilute solution of potassium permanganate when the two liquids are shaken together, but amylene is readily oxidised.

The lower olefines may be distinguished or identified by an explosion method as given in the case of the paraffins (p. 30) ; a more convenient process is to convert the olefine into the dibromide, which may then perhaps be identified by its (melting- or) boiling-point.

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 shown in brackets : where isomerism occurs the given b.p. is that of the normal hydrocarbon containing the group, $CH_2{:}CH—$.

		b.p.			b.p.
Ethylene	C_2H_4	−105°	Amylene (5)	C_5H_{10}	+30°
Propylene	C_3H_6	−47·6°	Hexylene (13)	C_6H_{12}	+63·7°
Butylene (3)	C_4H_8	−6·3°			

Nomenclature. The names of the olefines are derived from those of the paraffins, by changing the termination *ane* into *ylene*, as above ; or into *ene*, as in *ethene*, *propene*, *butene*, *pentene*, etc. Some members of the series are conveniently regarded as derivatives of ethylene, and named accordingly, as already shown (p. 92), but the systematic nomenclature of the olefines is based on that of the normal hydrocarbons of the series just as in the case of the paraffins ; the position of the double binding or ethylenic link is then shown by adding before or after the name, the numeral or letter of that carbon atom *from* which the double binding starts. Thus the compounds

$CH_3 \cdot CH{:}CH \cdot CH_2 \cdot CH_3$ and $CH_3 \cdot CH(CH_3) \cdot CH{:}CH \cdot CH_2 \cdot CH_3$

are respectively pentene-2 or methylethylethylene and 2-methylhexene-3 or 2-methyl-3-hexene. An alternative is to indicate the position of the double bond by a number or letter following the

symbol Δ; the compounds just mentioned would then be called Δ^{α}- or Δ^{β}-pentene and 2-methyl-Δ^{β}-hexene respectively.

Methods of Preparation. (1) The alcohols (p. 106) are heated with sulphuric acid, phosphoric acid, zinc chloride, potassium hydrogen sulphate, etc., or their vapours are passed over heated alumina,

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

(2) The alkyl halides (p. 73) are heated with alcoholic potash,

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

as, with this reagent, the halogen is often displaced by —OEt to a very considerable extent, pyridine, quinoline or dimethylaniline (Part II) may be used instead.

(3) Quaternary ammonium hydroxides are decomposed at high temperatures (pp. 219, 597).

(4) Dihalides in which the halogen atoms are combined with adjacent carbon atoms are treated with zinc or magnesium,

$$CH_3 \cdot CHBr \cdot CHBr \cdot CH_3 + Zn = CH_3 \cdot CH{:}CH \cdot CH_3 + ZnBr_2.$$

(5) Allyl bromide (p. 339) is treated with a Grignard reagent (p. 235),

$$CH_2Br \cdot CH{:}CH_2 + RMgX = R \cdot CH_2 \cdot CH{:}CH_2 + MgXBr.$$

(6) Aqueous solutions of the alkali salts of certain dibasic acids are submitted to electrolysis (p. 86).

Many olefines occur among the products of cracked petroleum.

Physical Properties. The first two members of the series and the three isomeric butylenes are gases, but the higher members are liquids at ordinary temperatures; the boiling-point rises as the molecular weight increases, just as in the case of the paraffins. Olefines, like *all* hydrocarbons, are insoluble, or nearly so, in water, but soluble in alcohol and other organic liquids.

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 at ordinary temperatures the latter are acted on by chlorine only and give substitution products, the olefines, as a rule, combine directly with Cl_2, Br_2, HBr, HI, HClO, H_2SO_4, etc., and form saturated additive products.

The olefines are converted into paraffins on treatment with molecular hydrogen in the presence of a catalyst,

$$C_nH_{2n} + H_2 = C_nH_{2n+2}.$$

They combine with chlorine and bromine, sometimes with iodine, forming saturated compounds, which may also 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 hydrogen bromide and hydrogen iodide, but not, as a rule, with hydrogen chloride, yielding alkyl halides,

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

combination normally occurring in such a way that the halogen atom unites with that carbon atom which is combined with the smaller number of hydrogen atoms (*Markownikoff*); thus propylene yields with hydrobromic acid, *iso*propyl bromide, $CH_3 \cdot CHBr \cdot CH_3$, and not normal propyl bromide, $CH_3 \cdot CH_2 \cdot CH_2Br$; α- or 1-butylene, $CH_3 \cdot CH_2 \cdot CH{:}CH_2$, with hydriodic acid, gives secondary butyl iodide, $CH_3 \cdot CH_2 \cdot CHI \cdot CH_3$,[1] and so on, but allyl bromide (p. 339), the molecule of which contains one bromine atom, gives trimethylene dibromide.

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

$$CH_2{:}CH_2 + H_2SO_4 = CH_3 \cdot CH_2 \cdot O \cdot SO_2 \cdot OH,$$

and it is often possible to separate olefines by using an acid of suitable concentration; *iso*butylene, for example, is rapidly absorbed by 63% sulphuric acid, whilst the isomeric hydrocarbons are only absorbed by more concentrated acid (80%). Such methods are used in dealing with the complex mixtures formed from petroleum.

Hypochlorous and hypobromous acids convert the olefines into *chlorohydrins* and *bromohydrins* respectively (p. 243).

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

in the case of ethylene these reactions are carried out either by passing a mixture of ethylene and carbon dioxide into a suspension of bleaching-powder in water or by passing ethylene into bromine water. When a homologue of ethylene combines with hypochlorous acid or with sulphuric acid the HO— group of the former or the $—O \cdot SO_2 \cdot OH$ group of the latter generally unites with that carbon atom which is combined with the smaller number of hydrogen atoms. Unlike the paraffins, the olefines are readily oxidised by chromic acid and by potassium permanganate. When oxidation is carried out carefully, under suitable conditions, a product containing the same number of carbon atoms as the original olefine is obtained; ethylene, for example,

[1] Derived from *secondary* butyl alcohol (p. 117).

gives ethylene glycol (p. 240), α-butylene, the corresponding butylene glycol,

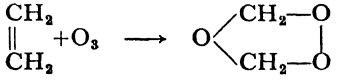
$$CH_2{:}CH_2+O+H_2O = CH_2(OH)\cdot CH_2\cdot OH,$$
$$CH_3\cdot CH_2\cdot CH{:}CH_2+O+H_2O = CH_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH.$$

Generally speaking, when a substance contains the group —CH=CH—, this group, on oxidation, is in the first place converted into —CH(OH)·CH(OH)—. The compounds thus formed readily undergo further oxidation in such a way that the originally unsaturated carbon atoms become separated. Propylene, on vigorous oxidation, yields ultimately acetic and formic acids; *a*-butylene gives propionic and formic acids,

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

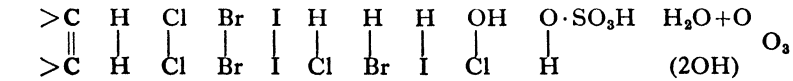
It follows, therefore, that the identification of the products of oxidation of an olefine may afford evidence of the *position* of the double binding in the molecule, or in other words, may establish the *structure* of the olefine; β- or 2-butylene, $CH_3\cdot CH{:}CH\cdot CH_3$, for example, would give acetic acid only.

Olefines (dissolved in an inert solvent) combine directly with ozone forming ozonides (Part III),



These compounds are often highly explosive and are decomposed by water or dilute acids giving aldehydes, ketones, or acids. Thus ethylene ozonide yields both formaldehyde and formic acid. This decomposition is also very useful for determining the position of a double binding in a molecule.

A general symbol for an olefine, and the atoms or groups with which an olefine combines, are shown below, but iodine and also hydrogen chloride often react only under particular conditions:



It has recently been shown that olefines will combine with carbon monoxide and hydrogen under pressure in the presence of catalysts containing cobalt compounds, giving aldehydes (*oxo*-reaction):

$$>C{:}C<+CO+H_2 = >CH\cdot C(CHO)<.$$

This appears to have important synthetical applications.

CHAPTER 7

HYDROCARBONS OF THE ACETYLENE SERIES

THE homologous hydrocarbons of the acetylene series are related to those of the olefine series just as the latter are related to the paraffins ; in other words, the molecules of the members of the acetylene series contain two atoms of hydrogen less than those of 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
Butane	C_4H_{10}	Butylene	C_4H_8	Crotonylene	C_4H_6

Acetylene, C_2H_2, the simplest member of the series, occurs in small proportions (about 0·06% by vol.) in coal-gas. It is formed when the electric arc is produced between carbon poles in a globe filled with hydrogen and through which a stream of the gas is passing (Berthelot),

$$2C+H_2 = C_2H_2.$$

This direct synthesis of acetylene and the conversion of the gas into benzene (p. 101) are reactions of very great theoretical and historical interest.

Acetylene is produced during the incomplete combustion of methane, ethyl alcohol, coal-gas, and other substances ; also when such substances are passed through a red-hot tube.

An ordinary Bunsen burner is lighted below, and a glass funnel, connected by tubing with a wash-bottle, containing an ammoniacal solution of cuprous chloride, is inverted over it ; with the aid of a water-pump, or aspirator, the products are drawn through the wash-bottle, when the red copper derivative of acetylene (p. 99) is precipitated. This product may be separated, washed with water, and warmed with hydrochloric acid, the liberated acetylene being collected over water.

Acetylene is also formed when ethylene dibromide is dropped into boiling alcoholic potash,

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

The reaction takes place in two stages, and the first product is vinyl bromide (p. 338),

$$C_2H_4Br_2+KOH = C_2H_3Br+KBr+H_2O,$$

which is then converted into acetylene,

$$C_2H_3Br+KOH = C_2H_2+KBr+H_2O.$$

The same apparatus is used as in the preparation of ethylene from ethyl bromide (p. 87), and the formation of acetylene is shown by passing the gas into an ammoniacal solution of cuprous chloride.

Acetylene is easily prepared in the laboratory, and is also manufactured, from *calcium carbide* (*calcium acetylide*), a very hard, grey, crystalline substance, prepared by heating a mixture of coke and calcium carbonate, or oxide, at a very high temperature in an electric furnace,

$$CaO+3C = CaC_2+CO.$$

When calcium carbide is placed in cold water, it is rapidly decomposed with a development of heat, and acetylene is evolved,

$$CaC_2+2H_2O = C_2H_2+Ca(OH)_2.$$

For laboratory and lecture experiments a small lump of the carbide is placed under an inverted gas-cylinder filled with water; but when a stream of gas is required the carbide is placed in a *small* flask, which contains a layer of sand and is provided with a dropping funnel and delivery tube; cold water is then dropped slowly on the carbide, when a steady stream of gas is obtained.[1]

This reaction, like the union of carbon and hydrogen, is a ***complete synthesis*** of acetylene because both calcium carbide and water can be prepared from their elements. As, moreover, acetylene can be reduced to ethylene, or converted into acetaldehyde (p. 101) and then into ethyl alcohol and acetic acid, these compounds also can be *completely* synthesised.

Acetylene boils at $-83°$ and has a characteristic smell, resembling that of garlic. It is a strongly endothermic compound, and can be detonated (with fulminate) under atmospheric pressure; a mixture of acetylene and air or oxygen, within wide limits, ***explodes with great violence*** when it is ignited, and it is dangerous to explode a mixture of acetylene and air or oxygen in a soda-water bottle, or

[1] Commercial calcium carbide may contain calcium phosphide, and the acetylene obtained in this way may contain hydrogen phosphide (phosphine) as well as other impurities.

even in an open gas-jar. When it is burnt in the latter or from an ordinary flat-flame burner, acetylene gives a very smoky flame, a behaviour which may be shown, to a less extent, by all hydrocarbons which contain a very large percentage of carbon ; when, however, suitably constructed burners are employed, smoking is prevented and the flame, almost dazzling in its brilliancy, is very rich in actinic rays. The illuminating power of acetylene is about 15 times as great as that of ordinary coal-gas.

Owing to the very high illuminating power of the acetylene flame, the discovery of a cheap method of manufacturing calcium carbide led to the expectation that acetylene would be the illuminating agent of the future ; hitherto, although acetylene is used alone in small quantities for such a purpose (domestic lighting, beacons, bicycle lamps), this expectation has not been realised. This is partly due to the fact that acetylene is liable to explode when it is under a pressure of more than 30 lb. per square inch, and, therefore, cannot be safely stored in the usual cylinders ; it should not be stored in metallic holders even under atmospheric pressure, as explosive metallic derivatives may be formed. As acetylene is readily soluble in acetone (24 vol. dissolve in 1 vol. of acetone under atmospheric pressure), solutions of the gas in this solvent are used instead of the compressed gas.

Acetylene is now employed on a large scale for welding and cutting metals, because when it is burned with oxygen, the *oxy-acetylene flame* reaches a temperature of 3000° or so. In welding, the proportions of oxygen and acetylene are so controlled that carbon monoxide and water are formed, thus avoiding the oxidation of the metal. For cutting purposes, an excess of oxygen is used and the metal burns. An oxyacetylene flame is capable of cutting nickel-chrome armour plate 17 in. thick at the rate of one foot in five minutes.

Acetylene is also used in the commercial preparation of many very important compounds (pp. 100, 369), but, owing to the very high temperature required for making calcium carbide, mainly only in those countries (U.S.A., Canada, Norway) which have a large hydro-electric supply.

Cuprous acetylide, C_2Cu_2, is a brownish-red, amorphous compound which is precipitated when acetylene is passed into an ammoniacal solution of cuprous chloride ; its formation serves as a delicate test for acetylene, and with the aid of this compound

acetylene is easily separated from other gases. The dry substance explodes when struck on a hard surface, or when heated at about 120°. It is decomposed by hydrochloric acid, with the formation of acetylene.[1] **Silver acetylide,** C_2Ag_2, is obtained as a colourless, amorphous compound, when acetylene is passed into an ammoniacal solution of silver nitrate. It is far more readily explosive than the copper compound, and detonates when it is gently rubbed with a glass rod, or heated; about 0·1 g. of *air-dried* silver acetylide, wrapped in a filter-paper, which is suspended by a wire to a retort-stand and then ignited, gives a harmless explosion.

When acetylene is passed over heated sodium or potassium, hydrogen is liberated, and metallic substitution products, such as C_2HNa and C_2Na_2, are formed.

Potassium acetylide was first obtained by Davy, in the preparation of potassium by heating together charcoal and calcined tartar (carbonised potassium hydrogen tartrate) in an iron bottle; he showed that this compound was decomposed by water, giving a gas 'bicarburet of hydrogen' (acetylene), which burnt with a luminous flame.

Acetylene combines *directly* with nascent hydrogen, and is converted first into ethylene, then into ethane; in the presence of finely divided nickel or platinum, it unites with molecular hydrogen, giving the same two products.

It combines *directly* with chlorine, forming dichloroethylene and tetrachloroethane (acetylene tetrachloride),

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

and with bromine, forming dibromoethylene and tetrabromoethane.

Acetylene may react with chlorine with explosive violence. When a small piece of calcium carbide is placed under a gas-jar, which is partly filled with chlorine (free from air) and is standing mouth downwards in a trough of water, the bubbles of acetylene 'puff' when they rise into the chlorine, and a deposit of carbon is formed. The reaction which occurs under these conditions may be expressed by the equation,

$$C_2H_2+Cl_2 = 2C+2HCl.$$

Acetylene tetrachloride, $C_2H_2Cl_4$ (b.p. 146–147°), known as *Westron*, is prepared on the commercial scale by treating acetylene

[1] Traces of vinyl chloride (p. 338) are also formed, but when cuprous acetylide is warmed with a solution of potassium cyanide, it yields pure acetylene.

with chlorine in the presence of antimony pentachloride; the tetrachloride may be converted into *trichloroethylene* (*Westrosol*), C_2HCl_3 (b.p. 88°), by warming it with milk of lime. These compounds are non-inflammable and are used in the extraction of fat from wool, and in the manufacture of varnishes and paints.

Acetylene combines with the halogen acids under certain conditions, giving in the first place substitution products of ethylene, such as vinyl chloride, C_2H_3Cl (p. 338), and then an ethylidene derivative such as $CH_3 \cdot CHCl_2$.

Sulphuric acid absorbs acetylene.[1] When the solution is diluted with water, and then distilled, acetaldehyde (p. 138) passes over. This change takes place in two stages, and is comparable with the conversion of ethylene into ethyl alcohol (p. 195),

$$C_2H_2 \xrightarrow{H_2SO_4} \begin{matrix} CH_3 \\ | \\ CH(O \cdot SO_3H)_2 \end{matrix} \xrightarrow{H_2O} \begin{matrix} CH_3 \\ | \\ CHO \end{matrix}$$

When acetylene is heated at a dull-red heat it is converted into benzene (p. 376),

$$3C_2H_2 = C_6H_6.$$

Constitution of Acetylene. As the two carbon atoms in the molecule of acetylene must be directly united, the first matter to consider is whether the two hydrogen atoms are united to the same or to different carbon atoms—that is to say, whether the expression, CH_2—C or CH—CH, represents the arrangement of the atoms in the molecule. Now, in the formation of ethylene, $CH_2{=}CH_2$, from ethyl bromide, CH_3—CH_2Br, an atom of hydrogen and an atom of bromine are removed from *different* carbon atoms. As the formation of acetylene from ethylene dibromide, CH_2Br—CH_2Br, apparently, is a change of the same kind, but one which involves the loss of two molecules of hydrogen bromide, it may be inferred that this loss takes place in two stages, each of which is similar to that which occurs in the production of ethylene. This argument, which is based on analogy, clearly points to the arrangement, CH—CH.

But since carbon is quadrivalent, and acetylene combines directly with four univalent atoms of certain elements, the structure of the hydrocarbon is represented by the formula, H—C≡C—H, or CH≡CH, or CH:CH, which is intended to show that the two

[1] This can be shown with the aid of Hempel's gas-analysis apparatus, as in the case of ethylene.

carbon atoms in the molecule are unsaturated and to a greater extent than are those in the molecule of ethylene. This view of the constitution of acetylene accords well with all that is known of the hydrocarbon.

Thus, its formation by the electrolysis of a salt of fumaric acid (p. 348) is a reaction which lends support to the above structural formula (compare pp. 53, 86),

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

The two carbon atoms in the molecule of acetylene are said to be united by a **treble bond** or treble linking; this treble bond, like the double bond, is merely a convenient expression of certain facts—namely, that the carbon atoms which are represented as being trebly bound are capable of uniting with *four* univalent atoms of certain elements.

When acetylene combines with two univalent atoms it becomes less unsaturated, and the two carbon atoms, which before were represented as being trebly bound, are now represented as being united by a double linking, as in the olefines,

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

When these *additive* compounds, which are still unsaturated, again combine with two univalent atoms, they are converted into saturated compounds,

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

Allylene (methylacetylene), $CH_3 \cdot C{:}CH$, is prepared by heating propylene dibromide (dibromopropane) with alcoholic potash,

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

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

Crotonylene (dimethylacetylene), $CH_3 \cdot C{:}C \cdot CH_3$, prepared by warming β-butylene dibromide (p. 92) with alcoholic potash,

$$CH_3 \cdot CHBr \cdot CHBr \cdot CH_3 + 2KOH = CH_3 \cdot C{:}C \cdot CH_3 + 2KBr + 2H_2O,$$

is a liquid boiling at 27°; it does *not* form copper or silver derivatives with ammoniacal solutions of cuprous chloride or silver nitrate, as this property is shown *only* by hydrocarbons which contain the

group, —C:CH. Nevertheless crotonylene, like allylene, is a homologue of acetylene.

SUMMARY AND EXTENSION

The hydrocarbons of the C_nH_{2n-2} series show isomerism which begins with the member containing three carbon atoms; thus the molecular formula C_3H_4 represents the following two compounds:

$CH_3 \cdot C:CH$	$CH_2:C:CH_2$.
Allylene or Methylacetylene	Allene

Allylene, like acetylene, contains two trebly bound carbon atoms, whereas allene resembles ethylene in constitution, and contains what may be regarded as two pairs of doubly bound carbon atoms; allene, therefore, is *not* a homologue of acetylene.

The hydrocarbons, C_nH_{2n-2}, are therefore classed in two groups: (1) The acetylene series, consisting of those compounds which, like *acetylene*, contain the *acetylenic binding*, —C:C—; and (2) the *diolefines*, or hydrocarbons, such as *allene*, $CH_2:C:CH_2$, and *butadiene*, $CH_2:CH \cdot CH:CH_2$, which resemble the olefines in constitution and contain two *ethylenic* bindings. The former behave on the whole like acetylene, whereas the latter are similar to the olefines.

The Acetylene Series. The more important members of this series are the gases, *acetylene*, CH:CH, and *allylene*, $CH_3 \cdot C:CH$, and *crotonylene*, $CH_3 \cdot C:C \cdot CH_3$, a liquid.

Nomenclature. The members of this series have been given names derived from those of the paraffins and ending in **yne**, as for example, eth**yne**, prop**yne**, but**yne**, etc. Where isomerism occurs the position of the acetylenic linkage is shown by a numeral, as for example, $CH:C \cdot CH_2 \cdot CH_3$, butyne-1, $CH_3 \cdot C:C \cdot CH_3$, butyne-2. The radical CH:C— is called *ethynyl*.

Methods of Preparation. (1) The monohalogen substitution products, or the dihalogen addition products of the olefines, are heated with alcoholic potash,

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

Dihalogen compounds, containing the group $—CX_2—$ or $CHX_2—$, such as those obtained by treating ketones or aldehydes with a pentahalide of phosphorus, may also be used,

$$CH_3 \cdot CBr_2 \cdot CH_3 + 2KOH = CH_3 \cdot C:CH + 2KBr + 2H_2O.$$

(2) Sodium acetylide is treated with an alkyl halide dissolved in liquid ammonia, or the Grignard compound of acetylene (p. 105) is treated with an alkyl halide.

(3) Aqueous solutions of the alkali salts of certain unsaturated dibasic acids are submitted to electrolysis,

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

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 soluble in alcohol and other organic liquids, and burn with a luminous, very smoky flame.

Those which contain the group, $\equiv CH$, form metallic compounds such as cuprous acetylide, C_2Cu_2, and silver acetylide, C_2Ag_2, when treated with ammoniacal solutions of cuprous chloride or of silver nitrate. The copper compounds are red, the silver compounds colourless, and both classes are explosive, the latter more so than the former. These compounds are decomposed by hydrochloric acid and also by warm potassium cyanide solution, the acetylenes being regenerated. The di-olefines, and those members of the acetylene series, such as $CH_3\cdot C\vdots C\cdot CH_3$, which do not contain the group, $\equiv CH$, do not form such metallic derivatives.

The hydrocarbons of the acetylene series may be caused to combine with the elements of water by dissolving them in strong sulphuric acid, and warming the diluted solution; or by shaking them with a concentrated aqueous solution of mercuric chloride or nitrate, and then decomposing the precipitate which is formed with a dilute mineral acid; or, in some cases, by merely heating them with water at about 325°,

$$CH\vdots CH + H_2O = CH_3\cdot CHO,$$
$$CH_3\cdot C\vdots CH + H_2O = CH_3\cdot CO\cdot CH_3.$$

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 propionaldehyde.

The acetylenic hydrocarbons combine directly with two molecules of chlorine, bromine, halogen acids, etc., and with nascent hydrogen, the action taking place in two stages,

$$CH_3\cdot C\vdots CH + Br_2 = CH_3\cdot CBr{:}CHBr,$$
$$CH_3\cdot CBr{:}CHBr + Br_2 = CH_3\cdot CBr_2\cdot CHBr_2;$$

they also combine with halogen acids and in the final product both the halogen atoms are united to the same carbon atom,

$$CH_3\cdot C\vdots CH + 2HBr = CH_3\cdot CBr_2\cdot CH_3.$$

Like the olefines, they are readily oxidised and finally converted into

products which contain a smaller number of carbon atoms in their molecules than the original compounds.

They combine with one molecule of ozone forming ozonides, whereas di-olefines unite with two molecules of ozone to give di-ozonides.

Those compounds containing the group, $\equiv CH$, react with ethyl magnesium bromide giving ethane and substances, $\equiv C \cdot MgBr$, which can be used for the synthesis of acetylenic derivatives.

Dipropargyl is an interesting member of the *di-acetylene* series and is isomeric with benzene (p. 376); it may be prepared from diallyl (below). It boils at 85·4°, and resembles acetylene in forming copper and silver derivatives.

The Di-olefine Series. Allene (p. 103), the simplest di-olefine, is of little importance.

Butadiene, $CH_2{:}CH \cdot CH{:}CH_2$, may be prepared by passing 1:3-butylene glycol (obtained from aldol) over heated lime,

$$CH_2(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_3 = CH_2{:}CH \cdot CH{:}CH_2 + 2H_2O.$$

It boils at −3° and is used in the manufacture of synthetic rubber (Part III).

Isoprene (β-methylbutadiene), $CH_2{:}C(CH_3) \cdot CH{:}CH_2$, may be obtained by the destructive distillation of natural rubber; it boils at 34·1°. When it is heated under pressure or treated with sodium it undergoes polymerisation, giving a product which is like rubber. Various syntheses of isoprene are given later (Part III).

Diallyl, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$, is also a hydrocarbon of the *di-olefine* series. It boils at 59·4° and may be prepared by warming allyl iodide (p. 339) with sodium or magnesium in ethereal solution,

$$2CH_2{:}CH \cdot CH_2I + 2Na = CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2 + 2NaI.$$

It combines directly with *two* molecules of bromine, yielding *diallyl tetrabromide*, which, when dropped into hot alcoholic potash, is converted into *dipropargyl*,

$$CH_2Br \cdot CHBr \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CH_2Br + 4KOH = CH{\vdots}C \cdot CH_2 \cdot CH_2 \cdot C{\vdots}CH + 4KBr + 4H_2O.$$

CHAPTER 8

THE MONOHYDRIC ALCOHOLS

THE monohydric alcohols form a homologous series of the general formula, $C_nH_{2n+1}\cdot OH$, or $R\cdot OH$.[1] They may be regarded as derived from the paraffins by the substitution of the univalent hydroxyl group for one atom of hydrogen.

Methyl alcohol, $CH_3\cdot OH$, derived from methane, $CH_3\cdot H$
Ethyl alcohol, $C_2H_5\cdot OH$, derived from ethane, $C_2H_5\cdot H$
Propyl alcohol, $C_3H_7\cdot OH$, derived from propane, $C_3H_7\cdot H$, etc.

Methyl alcohol, *methanol*,[2] or *wood-spirit*, $CH_3\cdot OH$, occurs in a combined form in certain essential oils—as, for example, in oil of winter-green (*Gaultheria procumbens*), which contains methyl salicylate (p. 534). It may be obtained from methane by first converting the hydrocarbon into methyl chloride, and then heating the latter with a dilute aqueous solution of potassium hydroxide in closed vessels,

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

These operations are difficult to carry out and are only of theoretical interest as stages in a complete synthesis of the alcohol.

Methyl alcohol is manufactured synthetically from carbon monoxide and hydrogen; the mixture (water-gas) is passed under pressure over a catalyst, at about 300–400°,

$$CO+2H_2 = CH_3\cdot OH,$$

and the product, which also contains propyl and *iso*butyl alcohols (p. 367) and many other compounds, is submitted to fractional distillation; it is also made by the direct oxidation of methane.

Methyl alcohol used to be prepared on the large scale from the products of the destructive distillation of wood, a process now little used. When wood is heated in iron retorts out of contact with the air, gases are evolved; water, *methyl alcohol*, *acetic acid*, acetone, tar, and other products collect in the receiver, and *wood charcoal* remains.

[1] R represents an alkyl radical (compare p. 80).

[2] The termination **ol** is used in the systematic names of all compounds, R·OH (p. 121).

After the distillate has settled, the brown aqueous layer (*pyroligneous acid*), which contains the above named and many other substances, is separated from the wood tar and distilled from a copper vessel; the vapours are first passed through hot milk of lime, to free them from acetic acid, and then through a series of rectifiers or fractionating columns, whereby 'crude wood alcohol' is obtained. This product contains about 70% of methyl alcohol, 16% of acetone and other ketones (p. 144), 8% of water, and 6% of a mixture of aldehydes, methyl acetate, amines, and oily matter. By further fractional distillation, after treatment with sulphuric acid, caustic soda, etc., methyl alcohol up to about 99% purity may be obtained.

Pure methyl alcohol can be prepared in the laboratory by warming this impure liquid with anhydrous oxalic acid, when crystalline dimethyl oxalate is produced (p. 275),

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

this is well drained on a filter-pump, washed with a little water, and hydrolysed with alkali. The methyl alcohol, distilled from the alkaline solution, is then freed from water by distillation first with quicklime and then with calcium (or with magnesium methoxide, compare p. 114).

Methyl alcohol is a mobile liquid of sp. gr. 0·796 at 15°; it boils at 64·7°, and has an agreeable vinous or wine-like odour and a burning taste; it is poisonous, causing blindness and madness. It is miscible with water, a slight contraction in volume taking place, with the development of heat; 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 making methylated spirit (p. 115), as a solvent in the manufacture of dyes and varnishes, and as an anti-freeze in radiators; also for the preparation of methyl chloride, formaldehyde, perfumes, fine chemicals, and many methyl esters.

Methyl alcohol is rapidly attacked by sodium and potassium, with the evolution of hydrogen and formation of metallic compounds called *methoxides* or *methylates*,

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

a reaction which is similar to that of 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 dry hydrogen ; it is a crystalline, very deliquescent compound, which rapidly absorbs carbon dioxide from the air, and is completely decomposed by water with the regeneration of methyl alcohol,

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

Potassium methoxide has similar properties.

Although neutral to indicators, methyl alcohol acts like a very weak basic hydroxide, and with acids it gives *esters* and water ; when saturated with hydrogen chloride, it is partly converted into methyl chloride (compare p. 70),

$$CH_3 \cdot OH + HCl \rightleftarrows CH_3Cl + H_2O,$$

and, when warmed with sulphuric acid, it gives methyl hydrogen sulphate, and very small proportions of dimethyl sulphate,

$$CH_3 \cdot OH + H_2SO_4 \rightleftarrows CH_3 \cdot HSO_4 + H_2O,$$
$$2CH_3 \cdot OH + H_2SO_4 \rightleftarrows (CH_3)_2SO_4 + 2H_2O.$$

It also reacts with organic acids such as acetic acid,

$$CH_3 \cdot OH + HO \cdot OC \cdot CH_3 \rightleftarrows CH_3O \cdot OC \cdot CH_3 + H_2O.$$

These reactions may be compared with those which occur when a metallic hydroxide is treated with an acid, *but they take place incompletely even in the presence of a large excess of the acid* (p. 188).

With acetic anhydride (p. 176) or acetyl chloride (p. 173), methyl alcohol gives methyl acetate (p. 186). With phosphorus bromides or oxybromide, methyl bromide is formed,

$$3CH_3 \cdot OH + PBr_3 = 3CH_3Br + H_3PO_3,$$
$$CH_3 \cdot OH + PBr_5 = CH_3Br + HBr + POBr_3,$$
$$3CH_3 \cdot OH + POBr_3 = 3CH_3Br + H_3PO_4,$$

and a mixture of red phosphorus and iodine gives methyl iodide.

The chlorides and oxychloride of phosphorus give, however, only a small proportion of methyl chloride.[1]

[1] The principal products are esters derived from phosphorous or phosphoric acid,

$$3CH_3 \cdot OH + PCl_3 = CH_3Cl + 2HCl + P(OH)(OCH_3)_2,$$
$$3CH_3 \cdot OH + PCl_5 = PCl_2(OCH_3)_3 + 3HCl.$$

Similar reactions occur with other alcohols (and phenols).

Methyl alcohol is readily oxidised,[1] giving first formaldehyde, then formic acid, and finally carbonic acid,

$$CH_3 \cdot OH + O = CH_2O + H_2O, \qquad CH_2O + O = H \cdot COOH.$$

The presence of water in methyl alcohol may be detected by a sp. gr. determination or by adding a large volume of benzene (which gives a turbidity); acetone, a common impurity in wood-spirit, may be detected by means of the iodoform reaction (p. 112).

Constitution of Methyl Alcohol. As it may be assumed that the atoms in the molecule, CH_4O, have their normal valencies, the only possible structural formula for methyl alcohol is

$$CH_3 \cdot OH \quad \text{or} \quad \begin{array}{c} H \\ | \\ H-C-O-H \\ | \\ H \end{array}$$

and a study of the methods of formation and chemical properties of methyl alcohol leads conclusively to the adoption of this formula.

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; further, methyl alcohol is formed by the action of dilute alkalis on methyl chloride,

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

and the three hydrogen atoms in methyl chloride, which are known to be combined with carbon, are not displaceable by metals. It is clear, therefore, that the displaceable hydrogen atom in methyl alcohol is not combined with carbon, but with oxygen. The above formula also accounts for the fact that the oxygen atom cannot be displaced without one of the hydrogen atoms accompanying it; when the alcohol is treated with HCl, PBr_3, PBr_5, etc., the univalent hydroxyl group is displaced by *one* atom of the univalent halogen. Methyl alcohol, in fact, is *methyl hydroxide*, and may be regarded as derived from water, H—O—H, by the substitution of the univalent CH_3— group for one atom of hydrogen, just as sodium hydroxide, Na—OH, is obtained by the substitution of one atom of sodium. Like very weak basic hydroxides, it reacts with acids

[1] The common *oxidising agents* used in organic chemistry are listed before the Index.

until an equilibrium is established (p. 188), and like water, it contains hydrogen displaceable by metals, but it differs widely from metallic hydroxides in most respects. It may also be considered as a hydroxy-substitution product of the paraffin, methane; it is termed a *monohydric* alcohol because its molecule contains one hydroxyl group.

Ethyl alcohol, *ethanol*, alcohol, or *spirit of wine*, $C_2H_5 \cdot OH$, has been known from very early times, as it is contained in all fermented liquors; it occurs in many plants in combination with organic acids.

It may be obtained from ethane by converting the hydrocarbon into ethyl chloride (p. 71) and heating the latter with dilute alkalis under pressure, a method of theoretical interest only,

$$C_2H_5Cl + KOH = C_2H_5 \cdot OH + KCl;$$

also by passing ethylene into fuming sulphuric acid, and then boiling the solution of ethyl hydrogen sulphate with water (pp. 194, 195), or from ethylene and steam under pressure in the presence of a suitable catalyst,

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

and by reducing acetaldehyde (p. 138) with hydrogen in the presence of nickel,

$$C_2H_4O + 2H = C_2H_6O.$$

Since ethylene can be obtained from cracked petroleum and acetaldehyde from acetylene, these reactions are of importance in the manufacture of ethyl alcohol.

Alcohol may be prepared by adding brewer's yeast (5 g.) to a 5–10% aqueous solution (500 c.c.) of ordinary sugar (*sucrose*) and keeping the mixture at about 25°. In the course of a few hours the liquid begins to 'work' or 'ferment' and frothing occurs, owing to the evolution of carbon dioxide; very complex changes are brought about by the yeast (p. 332), but the formation of the main products may be summarised as follows:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6},$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} = 2C_2H_6O + 2CO_2.$$

After the lapse of twenty-four hours or so, the yeast is separated by filtration, and the solution is distilled until about one third, which contains practically *all* the alcohol, has passed over. A more concentrated sample, which burns readily when ignited, may be

obtained by a second fractional distillation, and this product may then be further dehydrated by leaving it in contact with quicklime during about twenty-four hours and again distilling. Alcohol containing about 0·2% of water can be thus obtained, but it is impossible to remove the water completely by distillation over lime (compare p. 114).

Alcohol is a mobile liquid of sp. gr. 0·790 at 15° ; it has a pleasant vinous odour and a burning taste ; it boils at 78·5°, but does not solidify until about −112° (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 the development of heat and a diminution of volume ; 52 vol. of alcohol and 48 vol. of water give a mixture occupying only 96·3 vol.

Alcohol is used in large quantities for the manufacture of methylated spirit, ether, acetaldehyde, chloral, chloroform, esters, etc. It is a very important solvent for gums, resins, and other substances, in the preparation of tinctures, varnishes, perfumes, etc. ; it is also used as a fuel for internal combustion engines, as an anti-freeze in radiators, and for the preservation of biological specimens.

Ethyl alcohol closely resembles methyl alcohol in chemical properties. It is rapidly acted on by sodium and potassium, with the evolution of hydrogen and formation of *ethoxides* or *ethylates*,

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

These compounds are readily soluble in alcohol, but may be obtained in a solid condition by evaporating the solvent in a stream of hydrogen or by heating anhydrous alcohol, dissolved in toluene, with the theoretical quantity of the metal until action ceases. They are crystalline and hygroscopic, rapidly absorb carbon dioxide from the air, and are immediately decomposed by water, with the regeneration of alcohol.

Sodium ethoxide is an important reagent in organic chemistry.

Aluminium ethoxide (or *ethylate*), $Al(OC_2H_5)_3$, is formed by treating alcohol with amalgamated aluminium in the presence of iodine ; it melts at 140° and differs notably from the ethoxides of the alkali metals inasmuch as it may be distilled under greatly reduced pressure.

Although neutral to indicators, alcohol acts like a weak basic hydroxide, and with acids it gives esters and water,

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

With sulphuric acid, it first gives ethyl hydrogen sulphate (p. 194) and then ethylene (p. 86) or ether (p. 126), according to the conditions of the experiment. It reacts violently with phosphorus pentachloride, giving some ethyl chloride (footnote, p. 108), and with the bromides of phosphorus, or with red phosphorus and iodine, it is converted into ethyl bromide or iodide respectively,

$$6C_2H_5 \cdot OH + 2P + 3I_2 = 6C_2H_5I + 2H_3PO_3.$$

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

$$C_2H_5 \cdot OH + O = C_2H_4O + H_2O, \qquad C_2H_4O + O = C_2H_4O_2.$$

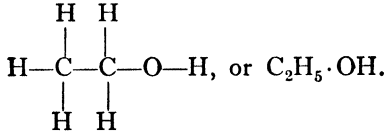
In the presence of the ferment, *Bacterium aceti*, under certain conditions (p. 169), it is oxidised to acetic acid at ordinary temperatures by atmospheric oxygen.

The presence of alcohol in dilute aqueous solutions is very easily detected. (1) The solution (2–3 c.c.) is gently warmed with a little potassium dichromate and dilute sulphuric acid; if alcohol is present the highly characteristic odour of *acetaldehyde* is observed, and the dichromate is reduced. (2) The solution is gently warmed with a few small crystals of iodine, and a solution of sodium hydroxide is then added drop by drop until the colour of the iodine disappears. If alcohol is present, a yellow precipitate of *iodoform* is produced either immediately or after some time;[1] iodoform may be recognised by its odour and by the characteristic appearance under the microscope of its six-sided crystals. By this test (*Lieben's iodoform reaction*) it is possible to detect 1 part of alcohol in 2000 parts of water. The iodoform reaction, which may also be carried out with a hypochlorite and an iodide, instead of with iodine and alkali (p. 78), is especially valuable for distinguishing ethyl from methyl alcohol (or for testing for ethyl alcohol in methyl alcohol), as the latter does *not* give the iodoform reaction; but as many other substances, such as acetone and acetaldehyde, give the reaction (p. 146), the formation of iodoform may not be a proof of the presence of ethyl alcohol.

[1] Iodoform is soluble in alcohol; if the solution is rich in alcohol a precipitate may not be produced until after the addition of water.

The presence of water in alcohol may be detected, but not very easily if the proportion is small, by the following tests : (1) A little anhydrous copper sulphate is added to the sample ; if water is present the colourless powder slowly turns blue, owing to the formation of the hydrated salt. (2) A large volume of petroleum ether is added to the sample ; if water is present the mixture is turbid, owing to the separation of droplets. The presence of water may also be detected, and its quantity may be estimated by determining the sp. gr. of the sample (p. 115).

The *constitution* of ethyl alcohol has already been discussed (p. 46), and it has been shown that the methods of formation and the chemical behaviour of this compound can only be accounted for satisfactorily with the aid of the following structural formula :



Ethyl alcohol, like methyl alcohol, is a monohydroxy-substitution product of a paraffin and a *monohydric* alcohol ; the two compounds are similar in properties *because* they are similar in structure.

Manufacture of Alcohol. Alcohol is prepared on the large scale (*a*) from cane- or beet-sugar, (*b*) from potatoes, grain, and various other substances rich in starch, (*c*) from ethylene (p. 110), and (*d*) from acetaldehyde (pp. 110, 369) ; the method used depends on the raw materials available in the country of manufacture.

(*a*) Instead of the refined sugar, the syrupy mother liquor (molasses or treacle), from which the sugar has been separated (p. 322), is employed, and after dilution the solution is fermented with yeast (pp. 110, 331).

(*b*) The raw material is reduced to a pulp or paste with water, mixed with a little malt, and the mixture kept at about 55° during 30–60 minutes, when *diastatic fermentation* (p. 332) takes place, and the starch is converted into maltose and dextrin,

$$\underset{\text{Starch}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{C_6H_{10}O_5}.^1$$

[1] Starch and dextrin have the same empirical formula, but their molecular formulae are uncertain (p. 327).

The solution is then cooled to about 25°, yeast is added, and the mixture is kept until alcoholic fermentation is at an end ; during this process both the maltose and the dextrin are first converted into glucose (p. 110).

Diastatic and alcoholic fermentations are brought about by substances, which are known as *enzymes*, contained in sprouted barley (malt) and yeast respectively. The reactions which occur are discussed later (p. 330).

Starch may be converted directly into alcohol by suitable moulds (*Rhizopus Delemar*). The organism (which during its growth secretes the enzymes necessary to bring about the change) is extremely efficient, and about 0·5 g. of the mould is all that is required to ' seed ' a tank containing up to 20,000 gallons of starch pulp. The operation occupies about four days and is known as the *amylo-*process. It is possible to obtain alcohol from starch by other methods, since starch is converted into glucose when it is heated with dilute sulphuric acid, and the solution, having been neutralised with lime, can be fermented with yeast.

Alcohol may also be produced from the cellulose contained in sawdust and other vegetable products, because cellulose, heated under pressure with hydrochloric acid, is partially converted into glucose, which may then be fermented with yeast.

The weak solution of alcohol, obtained by any of these methods, is submitted to fractional distillation in various forms of continuous ' stills ' of a complex structure, whereby a product which contains about 96% of alcohol is obtained.

The remainder of the water cannot be separated by fractionation as a mixture of constant boiling-point, containing 95·6% of alcohol and boiling at 78·15°, passes over. When, however, a little benzene is added distillation affords : (1) a small fraction of water, benzene, and alcohol (b.p. 64·8°) ; (2) a small fraction of benzene and alcohol (b.p. 68·2°) ; and (3) alcohol (b.p. 78·5°), containing only traces of water, if any.

For some purposes, alcohol free from even traces of water is required ; this may be obtained by boiling a highly concentrated sample with *calcium* or *calcium carbide* during several hours and then distilling.

A better method is to treat the sample (50–75 c.c.) with magnesium (4–5 g.) in the presence of iodine (0·4–0·5 g.) in order to produce *magnesium ethoxide* ; the rest (say 900 c.c.) of the alcohol

is then added, and the mixture is boiled during about 30 minutes. Any water which may be present reacts with the magnesium ethoxide, giving magnesium hydroxide, from which the anhydrous alcohol is then distilled.

As alcohol is very hygroscopic, care must be taken to exclude moisture during its dehydration ; anhydrous alcohol is often called *absolute alcohol.*

Fusel oil is an important by-product in the manufacture of alcohol (p. 332) ; it consists mainly of two amyl alcohols (p. 120), but the crude mixture also contains propyl and *iso*butyl alcohols.

Methylated spirit. All alcoholic beverages are subject to an excise duty, and for that reason the manufacture of alcohol in general is strictly controlled by the Government ; nevertheless, the production and use of ' duty-free spirit ' for scientific work are permitted (under licence), and also its employment for general industrial and other purposes when it is in the ' denatured ' form of ' methylated spirit.' This commercial mixture, of which various blends are made, may consist of about 90% of distilled alcohol (containing 5–20% of water), about 10% of partially purified wood-spirit or methyl alcohol, and a small quantity of pyridine ; the wood-spirit and pyridine render the alcohol noxious and unfit to drink, without greatly affecting its usefulness for other purposes (small quantities of a dye, such as methyl violet, are also often added).

Alcoholometry. In order to ascertain the concentration of a sample of alcohol—that is, the percentage of pure alcohol in aqueous spirit—it is only necessary to determine the specific gravity of the sample at a standard temperature, and then to refer to published tables, in which the sp. gr. of any mixture 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% 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% by weight, or 57·1% 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 vol. of this spirit, diluted with water, would yield 120 vol. of proof-

spirit, whilst 20° under proof means that 100 vol. of the sample contain as much alcohol as 80 vol. of proof-spirit.

The name *proof-spirit* owes its origin to the ancient practice of testing the strength of a sample of alcohol by pouring it on to gunpowder and then applying a light. If the sample contained more than a certain proportion of water, it did not inflame, or the alcohol burnt away, leaving the powder so damp that it did not ignite ; but if the proportion of water was below a certain limit, the alcohol burnt away and the gunpowder then took fire. A sample which ignited the powder was called proof-spirit.

For the *determination of alcohol* in beers, wines, and spirits, a measured quantity of the sample is distilled until about one third has passed over. The distillate, which contains the whole of the alcohol, is then diluted with water to the volume of the original sample, at the standard temperature, and its sp. gr. is determined; the percentage of alcohol is found by referring to the tables already mentioned. Distillation is necessary because the sugars and other dissolved matter, contained in the sample, influence the sp. gr. so much that a direct observation would be of no value.

Homologues of Ethyl Alcohol. All the members of the series of monohydric alcohols may be considered as derived from the paraffins by the substitution of the univalent HO— radical for one atom of hydrogen. Except the first two members, they all show isomerism, and as two or more isomerides may be derived from one hydrocarbon, the number of isomeric alcohols is greater than that of the corresponding paraffins. There is, for example, only one hydrocarbon, C_3H_8 (propane), but two isomeric alcohols are derived from it—namely, propyl alcohol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$, and *iso*-propyl alcohol, $CH_3 \cdot CH(OH) \cdot CH_3$. From C_4H_{10} four, and from C_5H_{12} eight, isomerides are derived, the number increasing rapidly as the series progresses.

In order to distinguish the various isomerides by names expressive of their structures, the alcohols may be considered as derivatives of methyl alcohol, $CH_3 \cdot OH$, which for this particular purpose is called *carbinol*. 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 the displacement of one atom of hydrogen by the ethyl group, C_2H_5—. *Iso*propyl alcohol, $(CH_3)_2CH \cdot OH$, may be called dimethyl carbinol, and regarded as derived from carbinol by the substitution of two methyl or CH_3— groups for two atoms of hydrogen. Such names as these serve to express the *constitutions*

of the substances, as will be seen by considering the case of the four isomeric butyl alcohols, $C_4H_9 \cdot OH$:

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	Normal[1] primary butyl alcohol, or propyl carbinol.
$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_3$	Secondary butyl alcohol, or methyl-ethyl carbinol.
$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot OH$	Primary *iso*butyl alcohol, or *iso*propyl carbinol.[2]
$\begin{matrix} CH_3 \\ CH_3 \!-\! C \cdot OH \\ CH_3 \end{matrix}$	Tertiary butyl alcohol, or trimethyl carbinol.

Classification of Alcohols. Three types of monohydric alcohols are distinguished—namely, primary, secondary, and tertiary alcohols.

Primary alcohols, as, for example, normal propyl alcohol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$, contain the group, $-CH_2 \cdot OH$; and may be considered as mono-substitution products of carbinol. On oxidation with chromic acid, etc., they are converted first into aldehydes (p. 133) and then into fatty acids (p. 160), the group, $-CH_2 \cdot OH$, being transformed first into $-CHO$, and then into $-COOH$,

$$CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CHO + H_2O,$$
$$CH_3 \cdot CHO + O = CH_3 \cdot CO \cdot OH.$$

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

Secondary alcohols, for example, *iso*propyl alcohol, $(CH_3)_2CH \cdot OH$, contain the group, $>CH \cdot OH$; and may be regarded as di-substitution products of carbinol. On oxidation they are converted into ketones each of which contains the *same* number of carbon atoms in the molecule as the alcohol from which it is derived, the group, $>CH \cdot OH$, becoming $>CO$, by the loss of hydrogen (p. 144),

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

Tertiary alcohols, such as tertiary butyl alcohol, $(CH_3)_3C(OH)$, contain the group, $R_3C \cdot OH$, and may be regarded as tri-substitution

[1] The term '*normal*' is applied to those alcohols which are derived from normal paraffins (p. 60).

[2] The term '*iso*' is often applied to those *primary* (*or secondary* in the case of *iso*propyl alcohol) alcohols the molecules of which contain the group $(CH_3)_2CH-$.

products of carbinol. On oxidation their molecules are broken up with the formation of ketones and acids, products which necessarily contain a *smaller* number of carbon atoms in their molecules than the alcohols from which they are derived. Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3C(OH)$, for example, yields acetone, $CH_3 \cdot CO \cdot CH_3$, acetic acid, $CH_3 \cdot CO \cdot OH$, and carbon dioxide.

The three classes of alcohols may also be distinguished by passing their vapours over heated nickel, as, under these conditions, primary alcohols give the corresponding aldehydes and hydrogen, secondary alcohols give the corresponding ketones and hydrogen, whilst tertiary alcohols give olefines and water.

Tertiary alcohols usually decompose very readily when they are warmed with zinc chloride, phosphorus pentoxide, etc., or even when they are heated alone, giving an olefine and water. Tertiary butyl alcohol, for example, yields iso*butylene*, $(CH_3)_2C{:}CH_2$. Esters of tertiary alcohols behave similarly, giving an olefine and an acid.

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,

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

The olefine is then dissolved in anhydrosulphuric acid, when an alkyl hydrogen sulphate is formed, the $-SO_4H$ group uniting with that carbon atom which is combined with the smaller 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 it 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 *iso*butyl alcohol, may be converted into the tertiary alcohol, trimethyl carbinol,

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

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} CH_3 \\ SO_4H \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} CH_3 \\ OH \end{matrix}$$

Propyl alcohol (normal), $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$, is one of the

components of fusel oil (p. 332), from which it may be obtained by fractional distillation; it is also manufactured from carbon monoxide (p. 106). It is formed when propyl iodide is heated with freshly precipitated silver oxide and water,

$$C_3H_7I+Ag\cdot OH = C_3H_7\cdot OH+AgI.$$

It is a liquid of sp. gr. 0·804 at 20°, boiling at 97°, and is miscible with water. On oxidation with chromic acid, it gives first propionaldehyde, and then propionic acid,

$$CH_3\cdot CH_2\cdot CH_2\cdot OH+O = CH_3\cdot CH_2\cdot CHO+H_2O,$$
$$CH_3\cdot CH_2\cdot CH_2\cdot OH+2O = CH_3\cdot CH_2\cdot CO\cdot OH+H_2O.$$

***Iso*propyl alcohol,** $(CH_3)_2CH\cdot OH$, may be prepared by the reduction of acetone with sodium amalgam and water or with hydrogen and nickel (p. 405),

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

It may also be produced by treating acetaldehyde with methyl magnesium iodide, and decomposing the product with a dilute acid (p. 238). It is now prepared commercially by passing propylene into sulphuric acid and warming the *iso*propyl hydrogen sulphate thus formed with water (p. 368),

$$CH_3\cdot CH{:}CH_2+H_2SO_4 = CH_3\cdot CH(SO_4H)\cdot CH_3,$$
$$CH_3\cdot CH(SO_4H)\cdot CH_3+H_2O = CH_3\cdot CH(OH)\cdot CH_3+H_2SO_4.$$

It is a liquid of sp. gr. 0·789 at 20°, and boils at 82°, 15° lower than does normal propyl alcohol. On oxidation it yields acetone (p. 145),

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

and when heated with zinc chloride it gives propylene.

There are four isomeric **butyl alcohols** $C_4H_9\cdot OH$. *Normal butyl alcohol*, a liquid boiling at 117°, may be obtained by reducing butyraldehyde, $CH_3\cdot CH_2\cdot CH_2\cdot CHO$. It is manufactured by reducing crotonaldehyde (p. 369) and has been produced on the large scale, together with acetone, by the fermentation of potato-starch, or maize, with certain bacteria (Fernbach's culture). This organism converts starch into butyl alcohol (30–50%), acetone (14–28%), and hydrogen. During the War of 1914–18 when acetone was manufactured by this process the butyl alcohol was a more or less useless by-product; now, however, the esters of butyl alcohol, such as butyl acetate and lactate, are valuable solvents

(especially for cellulose esters used in lacquers) and plasticisers. Butyl alcohol can also be used for the production of butadiene, $CH_2{:}CH \cdot CH{:}CH_2$, and then synthetic rubber (p. 369).

Iso*butyl alcohol*, or *iso*propyl carbinol, $(CH_3)_2CH \cdot CH_2 \cdot OH$, is contained in fusel oil and in the product from carbon monoxide and hydrogen (p. 106). It boils at 108°.

Methylethyl carbinol, $CH_3 \cdot CH(OH) \cdot C_2H_5$, may be obtained by reducing methylethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$ (p. 152), or by treating acetaldehyde with ethyl magnesium bromide, and then decomposing the product with an acid (p. 238); it is prepared commercially from the butylenes contained in cracked petroleum (p. 368). It boils at 99°.

Trimethyl carbinol, $(CH_3)_3C \cdot OH$, may be prepared from acetone or ethyl acetate with the aid of methyl magnesium iodide (p. 238); also from *iso*butyl alcohol (p. 118) or *iso*butylene. Trimethyl carbinol is one of the few alcohols of low molecular weight which is solid at ordinary temperatures. It melts at 25°, and boils at 83°.

Amyl alcohols, $C_5H_{11} \cdot OH$. Of the eight structural isomerides theoretically capable of existing, all of which are known, the following are the main components of fusel oil (p. 332):

*Iso*amyl alcohol (3-Methylbutanol-1) $\quad (CH_3)_2 > CH \cdot CH_2 \cdot CH_2 \cdot OH$. B.p. 131°.

Active amyl alcohol (2-Methylbutanol-1) $\quad CH_3 \cdot CH_2 \cdot (CH_3) > CH \cdot CH_2 \cdot OH$. B.p. 128°.

Commercial amyl alcohol is prepared from fusel oil by fractionation, and contains about 87% of *iso*butyl carbinol and about 13% of active amyl alcohol, for the separation of which (rarely carried out) chemical methods would be necessary. It has a pungent, unpleasant smell, boils at about 130°, and is used as a solvent and in the preparation of essences and perfumes (p. 198). Other commercial mixtures of amyl alcohols are prepared from petroleum pentane by chlorination, followed by hydrolysis, and also from the amylenes of cracked petroleum (p. 368). The esters of amyl alcohols are largely used as solvents for cellulose lacquers.

SUMMARY AND EXTENSION

The Monohydric Alcohols. Hydroxy-derivatives of the paraffins of the general formula, $C_nH_{2n+1} \cdot OH$ or $R \cdot OH$. The more important members of the series are the following: the letters p., s., t., in

brackets, denote primary, secondary, and tertiary respectively, and the figure in brackets shows the number of structural isomerides.

		B.p.	Sp. gr. at 0°
Methyl alcohol (p.)	$CH_3 \cdot OH$	64·7°	0·810
Ethyl alcohol (p.)	$C_2H_5 \cdot OH$	78·5°	0·806
Propyl alcohol (p.)	$C_3H_7 \cdot OH$ (2)	97°	0·817
*Iso*propyl alcohol (s.)		82°	0·800
Butyl alcohol (p.)	$C_4H_9 \cdot OH$ (4)	117°	0·824
*Iso*butyl alcohol (p.)		108°	0·817
Methylethyl carbinol (s.)		99°	0·827
Trimethyl carbinol (t.)		83°	0·807
*Iso*amyl alcohol (p.)	$C_5H_{11} \cdot OH$ (8)	131°	0·824
Active amyl alcohol (p.)		128°	0·834

Nomenclature. The lower alcohols are still generally named as above, but more systematically the name is derived from that of the parent paraffin, the terminal **e** of **ane** being changed into **ol**, as in methan**ol**, ethan**ol**, etc. Consequently only those alcohols derived from normal hydrocarbons have names which directly express the number of carbon atoms in the molecule, because the parent hydrocarbons are themselves named in accordance with the system already explained (p. 60) : thus there are only three alcohols derived from normal hexane, namely, 1-, 2- and 3-n-*hexanols*,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH,$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot CH_3,$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_3,$$

the position of the hydroxyl group being shown by a number. Those derived from *iso*hexane, however, are 2-*methylpentanols*, and so on.

Special Methods of Preparation. Methyl alcohol is prepared from water-gas and from methane (p. 106). Ethyl alcohol is obtained by the fermentation of sugars ; the fusel oil produced at the same time contains propyl, *iso*butyl, *iso*amyl, and active amyl alcohols. It is also produced from starch by fermentation processes, and from sawdust, which is first converted into glucose.

Many alcohols (including ethyl alcohol) are prepared commercially from cracked petroleum (p. 368).

General Methods of Preparation. (1) The alkyl halogen compounds are heated with water, dilute aqueous alkalis, or moist, freshly precipitated silver oxide,

$$CH_3Br + KOH = CH_3 \cdot OH + KBr,$$
$$C_3H_7I + Ag \cdot OH = C_3H_7 \cdot OH + AgI.$$

In these, as in nearly all cases, the iodides react more easily than the bromides and the latter more easily than the chlorides.

(2) The alkyl halogen compounds are heated with silver (or potassium) acetate, and the products are hydrolysed,

$$C_2H_5I+C_2H_3O_2Ag = C_2H_5\cdot C_2H_3O_2+AgI,$$
$$C_2H_5\cdot C_2H_3O_2+KOH = C_2H_5\cdot OH+C_2H_3O_2K.$$

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 alkalis, are mainly converted into olefines,

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

and the yield of alcohol is small.

(3) The hydrocarbons of the olefine series are dissolved in (anhydro) sulphuric acid, and the solutions are boiled with water, an important commercial process,

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

(4) Primary amines are decomposed with nitrous acid (p. 215).

(5) Aldehydes and ketones are reduced with nascent hydrogen, molecular hydrogen and a catalyst, or by the Pondorff reagent (p. 156); aldehydes thus give primary, ketones secondary, alcohols (and pinacols, p. 155).

(6) Aldehydes, ketones, and esters are treated with a Grignard reagent (p. 238), and the products are decomposed with a mineral acid; in this way secondary alcohols are obtained from aldehydes (and esters of formic acid), tertiary alcohols from ketones and esters in general.

Some higher alcohols may be obtained by the reduction of esters (p. 198).

Physical Properties. Most of the members up to $C_{12}H_{26}O$ are liquids at ordinary temperatures; 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. Trimethyl carbinol is also a solid. 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, are only sparingly soluble. The lower alcohols are miscible with other organic liquids.

The specific gravity increases and the boiling-point rises as the molecular weight increases; *but* as a primary alcohol boils at a higher temperature than the corresponding secondary alcohol, and the latter

at a higher temperature than the tertiary isomeride (as shown in the table, p. 121), the regular variation in this, and in other physical properties, is obvious only when homologues of *similar constitution* are compared. It may also be pointed out that, as a rule, the first member of a homologous series shows a somewhat abnormal behaviour; methyl alcohol, for example, has a *higher* specific gravity than ethyl alcohol, and its boiling-point is only 13° lower than that of ethyl alcohol; in the case of the higher homologues, the difference between the boiling-points of two consecutive *normal* primary alcohols is about 20°.

Alcohols are associated in the liquid state and this accounts for their high boiling-points compared, for example, with those of their isomeric ethers.

A comparison of the properties of an alcohol, with those of the paraffin from which it is derived, shows that the substitution of the hydroxyl group for an atom of hydrogen in the molecule not only raises the boiling-point very considerably, but also greatly increases the solubility in water; on the other hand, as the hydrocarbon radical in the alcohol, $R \cdot OH$, increases in molecular weight, the influence of the hydroxyl group on the physical properties diminishes.

Chemical Properties. The fact that the alcohols react with many other compounds so much more readily than do the paraffins is due to the presence of the hydroxyl group in their molecules; it is this group only which is changed in most of their general reactions.

The alcohols are acted on by sodium and potassium, with the evolution of hydrogen; also by magnesium and aluminium in the presence of iodine and mercuric chloride, giving $Mg(OR)_2$ and $Al(OR)_3$ respectively. They react with acids, forming esters, such as CH_3Cl, C_2H_5Br, C_2H_5I, $C_3H_7 \cdot O \cdot SO_3H$, $C_2H_5OOC \cdot CH_3$.

They are partly converted into halogen derivatives of the paraffins when they are treated with PCl_5, PCl_3, $POCl_3$ (compare footnote, p. 108), but with the corresponding bromo-derivatives, or with red phosphorus and iodine, much larger proportions of the alkyl halide are formed,

$$2P+3I_2+6C_2H_5 \cdot OH = 6C_2H_5I+2H_3PO_3.$$

Except methyl alcohol, they are converted into olefines by sulphuric acid, phosphoric acid, zinc chloride, etc.,

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

In the case of secondary and tertiary alcohols the hydroxyl group is usually removed with a hydrogen atom from an adjoining $>CH$ or $>CH_2$ rather than a $-CH_3$ group: methylethyl carbinol, for example, gives 2- rather than 1-butylene,

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

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 product contains the same number of carbon atoms in the molecule as the alcohol from which it is 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 undergo a more profound change and are decomposed, giving a mixture of simpler acids, or of acid and ketone. The three classes of alcohols, therefore, can be *distinguished* by their different behaviour on oxidation; also by their different behaviour in the presence of heated nickel (p. 118).

CHAPTER 9

THE ETHERS, THIO-ETHERS, AND MERCAPTANS

THE ethers, such as dimethyl ether, $CH_3 \cdot O \cdot CH_3$, methylethyl ether, $CH_3 \cdot O \cdot C_2H_5$, etc., are substances of the type, R—O—R, and they contain two identical, or different, alkyl groups united to an oxygen atom. They may be regarded as oxides of the hydrocarbon radicals or as anhydrides of the alcohols and they form a homologous series $C_nH_{2n+2}O$.

Methyl ether (dimethyl ether), $CH_3 \cdot O \cdot CH_3$, may be prepared by the action of sulphuric acid on methyl alcohol; the reaction takes place in two stages, as described below.

It is a gas which liquefies at $-24°$ and is used as a refrigerant; 1 vol. of water dissolves 37 vol. of the ether at 18°.

Ethyl ether, *diethyl ether* or, simply, *ether*, $C_2H_5 \cdot O \cdot C_2H_5$, is formed when sodium ethoxide is warmed with ethyl iodide (Williamson),

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

It is prepared by heating ethyl alcohol with sulphuric acid under suitable conditions.

Concentrated sulphuric acid (100 c.c.) is *cautiously* added to ethyl alcohol (100 c.c.), containing not more than about 5% of water, and the mixture is slowly heated in a litre flask fitted with a tap-funnel and thermometer, and connected with a condenser (Fig. 19). The end of the latter is fitted into a distillation flask, the side tube of which is connected with a piece of rubber tubing leading over the edge of the working-bench so that the uncondensed ether vapour cannot catch fire. As soon as the temperature of the liquid rises to about 140°, ether begins to pass over.[1] Alcohol is now added from the tap-funnel at about the same rate as that at which the ether distils, and the temperature is kept at 140–145°; the tap-funnel should dip *below* the surface of the liquid. The crude product in the receiver is a mixture of ether, alcohol, and water, and may also contain sulphur dioxide. It is shaken with

[1] The bulb of the thermometer is immersed in the *liquid* (which, of course, is not usual). It is advisable to cool the receiver with ice in warm weather. Great care should be taken in working with ether and other readily volatile inflammable liquids.

dilute aqueous alkali in a separating-funnel, the aqueous solution is run off, and the ether is then well agitated with anhydrous calcium chloride ; the decanted or filtered liquid is distilled from a water-bath. The ether still contains some water and alcohol, and may

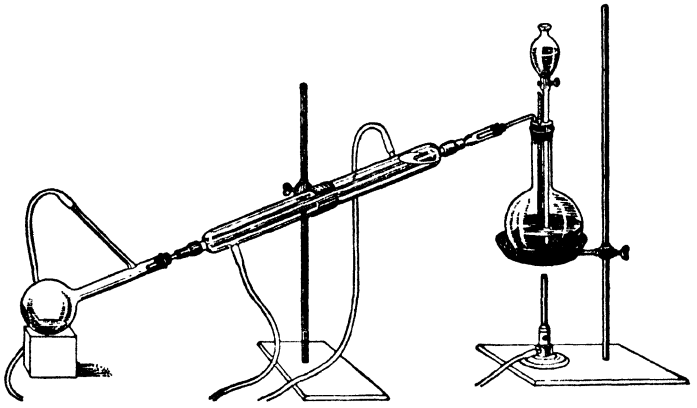


Fig. 19

be left in contact with bright pieces of sodium (in a flask closed with a calcium chloride tube) until the evolution of hydrogen ceases. The ether is finally distilled from the sodium ethoxide and sodium hydroxide, which have been produced.

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. 194),

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

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

$$C_2H_5 \cdot HSO_4 + HO \cdot C_2H_5 = C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4.$$

This explanation of the formation of ether was first given by Williamson, who proved 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 may be *reduced* by the alcohol, with the formation of sulphur dioxide. Nevertheless, as this method of preparing ether by the *continuous* addition of alcohol to a solution of alcohol in sulphuric acid is practicable within limits, it is termed the *continuous process*.

In the presence of anhydrous aluminium sulphate the reactions take place rapidly at about 135°. If, instead of sulphuric acid, benzenesulphonic acid (p. 475) is used, the process is really continuous, as this acid is not reduced by the alcohol, and the water which is produced is not retained by the acid, but distils with the ether,

$$C_6H_5\cdot SO_2\cdot OH+C_2H_5\cdot OH = C_6H_5\cdot SO_2\cdot OC_2H_5+H_2O,$$
$$C_6H_5\cdot SO_2\cdot OC_2H_5+C_2H_5\cdot OH = C_2H_5\cdot O\cdot C_2H_5+C_6H_5\cdot SO_2\cdot OH.$$

Ether may also be prepared by passing the vapour of ethyl alcohol[1] through copper tubes containing precipitated alumina, which is heated at about 260°; the alumina acts catalytically and the alcohol is converted into ether and water, but at higher temperatures ethylene is also formed.

Ether is obtained as a by-product in the manufacture of alcohol from ethylene (p. 368).

Ether is a mobile, neutral, pleasant-smelling liquid of sp. gr. 0·713 at 20°. It boils at 34–35°, and solidifies at about −120°. It is very volatile, and *highly inflammable*, and as its vapour forms an explosive mixture with air or oxygen,

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

all experiments with ether should be conducted at least ten feet away from flames or hot objects. Ether is soluble in about ten volumes of water, and is miscible with alcohol and most other organic liquids. When it contains water, it gives a turbidity if mixed with its own volume of carbon disulphide.

Compared with alcohol, ether is a very inactive substance. It is not acted on by sodium or potassium, by alkalis or weak acids, or by phosphorus pentachloride in the cold. Concentrated acids, however, decompose it, with the formation of esters (p. 185),

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

Ether vapour, usually mixed with nitrous oxide and oxygen, is used in surgery as an anaesthetic ; it is an important laboratory reagent (p. 236) and is also employed as a solvent for fats, oils, alkaloids, etc., and for the extraction of substances from aqueous solutions or suspensions.

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 univalent C_2H_5— group for the sodium atom, and its constitution may be expressed by the formula, $C_2H_5 \cdot O \cdot C_2H_5$. This view is confirmed by a study of the chemical properties of ether ; its molecule, unlike that of alcohol, does not contain a hydroxyl group, and therefore it is not acted on by sodium or potassium, or by phosphorus halides.

Ether may be regarded not only as an *anhydride* of alcohol but also as a di-substitution product of water, the mono-substitution product being the corresponding alcohol.

In the molecules of *dimethyl* and *diethyl* ethers the two hydrocarbon radicals united to the oxygen atom are *identical*; such compounds are called *simple* ethers, to distinguish them from *mixed* ethers in which two *different* radicals are combined with the oxygen atom, as, for example, *methylethyl ether*, $CH_3 \cdot O \cdot C_2H_5$.

Isomerism in the homologous series of ethers begins with the compounds $C_4H_{10}O$, of which there are three, one simple and two mixed ethers as shown below :

$CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_3$, Diethyl ether

$CH_3 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH_3$, Methylpropyl ether

$CH_3 \cdot O \cdot CH(CH_3)_2$. Methyl*iso*propyl ether

It will be realised from this example that isomerism is due to differences between the hydrocarbon radicals either in molecular formula or in structure. These three ethers are also isomeric with the four alcohols, $C_4H_{10}O$.

Isomerism of the type exhibited by the ethers is sometimes called *metamerism*, this term being used to denote isomerism of molecules in which *all* the carbon atoms are not directly united. Metamerism is also exhibited, for example by sulphides, amines, esters, etc.

The *homologues* of diethyl ether and, in fact, all ethers, closely resemble diethyl ether in their chemical behaviour.

Mercaptans and Sulphides

There are two classes of organic compounds derived from hydrogen sulphide—namely, the hydrosulphides and the sulphides, and the relation between them is similar to that between the alcohols and the ethers respectively,

Ethyl hydrosulphide	$C_2H_5 \cdot SH$	Diethyl sulphide	$(C_2H_5)_2S$
Ethyl hydroxide	$C_2H_5 \cdot OH$	Diethyl oxide	$(C_2H_5)_2O$.

The organic hydrosulphides are usually called **mercaptans** (*mercurium captans*) on account of their property of reacting readily with mercuric oxide to form 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 hydrogen sulphide,

$$C_2H_5 \cdot KSO_4 + KSH = C_2H_5 \cdot SH + K_2SO_4,$$

or by the interaction of ethyl iodide and potassium hydrogen sulphide. It is a liquid, having a most offensive smell, and boils at 37°.

Its low boiling-point, compared with that (78·5°) of alcohol, shows that ethyl mercaptan (like other mercaptans) is far less associated (if at all) than alcohol in the liquid state, just as liquid hydrogen sulphide is less associated than water.

The hydrogen atom of the HS— group is displaceable by metals more readily than that of the HO— group of the alcohols ; thus ethyl mercaptan reacts not only with sodium or potassium, giving *sodium* or *potassium mercaptide*, $C_2H_5 \cdot SNa$, or $C_2H_5 \cdot SK$, with the evolution of hydrogen, but when shaken with mercuric oxide it yields *mercuric mercaptide*,

$$2C_2H_5 \cdot SH + HgO = (C_2H_5 \cdot S)_2Hg + H_2O ;$$

this crystalline compound is decomposed by hydrogen sulphide, giving ethyl mercaptan,

$$(C_2H_5 \cdot S)_2Hg + H_2S = 2C_2H_5 \cdot SH + HgS.$$

Other mercaptans can be obtained by reactions similar to those given above ; 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 alkyl*sulphonic acids*,

$$C_2H_5\cdot SH+3O = C_2H_5\cdot SO_2\cdot OH.$$
Ethanesulphonic Acid

which contain the group $—SO_2\cdot OH$, and an alkyl radical combined with the sulphur atom, as proved by the formation of the acids from the mercaptans ; they are stable acids, forming salts, such as potassium ethanesulphonate, $C_2H_5\cdot SO_2\cdot OK$, which may be prepared by boiling alkyl halides with alkali sulphites,

$$C_2H_5I+K\cdot SO_3K = C_2H_5\cdot SO_3K+KI.$$

Diethyl sulphide, *ethyl sulphide*, $(C_2H_5)_2S$, may be obtained by heating 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 neutral, unpleasant-smelling, inflammable liquid, and boils at 92° ; 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 ; on oxidation with nitric acid, they are first converted into *sulphoxides*, R_2SO, and then into very stable crystalline compounds termed *sulphones*, of which *diethyl sulphone*, $(C_2H_5)_2SO_2$, m.p. 72°, is an example.

Sulphonal, $(CH_3)_2C(SO_2\cdot C_2H_5)_2$, is an important and interesting compound, largely used as a soporific. Although acetone and other ketones do not react readily with alcohols, giving acetals, as do aldehydes, they *condense* with mercaptans in the presence of hydrogen chloride ; acetone and ethyl mercaptan, for example, give *acetone diethylmercaptole* (b.p. 75°, 12 mm.),

$$(CH_3)_2CO+2C_2H_5\cdot SH = (CH_3)_2C(S\cdot C_2H_5)_2+H_2O.$$

When this mercaptole is oxidised with potassium permanganate, it unites directly with four atoms of oxygen, giving *sulphonal*, a crystalline compound melting at 126°. Analogous compounds, $CMeEt(SO_2\cdot C_2H_5)_2$ and $CEt_2(SO_2\cdot C_2H_5)_2$, named *trional* and *tetronal* respectively, are obtained from methylethyl ketone and diethyl ketone respectively.

$\beta\beta'$-Dichlorodiethyl sulphide, $(CH_2Cl\cdot CH_2)_2S$, a poison gas (known as mustard gas), may be prepared by passing ethylene into sulphur monochloride,

$$\begin{matrix}CH_2{:}CH_2\\CH_2{:}CH_2\end{matrix}\!\!>\!\!\begin{matrix}Cl\\Cl\end{matrix}\!\!>S_2 = \begin{matrix}CH_2Cl\cdot CH_2\\CH_2Cl\cdot CH_2\end{matrix}\!\!>S+S.$$

It has also been manufactured by treating ethylene chlorohydrin with sodium sulphide, or ethylene oxide with hydrogen sulphide, and then esterifying the product with hydrogen chloride.

It melts at 14·4°, boils at 217°, and is exceedingly toxic and vesicant.

SUMMARY AND EXTENSION

Ethers have the general formula, R—O—R′, where R and R′ represent identical or different hydrocarbon radicals, and their names show the alkyl groups which their molecules contain ; they and the sulphides, $R\cdot S\cdot R'$, form homologous series, $C_nH_{2n+2}O$ and $C_nH_{2n+2}S$, respectively.

		b.p.
Dimethyl ether	C_2H_6O	−24°
Methylethyl ether	C_3H_8O	11°
Diethyl ether	$C_4H_{10}O$	35°
Methylpropyl ether		39°
Methyl*iso*propyl ether		32°
Dipropyl ether	$C_6H_{14}O$	90°
Di-*iso*propyl ether		69°
Di-*iso*butyl ether	$C_8H_{18}O$	123°
Di-*iso*amyl ether	$C_{10}H_{22}O$	173°

Nomenclature. It will be seen that the name of an ether consists of those of the two hydrocarbon radicals together with *ether*.

General Methods of Formation. (1) The sodium derivatives of the alcohols are heated with the alkyl halides (Williamson),

$$CH_3\cdot ONa+CH_3I = CH_3\cdot O\cdot CH_3+NaI,$$
$$CH_3\cdot ONa+C_3H_7I = CH_3\cdot O\cdot C_3H_7+NaI.$$

(2) The alkyl halides are heated with silver oxide,

$$2C_3H_7I+Ag_2O = (C_3H_7)_2O+2AgI.$$

(3) The alcohols are heated with sulphuric acid, or their vapours are passed under pressure over heated aluminium sulphate ; these methods are usually applicable only in the case of the lower primary alcohols ; secondary alcohols generally, and tertiary alcohols always, give olefines.

When a mixture of two alcohols is treated with sulphuric acid, *three* ethers, two simple and one mixed, are formed. A mixture of

methyl and ethyl alcohols, for example, yields *dimethyl ether*, *diethyl ether*, and *methylethyl ether*. The formation of the first two compounds will be understood from the equations given above in the case of diethyl ether. Methylethyl ether is produced by the interaction (*a*) of methyl hydrogen sulphate and ethyl alcohol, (*b*) of ethyl hydrogen sulphate and methyl alcohol,

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

Mixed ethers are best obtained by Williamson's method (1); some are manufactured by treating an alkyl hydrogen sulphate, dissolved in sulphuric acid, with an olefine.

General Properties. With the exception of dimethyl ether, which is a gas, the ethers are volatile, non-associated, inflammable liquids, specifically lighter than water. In chemical properties they are very inert and closely resemble diethyl ether. They are not acted on by alkalis or alkali metals, and do not react with dilute acids, but they are decomposed when heated with strong acids, yielding esters,

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

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

$$CH_2Cl \cdot O \cdot CH_3, \quad C_2H_5 \cdot O \cdot C_2H_4Cl, \quad C_2H_5 \cdot O \cdot C_2H_3Cl_2, \quad \text{etc.}$$

CHAPTER 10

ALDEHYDES AND KETONES

ALDEHYDES

THE *aldehydes* form a homologous series of the general formula, $C_nH_{2n+1}\cdot CHO$, or $R\cdot CHO$; they are derived from the primary alcohols, $R\cdot CH_2\cdot OH$, by the elimination 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, a name originally given to acetaldehyde, because it is formed when hydrogen is taken from alcohol (by oxidation). An aldehyde derives its name from that of the acid which it yields on oxidation, *form*-aldehyde giving *form*ic acid; or from that of the corresponding paraffin, by changing the termination *ane* into *aldehyde* or *anal*.

Formaldehyde, *methaldehyde*, *methanal*, $H\cdot CHO$, has been considered to be an intermediate product in that wonderful process —the formation of starch and sugars from the carbon dioxide which a plant absorbs from the air; there is, however, no conclusive evidence that formaldehyde actually occurs in plants.

Formaldehyde is produced in small quantities when carbon dioxide is passed into water exposed to ultra-violet light, and it is formed when calcium formate is heated,

$$\left.\begin{matrix}H\cdot COO\\H\cdot COO\end{matrix}\right\rangle Ca = H\cdot CHO + CaCO_3.$$

It is prepared by passing a mixture of air and the vapour of methyl alcohol through a tube containing a roll of copper or silver gauze, or platinised asbestos, heated at about 400°;[1] the alcohol is decomposed catalytically into formaldehyde and hydrogen,

$$CH_3\cdot OH = H\cdot CHO + H_2,$$

and the latter combines with the atmospheric oxygen.

[1] Unless special precautions are taken, explosions may occur.

The pungent-smelling aqueous solution which collects in the receiver may contain, under favourable conditions, as much as 30–40% of formaldehyde, together with methyl alcohol; when the solution is evaporated, even at ordinary temperatures, it gives a solid, which is a complex mixture, produced from the (hydrated) aldehyde, and is known as *paraformaldehyde* (p. 135).

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

Formaldehyde is a gas at ordinary temperatures, but it may be condensed to a liquid, b.p. $-21°$. Even at this temperature it may slowly change into *trioxymethylene* (p. 136), and at ordinary temperatures it does so with great rapidity, and with a considerable development of heat. Aqueous solutions of formaldehyde have a very penetrating, suffocating odour, and a neutral reaction; they have also a strong reducing action, since formaldehyde readily undergoes oxidation, yielding formic acid,

$$H\cdot CHO+O = H\cdot CO\cdot OH.$$

Thus an aqueous solution of formaldehyde reduces an ammoniacal solution of silver oxide, and silver is precipitated,

$$H\cdot CHO+Ag_2O = H\cdot CO\cdot OH+2Ag;$$

when the solution is only gently warmed the metal may be deposited on the walls of the containing vessel in the form of a mirror. Mercuric chloride and alkaline solutions of cupric hydroxide (Fehling's solution, p. 312) are also reduced, the former giving mercurous chloride and then mercury, the latter, cuprous oxide.

When formaldehyde is treated with dilute caustic soda it is converted into methyl alcohol and sodium formate,

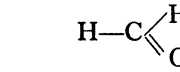
$$2H\cdot CHO+NaOH = CH_3\cdot OH+H\cdot CO\cdot ONa.$$

Like acetaldehyde, formaldehyde reacts with a solution of sodium hydrogen sulphite (p. 139), with hydroxylamine (p. 149), and with phenylhydrazine (p. 150).

Formaldehyde is a strong antiseptic, and is fatal to bacteria of various kinds; an aqueous solution containing about 40% of formaldehyde and a little alcohol is sold under the name of ***formalin***,

and is an important article of commerce. Formalin is used as a reducing agent and as an antiseptic and disinfectant; also as a preservative for biological and anatomical specimens, which it hardens without increasing their opacity. Gelatin, a substance readily soluble in water, becomes insoluble when it is treated with formalin. Formaldehyde is also used in the preparation of synthetic resins, such as Bakelite (p. 484), which is produced from formaldehyde and phenol and is employed for a great many industrial purposes. Similar resins are also formed from formaldehyde and urea (p. 263) or thiourea (p. 364). Formaldehyde is also used in the preparation of dyes and other synthetic products.

Structure. Since carbon is quadrivalent, the constitution of formaldehyde must be expressed by the formula,



It will be seen that the oxygen atom in the molecule of formaldehyde is represented as being in a state of combination different from that in which it exists in the molecule of methyl alcohol. Formaldehyde, in fact, is not a saturated compound, and is capable of forming additive products under certain conditions; it must be carefully noted, however, that the atoms or groups with which formaldehyde unites directly are not, generally speaking, those which combine readily with two unsaturated carbon atoms. *A double binding between carbon and oxygen must be distinguished from a double binding between two carbon atoms*, although in both cases it may indicate unsaturation; nevertheless, the term unsaturated is often restricted to those compounds in which both parts of the addendum combine with *carbon* atoms.

The aldehyde group is written —CHO, and not —COH, as the latter would imply that the hydrogen is united to the oxygen atom.

Since formaldehyde is neutral to litmus, the percentage of the aldehyde in formalin may be estimated by first neutralising any acid impurities with dilute sodium hydroxide solution, and then adding an excess of standard ammonia, which converts the formaldehyde into hexamethylenetetramine (p. 137); the excess of ammonia is then titrated with standard acid. Formaldehyde is readily oxidised by hydrogen peroxide, giving formic acid; this reaction may also be used for its estimation.

Paraformaldehyde, obtained by evaporating an *aqueous solution*

of formaldehyde, is crystalline (m.p. 140–160°) and soluble in warm water ; mixed with sucrose, it is sold as *formamint* or *formalin*.

It is a complex mixture of compounds (α-polyoxymethylenes) which are derived from *methylene glycol*, $HO \cdot CH_2 \cdot OH$, and have the composition, $HO \cdot CH_2 \cdot O \cdot (CH_2 \cdot O)_n \cdot CH_2 \cdot OH$ where the value of *n* ranges from about 8 to 50. With concentrated sulphuric acid, formalin gives crystalline precipitates which are similar to, but more complex than, paraformaldehyde ; when these solids are heated at 100° under reduced pressure, the distillate contains *trioxymethylene* ; when they are left in contact with phosphorus pentoxide, they give gaseous formaldehyde.

Trioxymethylene, *trioxan* $(CH_2O)_3$, or $C_3H_6O_3$, is formed by the polymerisation of gaseous or liquid formaldehyde in the presence of traces of water, acids, or alkalis ; it is crystalline, sublimes readily, melts at 67–68°, and is freely soluble in water. 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, trioxymethylene is again produced if traces of water are present. When heated with a large quantity of water at about 140° it gives an aqueous solution resembling formalin.

Tetraoxymethylene, $(CH_2O)_4$, or $C_4H_8O_4$, is also a *polymeride* of formaldehyde, melting at 112° and readily soluble in water. It is obtained by heating the *diacetates* prepared from the polyoxymethylene derivatives contained in formalin.

Polymerisation. It will have been seen that formaldehyde readily changes, giving new compounds, which can be reconverted into formaldehyde, CH_2O, by simple means. As the new compounds have the *same* percentage composition as the parent substance, their molecules might be regarded as having been produced by the aggregation of *several* molecules of the latter. Such views led to the introduction of the word **polymerisation,**[1] which means the change of some (simple) substance into another of the same percentage composition, but having a molecular weight equal to several multiples of that of the parent substance ; the more complex compounds, thus formed, were then termed *polymers*, *polymerides*, or *polymeric modifications* of the original substance, and they received names, as in the case of paraformaldehyde, which indicated their origin or derivation. It is now recognised, however, that a poly-

[1] Gr. *meros*, part.

meric modification may show little or no structural relation to the parent substance; that its molecules are not merely *aggregates* or *collections* of simpler molecules, but are produced by the chemical union of two or more molecules of the latter to form a new and distinct compound, which in many cases cannot be reconverted into the original substance.

Polymerisation, then, is merely a chemical change, resulting in the formation of a compound, whose molecular formula is a multiple of that of the original substance because the polymeride is produced by the direct union of two or more molecules of the latter; other examples of this change are given later (p. 141).

Formaldehyde gives several other polymerides, and the readiness with which it undergoes polymerisation is one of its more 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; these reactions are *not* reversible, and are of great interest, since they show that complex vegetable substances, such as the sugars, may be formed by simple changes (p. 319).

Hexamethylenetetramine or **hexamine,** $(CH_2)_6N_4$, is rapidly formed when ammonia is added to formalin; it is crystalline, readily soluble in water, and is used in medicine in cases of gout and rheumatism. When strongly heated it sublimes and is partly decomposed, giving basic vapours; it is also decomposed by hot dilute sulphuric acid, giving formaldehyde, which is recognised by its pungent smell, and ammonium sulphate; it is *not* decomposed when it is boiled with an aqueous solution of an alkali, and although it is a mono-acidic base, it is neutral to litmus. Its structure is shown later (p. 159).

Methylal, $CH_2(OCH_3)_2$, is an important derivative of formaldehyde. It may be obtained by oxidising methyl alcohol with manganese dioxide and sulphuric acid, when the formaldehyde which is first produced combines with some of the unchanged methyl alcohol; it is usually prepared by boiling formalin with methyl alcohol and a small quantity of sulphuric acid,

$$H\cdot CHO + 2HO\cdot CH_3 = H\cdot CH{<}\begin{matrix}OCH_3\\OCH_3\end{matrix} + H_2O.$$

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 gives an aqueous solution of methyl alcohol and formaldehyde, but it is not decomposed by boiling aqueous alkali.

Acetaldehyde, *ethaldehyde, ethanal,* $CH_3 \cdot CHO$, is formed in very small quantities by atmospheric oxidation when alcohol is slowly filtered through charcoal, or exposed to the air in the presence of platinum black, or heated platinum; it is also formed when a mixture of calcium acetate and calcium formate (which may be regarded as a salt of the two acids) is submitted to dry distillation,

$$\left.\begin{matrix} H \cdot COO \\ CH_3 \cdot COO \end{matrix}\right\rangle Ca = CH_3 \cdot CHO + CaCO_3.$$

Acetaldehyde may be obtained in the laboratory by oxidising alcohol with potassium dichromate and sulphuric acid.

Coarsely powdered potassium dichromate (30 g.) and water (120 c.c.) are placed in a litre flask fitted with a tap-funnel and attached to a condenser, and the flask is gently heated on a water-bath; a mixture of alcohol (35 c.c.) and concentrated sulphuric acid (22 c.c.) is then added drop by drop, and the flask is shaken almost continuously during the operation. A vigorous action sets in, and a liquid, which consists of aldehyde, alcohol, water, and small proportions of acetal (p. 142), collects in the receiver. This product is now fractionally distilled from a water-bath, and the portion which passes over below 25° is collected and again fractionated, preferably with the aid of a *column*; the liquid which passes over between 20 and 22° consists of acetaldehyde, and is sufficiently free from impurities for most purposes.[1] The receiver should be well cooled with ice in all these operations.

Acetaldehyde is prepared on the large scale by passing alcohol vapour, mixed with air, over silver at a dull red heat; and also by passing acetylene into 20% sulphuric acid containing 1% of mercuric oxide and 5% of ferric sulphate, a little pyrolusite being added when the reactions begin to slow down. The acetaldehyde so obtained may be used for the manufacture of acetic acid (pp. 164, 369).

Acetaldehyde, or aldehyde, as it is often called, is a mobile, inflammable liquid of sp. gr. 0·785 at 16°; it boils at 21°. It has a characteristic, penetrating, and suffocating odour, by means of which it is easily identified; it is miscible with water, alcohol, and

[1] Pure acetaldehyde is best prepared from paraldehyde (p. 141), into which the crude acetaldehyde is easily converted.

ether. Aldehyde is slowly oxidised to acetic acid on exposure to the air,[1] and, like formaldehyde, it has marked reducing properties, giving cuprous oxide with Fehling's solution ; it also precipitates silver (in the form of a mirror) from ammoniacal solutions of silver oxide,

$$CH_3 \cdot CHO + Ag_2O = CH_3 \cdot CO \cdot OH + 2Ag.$$

When reduced with sodium amalgam and water, it is converted into alcohol. When aldehyde is shaken with a concentrated solution of sodium hydrogen sulphite (sodium bisulphite), direct combination occurs, and a substance, $CH_3 \cdot CH(OH) \cdot SO_3Na$, quickly separates in crystals. This compound is readily decomposed by acids, alkalis, and alkali carbonates, aldehyde being liberated. Aldehyde also combines directly with dry ammonia, to form *aldehyde ammonia*, $(C_2H_7ON)_3$,[2] a crystalline substance (m.p. 70–80°), which is decomposed by acids, aldehyde being regenerated. It also unites with hydrogen cyanide (p. 151), and condenses with hydroxylamine (p. 149) and hydrazines (p. 150).

Aldehyde very readily undergoes polymerisation on treatment with acids and other substances (p. 141). When it is very gently warmed with concentrated aqueous alkali a violent action occurs, and the aldehyde is converted into a mixture of brown substances, of unknown structure, having a characteristic smell, and called *aldehyde resin.*

Aldehyde is easily detected by its distinctive odour ; its reducing action on silver oxide and behaviour with alkalis may be used as confirmatory tests, but other aldehydes give these reactions. The magenta or rosaniline test (*Schiff's* reaction) may also be employed.

Sulphurous acid is added to a very dilute solution of rosaniline hydrochloride until the pink colour is just discharged.

When this reagent (1-2 c.c.) is treated with acetaldehyde, a violet or pink colour very soon appears. This behaviour, also, is not characteristic of acetaldehyde, as, with very few exceptions, all aldehydes and some ketones give this reaction.

Acetaldehyde is used in the commercial preparation of aldol, acetic acid and its derivatives, and various other compounds (p. 369).

[1] The first oxidation product is peracetic acid, $CH_3 \cdot CO_3H$, a very explosive substance which reacts with the aldehyde,

$$CH_3 \cdot CO_3H + CH_3 \cdot CHO = 2CH_3 \cdot COOH.$$

These reactions are catalysed by manganese salts.

[2] The structure of aldehyde ammonia is still doubtful.

Constitution. Aldehyde is formed by the oxidation of ethyl alcohol, just as formaldehyde is produced by the oxidation of methyl alcohol, and the final result in both cases is that two atoms of hydrogen are removed from the molecule of the primary alcohol. Now, it is known that, in the formation of formaldehyde, this change involves a hydroxyl group and a hydrogen atom, which are united to one and the same carbon atom,

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} H \\ OH \end{matrix} + O = \begin{matrix} H \\ H \end{matrix}\!\!>\!C{=}O + H_2O.$$

If, then, acetaldehyde is produced from ethyl alcohol in a similar manner,

$$CH_3\cdot CH_2\cdot OH + O = CH_3\cdot C\!\begin{matrix} \diagup \\ \diagdown \end{matrix}\!\!\begin{matrix} H \\ O \end{matrix} + H_2O,$$

—the constitution of acetaldehyde would be expressed by the formula (I), and *not* by either of the formulae (II) or (III), which from valency requirements are the only other theoretically possible structures,

$$CH_3{-}C\!\begin{matrix} \diagup \\ \diagdown \end{matrix}\!\!\begin{matrix} H \\ O \end{matrix} \qquad \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!\diagup\!\!\diagdown O \qquad CH_2{=}CH{-}OH$$

I II III

Judging from analogy, then, the constitution of aldehyde is expressed by the formula (I); this view accords with the whole chemical behaviour of the compound and in particular is fully confirmed by the relationship of aldehyde to chloral (p. 143). Aldehyde, unlike alcohol, does not contain a hydrogen atom displaceable by sodium or potassium, and does not form esters with acids; these facts are expressed by the above formula, which shows that aldehyde does not contain the HO— group. When aldehyde is treated with phosphorus pentachloride, one atom of oxygen is displaced by *two* atoms of chlorine (giving *ethylidene dichloride*), a change which is very different from that which occurs in the case of alcohol, and which affords further evidence that aldehyde is not a hydroxy-compound,

$$CH_3\cdot CHO + PCl_5 = CH_3\cdot CHCl_2 + POCl_3,$$
$$CH_3\cdot CH_2\cdot OH + PCl_5 = CH_3\cdot CH_2Cl + POCl_3 + HCl.$$

The fact that aldehyde has the property of combining directly with two univalent atoms or groups is also indicated by the above con-

since both are derived from the paraffins by the substitution of one atom of oxygen for two atoms of hydrogen.

Propionaldehyde	$CH_3 \cdot CH_2 \cdot CHO$	C_3H_6O.
Dimethyl ketone	$CH_3 \cdot CO \cdot CH_3$	
Butyraldehyde	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHO$	C_4H_8O.
Methylethyl ketone	$CH_3 \cdot CH_2 \cdot CO \cdot CH_3$	

Acetone, *propanone*, 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, with many other substances, during the destructive distillation of wood, sugar, gum, etc., and is obtained when *iso*propyl alcohol is oxidised with potassium dichromate and sulphuric acid,

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

It may be easily prepared in the laboratory by heating calcium (or barium) acetate (10 g.) in a hard glass tube, fitted with a cork and a downward delivery tube,[1]

$$CH_3 \cdot CO\,O \cdot Ca \cdot OOC \cdot CH_3 = CH_3 \cdot CO \cdot CH_3 + CaCO_3.$$

The distillate is shaken with a *saturated* solution of sodium hydrogen sulphite and the crystalline acetone sodium bisulphite, which is formed after a short time, is separated on a filter pump, and decomposed by distillation with a saturated solution of sodium carbonate ; the readily volatile product may then be freed from water with the aid of calcium chloride.

Acetone is manufactured by the oxidation of *iso*propyl alcohol with air in the presence of copper (p. 368), by passing a mixture of acetylene and steam over a heated mixture of ferric hydroxide and zinc oxide,

$$2C_2H_2 + 3H_2O = CH_3 \cdot CO \cdot CH_3 + 2H_2 + CO_2,$$

and, together with butyl alcohol, by the fermentation of starch (p. 119). It has also been made by passing a mixture of steam and ethyl alcohol vapour over a catalyst of iron and calcium acetate,

$$2C_2H_5 \cdot OH + H_2O = CH_3 \cdot CO \cdot CH_3 + CO_2 + 4H_2,$$

and by passing acetic acid vapour over heated lime or magnesia.

[1] The tube should be tapped gently to ensure a clear channel for the escape of the gaseous product.

Acetone is a mobile liquid of sp. gr. 0·792 at 20° ; it boils at 56·5°, has a peculiar and highly characteristic odour, by which it can be identified, and is miscible with water, alcohol, and ether.

In chemical properties acetone *resembles* acetaldehyde in several important particulars. When it is shaken with a concentrated aqueous solution of sodium hydrogen sulphite a considerable development of heat takes place, and *acetone sodium bisulphite*, $(CH_3)_2C(OH)\cdot SO_3Na$, an additive product, separates in crystals. This compound is readily soluble in water, and is quickly decomposed by dilute acids and alkalis, giving acetone.

When acetone is treated with phosphorus pentachloride, the oxygen atom in its molecule is displaced by two atoms of chlorine, and a dichloropropane is formed,

$$(CH_3)_2CO+PCl_5 = (CH_3)_2CCl_2+POCl_3 ;$$

on reduction, it is partially converted into *iso*propyl alcohol (p. 155).

Acetone, like acetaldehyde, reacts with hydroxylamine in aqueous solution, and forms *acetoxime*,

$$(CH_3)_2C{:}O+H_2N\cdot OH = (CH_3)_2C{:}N\cdot OH+H_2O,$$

a crystalline substance, melting at 59° ; also with phenylhydrazine, giving a phenylhydrazone, $(CH_3)_2C{:}N\cdot NH\cdot C_6H_5$ (m.p. 42°).

On the other hand, acetone *differs from* acetaldehyde in several very important respects. Thus, it does not readily undergo polymerisation, and does *not* reduce ammoniacal solutions of silver oxide ; it is oxidised, however, by certain reagents and its molecule is broken up, with the formation of 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, and is employed for the preparation of iodoform, chloroform, sulphonal, and other medicinal products, and for making plastics (p. 343); it is also a very important solvent.

Constitution. Acetone is formed when two atoms of hydrogen are removed from a molecule of *iso*propyl alcohol by oxidation. If, therefore, this process involves reactions analogous to those which occur in the oxidation of ethyl alcohol and methyl alcohol it may be represented as follows :

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}H\\OH\end{matrix}+O = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}O+H_2O.$$

This view of its constitution accords well with the whole chemical behaviour of acetone. That its molecule does not contain a hydroxyl group is shown by the fact that acetone, unlike the alcohols, is not attacked by acetyl chloride (p. 174), and also by the fact that its behaviour with phosphorus pentachloride is similar to that of aldehyde, but quite different from that of alcohol. These and many other considerations show that acetone has the constitution shown above ; its characteristic properties are determined by the presence of the bivalent **carbonyl** or **ketonic** group, $>C=O$, which is contained in the molecules of all ketones.

The similarity in chemical behaviour between acetone and aldehyde is expressed by their structural formulae ; both molecules contain the carbonyl group,

$$\text{Acetone, } \begin{matrix}CH_3\\CH_3\end{matrix}>C=O \qquad \text{Acetaldehyde, } \begin{matrix}H\\CH_3\end{matrix}>C=O,$$

and therefore those changes, in which only this group takes part, are common to both substances. Thus, they behave in a similar manner towards phosphorus pentachloride, and they both combine directly with hydrogen, hydrogen cyanide (p. 151), and sodium hydrogen sulphite ; in the last three, and in many other reactions, acetone, like aldehyde, behaves as an unsaturated compound. The difference between the two compounds as regards oxidation is also explained by the above formulae ; acetone does not contain the readily oxidisable hydrogen atom of the aldehyde group, and, therefore, it is less readily acted on than aldehyde, and does not reduce silver oxide. Both of these compounds, however, give the iodoform reaction.

Acetone and many other ketones give Schiff's reaction, but the colour usually appears more slowly than with aldehydes. The surest method of distinguishing between an aldehyde and a ketone is to study the oxidation products of the compound (p. 157).

Condensation of Acetone. When acetone is treated with certain dehydrating agents, it undergoes changes in which two or more molecules combine together with the elimination of one or more molecules of water,

$$(CH_3)_2CO+H_2CH\cdot CO\cdot CH_3 = \underset{\text{Mesityl oxide}}{(CH_3)_2C{:}CH\cdot CO\cdot CH_3}+H_2O,$$

$$(CH_3)_2C{:}CH\cdot CO\cdot CHH_2+OC(CH_3)_2 = \underset{\text{Phorone}}{(CH_3)_2C{:}CH\cdot CO\cdot CH{:}C(CH_3)_2}+H_2O.$$

These and similar changes, in which two or more molecules of the same or of different substances combine, with the formation of water, are termed **condensations,** and the substances which are formed, **condensation products**; the term ' condensation,' however, is applied to various types of reactions (p. 141).[1]

The production of mesityl oxide probably takes place in two stages, the first of which is a process of polymerisation, like that which occurs in the formation of aldol from acetaldehyde,

$$2CH_3 \cdot CO \cdot CH_3 = (CH_3)_2C(OH) \cdot CH_2 \cdot CO \cdot CH_3.$$

In the second stage the polymeride loses the elements of water, just as aldol gives crotonaldehyde; the condensation of mesityl oxide and acetone to phorone may be explained in a similar manner.

The above-named condensation products are formed when acetone is saturated with dry hydrogen chloride, and the solution is kept for some time; but when acetone is treated with sulphuric acid (about 80%), it yields a condensation product, *mesitylene* (p. 418), a derivative of benzene,

$$3(CH_3)_2CO = C_9H_{12} + 3H_2O.$$

Mesityl oxide, $C_6H_{10}O$, is best prepared by distilling diacetone alcohol (below) with a trace of iodine; it boils at 130°, has a strong peppermint-like smell, and when boiled with dilute sulphuric acid it is decomposed, with the regeneration of acetone.

Phorone, $C_9H_{14}O$, crystallises in pale-yellow prisms, melting at 28°; it boils at 198°, has a pleasant aromatic odour, and is decomposed by boiling dilute sulphuric acid, with the formation of acetone.

When a saturated solution of ammonia in acetone is kept during some weeks a considerable proportion of the ketone is converted into *diacetonamine*, $CH_3 \cdot CO \cdot CH_2 \cdot C(CH_3)_2 \cdot NH_2$, an additive product of mesityl oxide and ammonia.

Diacetone alcohol, $(CH_3)_2C(OH) \cdot CH_2 \cdot CO \cdot CH_3$, is prepared by treating acetone with barium hydroxide,

$$(CH_3)_2CO + H \cdot CH_2 \cdot CO \cdot CH_3 = (CH_3)_2C(OH) \cdot CH_2 \cdot CO \cdot CH_3.$$

It boils at 164°, is miscible with water, and is used as a solvent, especially for cellulose nitrates; it is a polymeride of acetone just as aldol is of acetaldehyde and is formed by a similar reaction.

Homologues of Acetone may be obtained by the oxidation of the corresponding secondary alcohols and by the destructive

[1] Reactions in which combination occurs with the separation of alcohol, for example, are also spoken of as condensations.

distillation of the calcium salts of the higher fatty acids, but are not of much importance ; they resemble acetone very closely in chemical properties.

Oximes (or *hydroximes*). Aldehydes and ketones usually react readily with hydroxylamine and give compounds which are called *oximes* ; those formed from aldehydes are called *aldoximes*, and those obtained from ketones, *ketoximes*. Acetaldehyde, for example, yields *acetaldoxime*,

$$CH_3 \cdot CH{:}O + H_2N \cdot OH = CH_3 \cdot CH{:}N \cdot OH + H_2O,$$

and acetone gives *acetoxime* (*dimethyl ketoxime*),

$$(CH_3)_2C{:}O + H_2N \cdot OH = (CH_3)_2C{:}N \cdot OH + H_2O.$$

The oximes are usually prepared by adding to (an alcoholic solution of) the aldehyde or ketone (2 mol.) a very concentrated aqueous solution of hydroxylamine hydrochloride, $NH_2 \cdot OH,HCl$ (2 mol.), and then a concentrated solution of sodium carbonate (1 mol.), which decomposes the hydrochloride and sets free the base (and generally gives a precipitate of sodium chloride). The mixture is kept at the ordinary temperature, or heated gently, during some hours, and most of the alcohol is then evaporated on the water-bath. At this stage, or on the addition of water, the oxime is usually deposited in crystals ; if not, it is extracted with ether.

The formation of the oxime is often facilitated by making the solution strongly alkaline with alcoholic potash ; in such cases, after the alcohol has been evaporated, it is sometimes necessary to add an excess of dilute acid in order to liberate the oxime from its potassium derivative.

The lower aldoximes are mostly odourless, volatile compounds, which distil without decomposition under greatly reduced pressure, and are very soluble in water ; the higher members are only sparingly soluble in water. The ketoximes have similar properties. Many oximes are decomposed when they are heated with moderately concentrated hydrochloric acid, with the 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 often converted into compounds readily soluble in water, such as $CH_3 \cdot CH{:}N \cdot ONa$ and $(CH_3)_2C{:}N \cdot OK$, by caustic alkalis ; but they are not otherwise changed even by boiling alkalis. Oximes

are easily reduced to primary amines (p. 220); those which are crystalline may serve for the *identification* of ketones and aldehydes which are liquid at ordinary temperatures.

Many oximes unite directly with hydrogen chloride (1 mol.) to form unstable *hydrochlorides*, which are decomposed by water.

The hydrogen atom of the $=N\cdot OH$, or *oximino*-group may be displaced by an alkyl or acid radical. These derivatives are produced by the action of alkyl halides and acid chlorides respectively on the sodium derivatives of the oximes. Many oximes exhibit a type of isomerism, the nature of which is discussed later (Part III).

One important difference between aldoximes and ketoximes is, that the former are decomposed by acetyl chloride, yielding cyanides or nitriles (p. 360),

$$CH_3\cdot CH{:}N\cdot OH = CH_3\cdot CN + H_2O,$$

whereas the latter are either converted into acetyl derivatives,

$$(CH_3)_2C{:}N\cdot OH + CH_3\cdot COCl = (CH_3)_2C{:}N\cdot O\cdot CO\cdot CH_3 + HCl,$$

or else undergo an *isomeric change* (p. 263) and give alkyl substituted amides (*Beckmann* reaction, Part III),

$$\underset{\text{Acetoxime}}{(CH_3)_2C{:}N\cdot OH} = \underset{\text{Methylacetamide}}{CH_3\cdot CO\cdot NH\cdot CH_3}.$$

Phenylhydrazones. Aldehydes and ketones react readily, as a rule, with phenylhydrazine (p. 459), and give compounds which are called *phenylhydrazones*; these substances were discovered by E. Fischer, and they are formed according to the equation,

$$>CO + H_2N\cdot NH\cdot C_6H_5 = >C{:}N\cdot NH\cdot C_6H_5 + H_2O.$$

Acetaldehyde phenylhydrazone, $CH_3\cdot CH{:}N\cdot NH\cdot C_6H_5$, and *acetone phenylhydrazone*, $(CH_3)_2C{:}N\cdot NH\cdot C_6H_5$, for example, are the two products obtained from acetaldehyde and acetone respectively. The phenylhydrazones, like the oximes, may be decomposed by hot concentrated hydrochloric acid, with the regeneration of the aldehyde or ketone, and they may be reduced to *primary amines* (p. 220).

Phenylhydrazine is a very important reagent, as it serves for the detection of aldehydes and ketones; also for their isolation and identification (p. 460).

Hydrazine, $NH_2\cdot NH_2$, also reacts with aldehydes and ketones, and *azines* are produced,

$$>CO + H_2N\cdot NH_2 + OC< = >C{:}N\cdot N{:}C< + 2H_2O.$$

In the preparation of azines the aldehyde or ketone is treated with hydrazine sulphate and sodium carbonate (or sodium acetate) in aqueous alcoholic solution.

Semicarbazones are formed by the interaction of an aldehyde, or ketone, and semicarbazide (p. 266),

$$>CO+NH_2\cdot NH\cdot CO\cdot NH_2 = >C{:}N\cdot NH\cdot CO\cdot NH_2+H_2O.$$

Acetone semicarbazone, for example, separates in crystals (m.p. 191°) when a dilute aqueous solution of acetone is treated with semicarbazide hydrochloride and sodium acetate. As the semicarbazones are usually crystalline, sparingly soluble compounds of high melting-point, semicarbazide is a very important reagent for the detection and identification of aldehydes and ketones.

Cyanohydrins. Aldehydes and ketones unite directly with hydrogen cyanide, forming *cyanohydrins*, $>C(OH)\cdot CN$ (hydroxycyanides), a *most important* reaction, which is very often used in synthesising hydroxy-acids (compare pp. 270, 282, 537); cyanohydrins are usually prepared by treating the bisulphite compound of an aldehyde (p. 139) or ketone (p. 146) with an aqueous solution of potassium cyanide (p. 537).

SUMMARY AND EXTENSION

The **Aldehydes** form a homologous series of the general formula, $C_nH_{2n}O$, 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.	Sp. gr. at 0°
Formaldehyde, methanal	CH_2O	−21°	—
Acetaldehyde, ethanal	C_2H_4O	+20·8°	0·801
Propionaldehyde, propanal	C_3H_6O	49°	0·832
Butyraldehyde, *n*-butanal	C_4H_8O	75°	0·911
*Iso*butyraldehyde, *iso*butanal		63°	0·862
Valeraldehyde, *n*-pentanal	$C_5H_{10}O$	103°	0·818 (11°)
*Iso*valeraldehyde, *iso*pentanal		92°	0·821
Caproaldehyde, *n*-hexanal	$C_6H_{12}O$	128°	0·850
Heptaldehyde, *n*-heptanal	$C_7H_{14}O$	155°	0·823 (15°)

The **Ketones** form a homologous series of the general formula, $C_nH_{2n}O$, or $R\cdot CO\cdot R'$, and are derived from the *secondary* alcohols by the loss of two atoms of hydrogen from the $>CH\cdot OH$ group. When the alkyl radicals R and R′ are identical the substance is a

simple ketone, but when R and R′ are different it is a *mixed ketone* (compare ethers, p. 128). The more important ketones are :

		B.p.	Sp. gr. at 0°
Acetone, dimethyl ketone	$(CH_3)_2CO$	56·5°	0·818
Methylethyl ketone	$CH_3(C_2H_5)CO$	80°	0·830
Propionone, diethyl ketone	$(C_2H_5)_2CO$	103°	0·833
Butyrone, dipropyl ketone	$(C_3H_7)_2CO$	144°	0·831
*Iso*butyrone, di-*iso*propyl ketone	$(C_3H_7)_2CO$	124°	0·823
		M.p.	
Oenanthone, dihexyl ketone	$(C_6H_{13})_2CO$	33°	
Palmitone	$(C_{15}H_{31})_2CO$	83°	
Stearone	$(C_{17}H_{35})_2CO$	88°	

Ketones and aldehydes which contain the same number of carbon atoms are isomeric, and the number of isomeric aldehydes of a given molecular formula is greater than that of the isomeric ketones. Thus, whereas there are four aldehydes of the molecular formula, $C_5H_{10}O$, —namely, in addition to the two given in the table,

$CH_3 \cdot CH_2 \cdot CH < {CHO \atop CH_3}$ and $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C < {CHO \atop CH_3}$

2-Methylbutanal — 2:2-Dimethylpropanal

—there are only three ketones—namely,

$CH_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3$, Diethyl ketone, Pentan-3-one

$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3$, Methylpropyl ketone, Pentan-2-one

$CH_3 \cdot CO \cdot CH < {CH_3 \atop CH_3}$ Methyl*iso*propyl ketone, 2-Methylbutan-3-one,

Both aldehydes and ketones may be regarded as derived from the paraffins, by the substitution of one atom of oxygen for two atoms of hydrogen of a CH_3— or —CH_2— group respectively.

Nomenclature. The aldehydes are generally named after the fatty acids which they yield on oxidation, or after the alcohols of which they are oxidation products.

The simple ketones (first obtained by the destructive distillation of a salt of a fatty acid) are named after the acid from which they were prepared ; acetone, for example, from acetic acid, propionone from propionic acid. The mixed ketones are named according to the alkyl groups which they contain, as exemplified above in the case of the isomerides of the composition, $C_5H_{10}O$.

Aldehydes and ketones in general are also named systematically after the paraffins from which they are theoretically derived, employing

the terminations **al** and **one** respectively in the place of the final **e** of **ane,** with a numeral, if necessary, as shown above.

Preparation. *Aldehydes* and *ketones* may be prepared by methods 1–5 ; aldehydes (only) by 6, 7 and 8 ; ketones by 9, 10 and 11.

(1) From alcohols by oxidation with various reagents (including air, pp. 133, 138, 145) ; *primary* alcohols give aldehydes,

$$CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CHO + H_2O,$$

whereas *ketones* are produced from *secondary* alcohols,

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

(2) From alcohols by passing the vapour over copper or nickel, heated at 250–320° ; primary alcohols thus give hydrogen and an aldehyde, whereas secondary alcohols give hydrogen and a ketone (*dehydrogenation*).

(3) From fatty acids by the destructive distillation of a calcium salt or a mixture of calcium salts. When a calcium salt is heated alone a simple ketone is produced (except calcium formate which gives formaldehyde, p. 133),

$$(CH_3 \cdot COO)_2Ca = CH_3 \cdot CO \cdot CH_3 + CaCO_3,$$

whereas a mixture of the calcium salts of two fatty acids (other than formic acid) gives a mixed ketone,

$$(CH_3 \cdot COO)_2Ca + (C_2H_5 \cdot COO)_2Ca = 2CH_3 \cdot CO \cdot C_2H_5 + 2CaCO_3 ;$$

in the latter case two simple ketones (acetone and propionone) are also produced by the independent decompositions of the two salts.

A mixture of a calcium salt with calcium formate gives an aldehyde,

$$(CH_3 \cdot COO)_2Ca + (H \cdot COO)_2Ca = 2CH_3 \cdot CHO + 2CaCO_3,$$
$$(C_3H_7 \cdot COO)_2Ca + (H \cdot COO)_2Ca = 2C_3H_7 \cdot CHO + 2CaCO_3.$$

Similar reactions occur when the vapour of an acid, or mixture of acids, is passed over heated thorium oxide or titanium dioxide.

Higher ketones, such as laurone, palmitone, etc., are conveniently prepared by heating the higher fatty acids with phosphorus pentoxide at about 200°.

(4) From ozonides by decomposition with water (p. 96).

(5) From those dihalogen derivatives of the paraffins in which both the halogen atoms are united to the same carbon atom (by hydrolysis),

$$>CCl_2 \longrightarrow >C(OH)_2 \longrightarrow >CO + H_2O ;$$

this method is of little use in the aliphatic series, as such dihalides are not readily obtained except from the corresponding aldehyde or ketone.

(6) From a cyanide (nitrile), by treating its ethereal solution with dry hydrogen chloride and anhydrous stannous chloride, and hydrolysing the product with warm water (*Stephen* reaction); the cyanide is first converted into an *imino-chloride* (Part III) which is reduced by the stannous chloride to an *aldimine*; this product, with water, then gives ammonia and an aldehyde,

$$R\cdot CN \longrightarrow R\cdot CCl{:}NH \longrightarrow R\cdot CH{:}NH \longrightarrow R\cdot CHO.$$

(7) From acid chlorides by catalytic reduction with hydrogen and palladium on barium sulphate (*Rosemund* reaction).

(8) From olefines by the *oxo*-reaction (p. 96).

(9) From ethyl acetoacetate and its derivatives, by hydrolysis; this is a synthetical method of great practical importance (p. 202).

(10) From hydrocarbons of the acetylene series by heating them with water at about 325°, with sulphuric acid and then with water, or with aqueous solutions of mercuric salts; acetylene gives acetaldehyde, the higher members give ketones,

$$CH_3\cdot C{:}CH + H_2O = CH_3\cdot CO\cdot CH_3.$$

(11) From acid chlorides by the action of zinc dialkyls (p. 233),

$$2CH_3\cdot CO\cdot Cl + Zn(CH_3)_2 = 2CH_3\cdot CO\cdot CH_3 + ZnCl_2.$$

Physical Properties. With the exception of formaldehyde, which is a gas at ordinary temperatures, the aldehydes and ketones up to about $C_{11}H_{22}O$ are mobile, neutral, volatile liquids; the higher members are solids. Aldehydes have usually a disagreeable, irritating smell, but ketones have generally a pleasant odour. The first two or three members of both classes of compounds are readily soluble in water, but the solubility rapidly decreases as the molecular weight increases, and the higher members are insoluble, or nearly so, in water, but readily soluble in alcohol, ether, etc. The boiling-point rises regularly in both homologous series; but the regularities are only observed when compounds of similar structure are compared—as, for example, the *normal* aldehydes.

Chemical Properties. Aldehydes and ketones have many chemical properties in common, because their molecules contain the carbonyl group, $>CO$, and most of their reactions involve changes in this particular group only. Owing to the presence of this group, they are capable of combining directly under certain conditions with two univalent atoms or groups.

All the lower aldehydes and many of the lower ketones, but usually only those which contain the group, $CH_3\cdot CO—$, form crystalline additive compounds when shaken with a concentrated aqueous solution of sodium hydrogen sulphite. This property is of great value in the purification of aldehydes and ketones, and especially in

their separation from substances which do not form bisulphite compounds, as illustrated in the case of acetone (p. 145). These bisulphite compounds are soluble in water, but usually insoluble, or nearly so, in alcohol and ether; they are readily decomposed when they are warmed with dilute alkalis (or acids), the aldehydes or ketones being regenerated,

$$>C(OH)\cdot SO_2\cdot ONa+NaOH = >CO+Na_2SO_3+H_2O.$$

The structures of these compounds are probably represented by the general formula, $>C(OH)\cdot SO_2\cdot ONa$, in which the sulphur atom is shown as directly united to carbon; they are thus salts of hydroxy-derivatives of sulphonic acids and their instability, in contrast to the great stability of the sulphonic acids (pp. 130, 365, 472), is due to the hydroxyl group, which is directly combined to the same carbon atom as the $—SO_3H$ group. This is another example of how the strength of a bond varies with the structure of the molecule as a whole (p. 46).

Aldehydes and ketones are readily acted on by reducing agents, such as sodium amalgam and water, or zinc and hydrochloric acid, with the formation of primary and secondary alcohols respectively,

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

The corresponding alcohol is not always the sole product of the reduction of a ketone, but is often accompanied by varying proportions of a *di-tertiary* alcohol belonging to the class of *pinacols*. Acetone, for example, yields not only *iso*propyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$, but also *pinacol*,

$$2(CH_3)_2CO+2H = (CH_3)_2C(OH)\cdot C(OH)(CH_3)_2.$$

The formation of a pinacol may be accounted for by assuming that, during reduction, a structure, $R_2C(OH)—$, is momentarily produced by the combination of the ketone with one atom of hydrogen. If so, such an intermediate product might then combine with another atom of hydrogen to form a secondary alcohol, $R_2CH\cdot OH$, or two structures might unite to form a pinacol, $R_2C(OH)\cdot C(OH)R_2$. Similar products (*di-secondary* alcohols) may be formed in the reduction of aldehydes, but usually in smaller proportions.

Pinacol may be prepared by reducing acetone with magnesium amalgam and water. It is decomposed on distillation with dilute sulphuric acid, yielding *pinacolone*,

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CH_3\\CH_3\end{matrix} = CH_3\cdot CO\cdot C(CH_3)_3+H_2O,$$

a very remarkable change, which involves the *migration* (the removal from one part of the molecule to another) of a methyl group. Pinacolone is a colourless liquid, boils at 106°, and has a very strong odour of peppermint. Its constitution is established by the fact that on oxidation with chromic acid it yields trimethylacetic acid and carbon dioxide,

$$(CH_3)_3C\cdot CO\cdot CH_3+4O = (CH_3)_3C\cdot COOH+CO_2+H_2O.$$

Aldehydes and ketones, reduced with *amalgamated* zinc and hydrochloric acid, give the corresponding *hydrocarbons* (Clemmensen); with molecular hydrogen and a catalyst, or with aluminium *iso*propoxide and an excess of *iso*propyl alcohol (*Ponndorf* reagent), they yield alcohols free from pinacols,

$$>CO+(CH_3)_2CH\cdot OH \rightleftarrows >CH\cdot OH+(CH_3)_2CO.$$

Aluminium ethoxide and ethyl alcohol are also used (Meerwein). These reagents are particularly useful when the aldehyde or ketone contains ethylenic or other groups, the reduction of which is not desired.

Aldehydes and ketones are readily acted on by phosphorus pentachloride or pentabromide with the formation of dihalogen derivatives of the paraffins, the oxygen atom of the carbonyl group being displaced by two atoms of halogen. Aldehyde, for example, gives *dichloroethane* or *ethylidene dichloride*, $CH_3\cdot CHCl_2$, and *dibromoethane* or *ethylidene dibromide*, $CH_3\cdot CHBr_2$,

$$CH_3\cdot CHO+PCl_5 = CH_3\cdot CHCl_2+POCl_3,$$

and acetone gives 2:2- or *ββ-dichloropropane* (acetone dichloride),

$$(CH_3)_2CO+PCl_5 = (CH_3)_2CCl_2+POCl_3.$$

The characteristic behaviour of aldehydes and ketones with hydroxylamine, phenylhydrazine, hydrazine, and semicarbazide (pp. 149-151) depends on the presence of the carbonyl group.

Aldehydes and ketones combine directly with hydrogen cyanide, forming additive products, termed *hydroxycyanides*, or *cyanohydrins* (p. 151); aldehyde, for example, giving *hydroxyethyl cyanide* or *acetaldehyde cyanohydrin*, $CH_3\cdot CH(OH)\cdot CN$, and acetone, *hydroxy*-iso*propyl cyanide* or *acetone cyanohydrin*, $(CH_3)_2C(OH)\cdot CN$. These compounds are decomposed by alkalis giving hydrogen cyanide and the aldehyde or ketone; but mineral acids hydrolyse them, yielding *hydroxycarboxylic acids*, the —CN group being transformed into —COOH,

$$CH_3\cdot CH(OH)\cdot CN+2H_2O = CH_3\cdot CH(OH)\cdot COOH+NH_3.$$

The cyanohydrins are of great importance in the study of the sugars.

Aldehydes and ketones are readily acted on by the Grignard reagents, and give products, which are decomposed by acids, yielding secondary and tertiary alcohols respectively (p. 238); they may be converted into β-hydroxy-acids by the *Reformatsky* reaction (p. 286).

Aldehydes and ketones usually react readily with ammonia, but in various ways. Formaldehyde, for example, gives a condensation product, hexamethylenetetramine (structure, p. 159), whereas acetaldehyde gives an unstable additive product, aldehyde ammonia (p. 139), which is soluble in water, but insoluble in ether. Acetone, at −65°, also gives an additive product, which is called *acetone ammonia*, or *β-amino-β-hydroxypropane*, $CH_3 \cdot C(OH)(NH_2) \cdot CH_3$, but at the ordinary temperature diacetonamine and other condensation products are formed (p. 605).

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 hydroxide, especially in the presence of a little caustic alkali, a silver mirror being formed. They also reduce alkaline solutions of cupric compounds (Fehling's solution). Ketones, on the other hand, are only attacked by stronger oxidising agents, and the difference between their behaviour and that of aldehydes, on oxidation, is used for determining whether a substance of unknown constitution is an aldehyde or a ketone.

Aldehydes, on oxidation, are converted into fatty acids, containing *the same number* of carbon atoms as the original compounds,

$$C_nH_{2n+1} \cdot CHO + O = C_nH_{2n+1} \cdot COOH.$$

Ketones, on oxidation, are decomposed with the formation, usually, of two acids, each of which, obviously, contains *a smaller number* of carbon atoms than the original ketone,

$$CH_3 \cdot CO \cdot CH_3 + 4O = CH_3 \cdot COOH + CO_2 + H_2O.$$
$$CH_3 \cdot CO \cdot [CH_2]_4 \cdot CH_3 + 3O = CH_3 \cdot COOH + CH_3 \cdot [CH_2]_3 \cdot COOH.$$

A ketone which contains branched chains may give more than two acids and in all cases the study of its oxidation products may afford important evidence as to its constitution.

Generally speaking, the oxidation of a mixed ketone follows the rule (Popoff's rule) that the carbonyl group remains united with the lower alkyl group, as represented in the second example given above. Popoff's rule, however, does not hold good in all cases.

Aldehydes give Schiff's reaction; ketones as a rule do not.

Aldehydes also *differ* from ketones in reacting readily with alcohols, in the presence of hydrogen chloride, to form *acetals*, which resemble

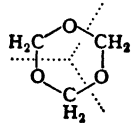
ethers in structure and in behaviour, except that they are hydrolysed by acids,

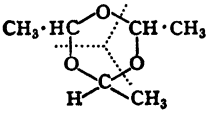
$$\begin{matrix}H\\R\end{matrix}\!\!>\!CO+2HO\cdot C_2H_5 = \begin{matrix}H\\R\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}O\cdot C_2H_5\\O\cdot C_2H_5\end{matrix}+H_2O.$$

Aldehydes, in the presence of small proportions of aluminium ethoxide, which acts catalytically, give esters,

$$2R\cdot CHO = R\cdot CO\cdot OCH_2R.$$

Aldehydes, especially the lower members of the series, very readily undergo polymerisation in the presence of aqueous acids, alkalis, and other substances. The most common form of polymerisation is the combination of three molecules of the aldehyde to form substances such as trioxymethylene and paracetaldehyde (paraldehyde), the constitutions of which are respectively represented by the formulae,





The method of combination of the three unsaturated molecules to form a polymeride will be readily understood with the aid of the dotted lines. These polymerides may be decomposed into the simple aldehydes under suitable conditions. They do not show the characteristic reactions of aldehydes because they do not contain the aldehyde group ; the unsuitable names, paraldehyde, metaldehyde, etc., were given to such substances when their constitutions were unknown.

Aldehydes are generally very unstable in the presence of alkalis, by which they are converted into brown resins of unknown nature. Formaldehyde, however, gives methyl alcohol and formic acid.

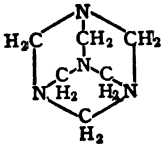
Ketones, as mentioned above, are much more stable than aldehydes ; they do not reduce alkaline solutions of silver, copper, etc., do not, as a rule, combine directly with ammonia, at ordinary temperatures, or with alcohols ; nor do they polymerise so readily as do the aldehydes.

When treated with suitable reagents, both aldehydes and ketones readily undergo condensation, two or more molecules combining with the loss of the elements of water, as in the production of croton-aldehyde from acetaldehyde (p. 141) and of mesityl oxide from acetone (p. 147). When condensations of this nature occur, the hydrogen atoms of one of the —CH_2— or CH_3— groups, which is in *direct combination* with the carbonyl group, take part in the reaction.

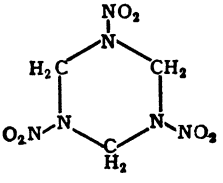
It is not necessary that the molecules undergoing condensation

should be identical ; two different ketones, two different aldehydes, or an aldehyde and a ketone, may condense together.

Cyclo*trimethylenetrinitramine* is formed by the action of nitric acid (sp. gr. 1·52) on hexamethylenetetramine. It is crystalline, m.p. 200-202°, and is an important explosive (cyclonite, hexogen, T.A.). Its structure, together with that of hexamethylenetetramine, (I), is shown below, (II).



I



II

CHAPTER 11

THE FATTY ACIDS

THE fatty acids form a homologous series of the general formula, $C_nH_{2n+1}\cdot CO\cdot OH$, 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
$H\cdot CH_3$	$H\cdot CH_2\cdot OH$	$H\cdot CHO$	$H\cdot CO\cdot OH$
$CH_3\cdot CH_3$	$CH_3\cdot CH_2\cdot OH$	$CH_3\cdot CHO$	$CH_3\cdot CO\cdot OH$
$C_2H_5\cdot CH_3$	$C_2H_5\cdot CH_2\cdot OH$	$C_2H_5\cdot CHO$	$C_2H_5\cdot CO\cdot OH$

The term '*fatty*' was given to the acids of this series because many of the higher members occur in a combined state in—and are obtained from—natural fats, and resemble fats in physical properties.

Formic acid, *methanoic acid*, CH_2O_2, or $H\cdot CO\cdot OH$, occurs in nature in nettles, ants (*formicae*), and certain other living organisms; the sting of an ant or nettle 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 is distilled, a very weak aqueous solution of formic acid collects in the receiver.

Formic acid can be obtained by oxidising methyl alcohol or formaldehyde with atmospheric oxygen and platinum black,

$$CH_3\cdot OH+2O = H\cdot CO\cdot OH+H_2O,$$
$$H\cdot CHO+O = H\cdot CO\cdot OH,$$

or by heating hydrocyanic acid with alkalis or mineral acids,

$$HCN+2H_2O = H\cdot CO\cdot OH+NH_3;^{1}$$

as a formate, it is produced by decomposing chloroform with alcoholic potash, or by heating carbon monoxide with moist potash,

$$CO+KOH = H\cdot CO\cdot OK.$$

When a large flask, moistened all over the inside with a concentrated solution of potash, is filled with carbon monoxide and heated in boiling water, the gas is slowly absorbed (as can be shown by providing the flask with a delivery tube, which dips under mercury).

[1] When an alkali is used, ammonia is liberated and a salt of formic acid is obtained; whereas when a mineral acid is employed, free formic acid and an ammonium salt are produced.

All the above-mentioned reactions illustrate complete syntheses of formic acid, as all the reagents can themselves be prepared from their elements.

Sodium formate is now manufactured by passing carbon monoxide, under pressure, over soda-lime or caustic soda at about 210°.

Formic acid may be prepared in the laboratory by heating oxalic acid with glycerol; it can be obtained by heating oxalic acid alone,

$$C_2O_4H_2 = H \cdot CO \cdot OH + CO_2,$$

but when this is done, a large proportion of the oxalic acid either sublimes without change, or is decomposed into carbon monoxide, carbon dioxide, and water.

When glycerol and oxalic acid are heated together, the anhydrous acid, produced from the hydrated crystals, $C_2H_2O_4,2H_2O$, reacts with the glycerol, forming *mono-oxalin*,

$$CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot O \cdot OC \cdot COOH,$$

which at higher temperatures decomposes into carbon dioxide and *monoformin*, $CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot O \cdot OC \cdot H$.

On the addition of a further quantity of the hydrated crystals of oxalic acid, the monoformin is decomposed by the water, giving formic acid, which distils, and the oxalic acid reacts with the regenerated glycerol, yielding mono-oxalin.

The glycerol, like the sulphuric acid in the manufacture of ether, is thus able, theoretically, to serve for the preparation of an unlimited quantity of formic acid.

Glycerol (about 50 c.c.) is placed in a retort connected with a condenser, crystallised oxalic acid (about 30 g.) is added, and the mixture is heated to about 100–110°; rather below this temperature an evolution of carbon dioxide commences, and dilute formic acid distils, but after some time the action ceases. A further quantity of oxalic acid is then added, the temperature of the liquid being kept at 100–110°, whereon carbon dioxide is again evolved, and a more concentrated solution of formic acid collects in the receiver. The addition of oxalic acid is repeated from time to time, until a sufficient quantity of formic acid has been obtained.

For the preparation of *lead formate*, the aqueous distillate is gently warmed with an excess of litharge; as soon as the litharge ceases to be dissolved the boiling solution is filtered, and the filtrate is evaporated to a small bulk, when crystals of lead formate are obtained. Crystallised *copper formate* may be obtained in a similar manner, using cupric oxide or carbonate.

Very concentrated formic acid may be prepared by gradually adding very finely divided, dry sodium formate (10 g.) to the theoretical quantity of concentrated sulphuric acid, which is continuously stirred at 0°; the pasty product is then placed in a very small distillation flask, which is immersed in a water-bath, and the formic acid is distilled under reduced pressure. Care must be taken not to inhale any carbon monoxide which may be formed during the experiment.

The concentrated acid may also be prepared by dehydrating the dilute solution with *anhydrous* oxalic acid.

Ethyl hydrogen oxalate is decomposed when it is heated under atmospheric pressure, giving carbon dioxide and *ethyl formate*, which boils at 54·5°.

Formic acid is a mobile, hygroscopic liquid of sp. gr. 1·22 at 20°; it solidifies at low temperatures, melting again at 8°, and boils at 101°. It has a pungent, irritating odour, recalling that of sulphur dioxide, and it blisters the skin like a nettle sting; it is miscible with water and alcohol. Formic acid has an acid reaction to litmus, decomposes carbonates, and dissolves certain metallic oxides; it behaves, in fact, like a weak mineral acid. Like the aldehydes, it has reducing properties, and precipitates silver from warm ammoniacal solutions of silver hydroxide, being itself oxidised to carbon dioxide and water,

$$H\cdot CO\cdot ONH_4+Ag_2O = 2Ag+NH_4HCO_3.$$

When gently warmed with concentrated sulphuric acid it is rapidly decomposed into carbon monoxide and water,

$$H\cdot CO\cdot OH = CO+H_2O,$$

and when heated alone at 160° in closed vessels it yields carbon dioxide and hydrogen,

$$H\cdot CO\cdot OH = CO_2+H_2.$$

Formic acid is used in the electroplating, tanning, and textile industries.

The **formates,** or salts of formic acid, are generally prepared by neutralising the acid with metallic hydroxides, or carbonates; they all dissolve in water, but some, such as the lead and silver salts, are only sparingly soluble;[1] they are all decomposed by warm concentrated sulphuric acid, with the evolution of carbon monoxide,

[1] When a solid or liquid dissolves in *about* 10 times its weight (or less) of a specified solvent, it is described as *readily* soluble in that solvent; *moderately* soluble, if *about* 10–20; and *sparingly* soluble, if more than *about* 20 times its weight of solvent are required for solution.

and by dilute mineral acids, yielding formic acid. The *sodium* salt, $H \cdot CO \cdot ONa$, and the *potassium* salt, $H \cdot CO \cdot OK$, are deliquescent; when heated at about 390°, they are converted into oxalates with the evolution of hydrogen, a reaction which is used for the manufacture of sodium oxalate,

$$2H \cdot CO \cdot ONa = C_2O_4Na_2 + H_2.^1$$

When *ammonium formate* is heated alone at about 230°, it is converted into formamide (p. 178), but when it is heated with phosphorus pentoxide it gives hydrogen cyanide (p. 354), water being eliminated in both stages,

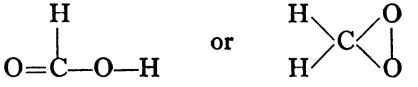
$$H \cdot CO \cdot ONH_4 = H \cdot CO \cdot NH_2 + H_2O,$$
$$H \cdot CO \cdot NH_2 = HCN + H_2O.$$

A mixture of ammonium formate and an excess of phosphorus pentoxide is heated in a glass tube and the gaseous products are passed into a solution of potassium hydroxide; the presence of a cyanide in the solution may then be demonstrated in the usual manner.

Silver formate, $H \cdot CO \cdot OAg$, is precipitated in lustrous crystals when silver nitrate is added to a *neutral* concentrated solution of a formate; but it is unstable, and quickly darkens when exposed to light or when warmed.

In order to test for formic acid or a formate, the solution, if acid, is neutralised with sodium carbonate, and a portion is warmed with an ammoniacal solution of silver oxide; if a black precipitate or mirror of silver is 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* (below 100°) with concentrated sulphuric acid, when carbon monoxide is evolved, and may be ignited at the mouth of the test-tube.

Constitution. Since formic acid has the molecular formula, CH_2O_2, it must have the constitution,



because these are the only formulae which can be constructed in accordance with the valencies of the atoms concerned. But the

[1] When a mixture of sodium formate and powdered arsenic (or an arsenic compound) is heated at about 400°, arsine is formed; the hydrides of antimony, phosphorus, sulphur, and of several other elements may be produced in a similar manner.

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 a metal; moreover, it does not accord with the fact that formic acid behaves in some respects like an aldehyde, and probably, therefore, contains in its molecule the aldehyde group, —CHO. For these and other reasons, which will be more clearly understood when the case of acetic acid has been considered (p. 166), the constitution of formic acid is represented by the first formula, which is usually written $H \cdot CO \cdot OH$, or $H \cdot COOH$. 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.

Formic acid, in fact, is an electrolyte, and the hydrogen atom of its HO— group is much more easily displaced by metals than that of an alcohol; *this is another good example of the variable nature of a bond between two given atoms* (pp. 46, 143).

Acetic acid, *ethanoic acid*, $C_2H_4O_2$, or $CH_3 \cdot CO \cdot OH$, occurs in nature in combination with alcohols in the essences or odoriferous, volatile oils of many plants, and is formed during the decay of certain organic substances. It can be produced by gently heating sodium methoxide in an atmosphere of carbon monoxide at about 180°, just as formic acid may be obtained from sodium hydroxide under similar conditions,

$$CH_3 \cdot ONa + CO = CH_3 \cdot CO \cdot ONa;$$

also by boiling methyl cyanide with alkalis or mineral acids,

$$CH_3 \cdot CN + 2H_2O = CH_3 \cdot CO \cdot OH + NH_3,$$

and by exposing alcohol or aldehyde, in contact with platinum black, to atmospheric oxidation.

Acetic acid is manufactured by oxidising acetaldehyde, in acetic acid solution at 70°, with atmospheric oxygen; the acetaldehyde used for this purpose is prepared commercially from acetylene as already described, or by the oxidation of alcohol.

Acetic acid is still prepared to some extent on the large scale from the brown aqueous distillate known as *pyroligneous acid*, which is obtained by the destructive distillation of wood.

This liquid is first distilled and the vapours are passed through milk of lime, as already described, to separate the methyl alcohol,

acetone, and other volatile neutral substances; the solution of calcium acetate is then evaporated in iron pans, and the residue is distilled *in vacuo* with concentrated sulphuric acid from cast-iron vessels. The crude 80% acetic acid which collects in the receiver is fractionated in a copper still, and the product, which now contains 99–99·5% of the acid, is treated with potassium permanganate or dichromate, by which means most of the impurities are oxidised; after a final distillation, practically pure *glacial* (ice-like, i.e. crystalline) acetic acid is obtained. The small quantity of water in commercial glacial acetic acid may be removed by separating the crystals from the more dilute mother liquor, melting them and then cooling and filtering again, repeating the processes until the melting-point becomes constant.

In some modern processes the acetic acid is extracted from the pyroligneous acid with solvents, such as ether or di-*iso*propyl ether.

Anhydrous acetic acid is a crystalline, hygroscopic solid, which melts at 16·7°, boils at 118°, and has a sp. gr. 1·05 at 20°; 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, and burns with a feebly luminous flame. It is miscible with water, alcohol, and ether, and is an excellent solvent for most organic compounds; it also dissolves many inorganic substances, such as sulphur, iodine, etc., which are insoluble in water. It is a fairly strong acid, and acts readily on certain metals and metallic hydroxides; unlike formic acid, it has no reducing properties. The pure acid does not decolourise a solution of potassium permanganate; if impure, it will probably do so.

Acetic acid is largely used in the manufacture of acetates, acetic anhydride, and (as anhydride) cellulose acetate silk; also for coagulating rubber latex and in curing meat and fish. It is an important laboratory reagent.

The **acetates,** or salts of acetic acid, are prepared by treating the acid with carbonates, hydroxides, or metals, or by double decomposition; they are mostly crystalline and soluble in water, and are decomposed by mineral acids with the liberation of acetic acid. *Sodium acetate*, $CH_3 \cdot COONa, 3H_2O$, is frequently used in the laboratory; it dissolves in its water of hydration when it is heated, but as the water is expelled, the salt solidifies. The anhydrous salt is hygroscopic, and is used as a dehydrating agent. *Potassium acetate*, $CH_3 \cdot COOK$, is deliquescent. *Ammonium acetate* is gradually decomposed into acetamide (p. 177) and water when it is distilled,

Silver acetate, $CH_3 \cdot COOAg$, is precipitated in lustrous crystals when silver nitrate is added to a concentrated neutral solution of an acetate ; it is sparingly soluble in cold water, and does not darken appreciably on exposure to light. *Lead acetate*, or ' sugar of lead,' $(CH_3 \cdot COO)_2Pb,3H_2O$, prepared commercially by dissolving litharge in acetic acid, has a sweet (sugary) astringent taste, is readily soluble in water, and is very poisonous ; when its solution is boiled with litharge various soluble basic salts are formed. *Calcium acetate*, $(CH_3 \cdot COO)_2Ca,H_2O$, is used for the laboratory preparation of acetone.

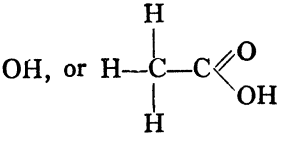
Copper acetate, $(CH_3 \cdot COO)_2Cu,H_2O$, is obtained by dissolving cupric oxide in acetic acid ; it is a dark, greenish-blue substance. *Verdigris*, $(CH_3 \cdot COO)_2Cu,Cu(OH)_2$, is a blue, hydrated, basic copper acetate, which is used as a pigment. Copper acetate and copper metarsenite form a beautiful emerald green, insoluble salt, $(CH_3 \cdot COO)_2Cu,3Cu(AsO_2)_2$, known as *Schweinfurter green*, *Paris green*, or *Emerald green*, formerly employed in colouring wall-papers, carpets, blinds, etc. The acetates of iron, aluminium and chromium are used as mordants (p. 657).

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, if acetic acid is present, a vapour, acid to litmus paper, is evolved and the acid can be recognised by its smell. A fresh portion of the solution is then neutralised, if necessary, with sodium carbonate and evaporated to dryness ; the residue is warmed with a few drops of alcohol and a little strong sulphuric acid. If acetic acid is present, ethyl acetate (p. 185) is formed, and is recognised by its pleasant, fruity odour (which is easily distinguished from that of alcohol and of ether).

Constitution. The formation of acetic acid by the oxidation of ethyl alcohol seems to be a reaction similar to that by which formic acid is produced from methyl alcohol ; if, therefore, the two changes take place in a similar manner,

$$H \cdot CH_2 \cdot OH + 2O = H \cdot CO \cdot OH + H_2O,$$
$$CH_3 \cdot CH_2 \cdot OH + 2O = CH_3 \cdot CO \cdot OH + H_2O,$$

the constitution of acetic acid would be expressed by the formula,

$CH_3 \cdot CO \cdot OH$, or 

Again, formic acid is produced when hydrogen cyanide is boiled with mineral acids (p. 355), whilst acetic acid is formed from methyl cyanide under the same conditions; if these two changes are analogous,

$$H\cdot CN+2H_2O = H\cdot CO\cdot OH+NH_3,$$
$$CH_3\cdot CN+2H_2O = CH_3\cdot CO\cdot OH+NH_3,$$

the constitution of acetic acid would be represented by the same formula as before.

If, now, other methods of formation are considered, together with the chemical behaviour of acetic acid, including its various decompositions and its relation to formic acid, it will be seen that the above constitutional formula, and *no other*, affords a satisfactory interpretation or summary of all the facts.

From the numerous arguments which might be advanced in support of this statement, the following may be given. (1) The molecule of acetic acid contains the HO— group, because its behaviour with phosphorus pentachloride is similar to that of alcohols. (2) It contains a CH_3— or methyl group—that is to say, three of the four atoms of hydrogen are *directly* combined with one carbon atom. This is shown by the fact that three of the four hydrogen atoms behave like those in CH_4,C_2H_6, etc., and are displaceable by (free) chlorine (pp. 70, 178); also by the production of ethane by the electrolysis of acetic acid, a change which can be formulated in a simple manner, only by assuming the presence of a CH_3— group,

$$\begin{matrix} CH_3\cdot CO\cdot OH \\ CH_3\cdot CO\cdot OH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + \begin{matrix} CO_2 \\ \\ CO_2 \end{matrix} + H_2.$$

Since, then, as shown by its chemical behaviour, the molecule of acetic acid contains a CH_3— and an HO— group, it must have the constitution shown above, which confirms the conclusion previously arrived at from other considerations.

The relation between formic and acetic acids, and their similarity in certain chemical properties, are also satisfactorily accounted for by the respective constitutional formulae,

$$H\cdot C\begin{matrix} \diagup\!\!\!= O \\ \diagdown OH \end{matrix} \quad \text{and} \quad CH_3\cdot C\begin{matrix} \diagup\!\!\!= O \\ \diagdown OH \end{matrix}$$

which thus confirm one another. The acids are both shown as derivatives of the univalent group of atoms, —CO·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, —CHO, 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 univalent group of atoms common to formic and acetic acids is named the **carboxyl** group, and is written —CO·OH, or —COOH. Soluble *carboxylic acids* are weak electrolytes.

As a good deal of the evidence given above is based on analogy, the constitution of acetic acid may be considered in another way altogether : Ethylene, C_2H_4, combines with hypochlorous acid to form ethylene chlorohydrin, C_2H_5ClO, which on oxidation gives chloroacetic acid, $C_2H_3ClO_2$; the latter is converted into trichloroacetic acid, $C_2HCl_3O_2$ (p. 179), by the direct action of chlorine, and this acid is decomposed by alkalis giving chloroform, $CHCl_3$, and carbon dioxide (as a carbonate). All these molecular formulae are fully established by the usual methods.

Now, of the three chlorine atoms in the final product, $CHCl_3$, one is present in ethylene chlorohydrin and the other two were introduced by the substitution of two atoms of chlorine for two atoms of hydrogen in chloroacetic acid ; this acid, therefore, contains the group $—CH_2Cl$, and the chlorohydrin from which it is formed must also contain this group in combination with $—CH_3O$, i.e. $—CH_2·OH$.

It is thus proved that ethylene must be $CH_2{:}CH_2$ and cannot be $CH_3·CH<$, that its chlorohydrin is $CH_2Cl·CH_2·OH$, not $CH_3·CHCl·OH$, and that chloroacetic acid is $CH_2Cl·COOH$, not

$$CHO·CHCl·OH \quad \text{or} \quad \begin{matrix} \ulcorner\!—O—\!\urcorner \\ CH_2—CCl·OH, \end{matrix}$$

as would be possible from considerations of valency alone. Furthermore, trichloroacetic acid, which can also be obtained from, and converted into, acetic acid directly, must be $CCl_3·COOH$, and acetic acid, $CH_3·COOH$.

It will be seen from the above that the structural formula of an organic compound is based not only on the whole behaviour of that compound, but on its relationship to many others, the structures of which have been established quite independently.

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,

$$CH_3 \cdot CH_2 \cdot OH + O_2 = CH_3 \cdot COOH + H_2O.$$

This change is not a simple atmospheric oxidation, but is the result of a process of fermentation brought about by a living ferment, *Bacterium aceti*. This ferment is present in the atmosphere and soon finds its way into the solution, where it grows, and in some manner causes the alcohol to react 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; the ferment is inactivated by strong alcohol, and cannot live in pure aqueous alcohol, since the latter does not contain nitrogenous substances, mineral salts, etc., which the ferment requires for food, and which are present in beers and wines.

Vinegar is merely 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 begun to turn sour, or of other dilute alcoholic liquids; it is prepared by various processes.

In the old *French* or *Orléans* process, some vinegar containing a small proportion of wine is placed in large vats covered with perforated lids, the vats having been previously soaked inside with warm vinegar; the ferment soon gets into the liquid, and vinegar is produced, the solution gradually becoming coated with a slimy film, known as 'mother-of-vinegar,' which is merely 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 are repeated with fresh quantities of wine.

In the more 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 is filled with beechwood 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% of alcohol, mixed with about 20% of vinegar, or with beer, or malt extract, to provide food for the ferment, is then sprayed in at the top, when it slowly trickles through the shavings, in contact with the ferment and with a free supply of air. The liquid which collects at the bottom is again sprayed over the shavings and the operations are

repeated 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 methods the fermenting liquid must be kept at a temperature of 25–30°.

Vinegar produced by the French process contains 6–10% of acetic acid ; whereas that produced by the German process from diluted ' raw-spirit ' contains only about 4–6% of the acid. Vinegar is used for table purposes and in the manufacture of white-lead and verdigris ; it is too dilute to be economically employed for the preparation of commercial acetic acid.

Homologues of Acetic Acid. As all the higher members of the series of fatty acids resemble acetic acid very closely in chemical properties, in their methods of formation, and in their transformations, their molecules must likewise 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 univalent 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, $C_nH_{2n}O_2$, $C_nH_{2n+1} \cdot COOH$, or $R \cdot COOH$, and are all monobasic or *monocarboxylic* acids.

Isomerism starts with the fourth member of the series and the number of isomerides theoretically possible in any given case is the same as that of the corresponding *primary* alcohols. The two isomeric acids, butyric and *iso*butyric,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH \quad \text{and} \quad \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\!\! CH \cdot COOH,$$

for example, correspond with the two primary alcohols,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH \quad \text{and} \quad \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\!\! CH \cdot CH_2 \cdot OH,$$

respectively.

Those isomerides which are derived from the normal paraffins, by the substitution of —COOH for one atom of hydrogen in a CH_3— group, are termed *normal* acids ; as, for example, normal butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, and normal valeric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$.

Those which contain the group, $(CH_3)_2CH$—, are often termed

iso-acids, as, for example, *iso*butyric acid, $(CH_3)_2CH \cdot COOH$, *iso*valeric acid, $(CH_3)_2CH \cdot CH_2 \cdot COOH$.

In order to distinguish other isomerides by names, which are also expressive of their constitutions, the acids may be regarded as derived from acetic acid, just as the alcohols may be 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)

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot COOH$

*Iso*valeric acid
(*Iso*propylacetic 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, *propanoic acid*, $CH_3 \cdot CH_2 \cdot COOH$, occurs in crude pyroligneous acid; it is formed when acrylic acid (p. 342) is reduced with sodium amalgam and water,

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

and when lactic acid (p. 267) is heated with concentrated hydriodic acid (a reaction which occurs in two stages),

$$CH_3 \cdot CH(OH) \cdot COOH + HI = CH_3 \cdot CHI \cdot COOH + H_2O,$$
$$CH_3 \cdot CHI \cdot COOH + HI = CH_3 \cdot CH_2 \cdot COOH + I_2.$$

It may be 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 liquid, which boils at 141°, has a pungent sour smell and is miscible with water. It is a monocarboxylic acid, and closely resembles acetic acid in chemical properties; its salts, the **propionates,** are soluble in water and of little importance.

Normal butyric acid, *butanoic acid*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, occurs in the vegetable and animal kingdoms; in combination with glycerol, it is an important component of butter (hence its name). It is formed during the decay of animal matter and during the butyric fermentation of lactic acid. When milk is left exposed to the air it turns sour, owing to the lactose or milk-sugar which it

contains having been converted into lactic acid by an airborne organism, the *lactic ferment*,

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O = 4\underset{\text{Lactic acid}}{C_3H_6O_3}.$$

The lactic ferment converts sugars other than lactose into lactic acid. When now a little mouldy cheese is added to the sour milk, and the solution is kept neutral by the addition of chalk,[1] *butyric fermentation* sets in, and the lactic acid is converted into butyric acid by the action of another organism, the *butyric ferment*, which is present in the cheese,

$$\underset{\text{Lactic acid}}{2C_3H_6O_3} = \underset{\text{Butyric acid}}{C_4H_8O_2} + 2CO_2 + 2H_2.$$

Butyric acid may be prepared by these processes of fermentation and separated by steam distillation, or by oxidising normal butyl alcohol with a dichromate and sulphuric acid.

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.

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, some of the salt separates in crystals.

***Iso*butyric acid,** *dimethylacetic acid*, $(CH_3)_2CH\cdot COOH$, may be prepared by the oxidation of *iso*butyl alcohol,

$$(CH_3)_2CH\cdot CH_2\cdot OH + 2O = (CH_3)_2CH\cdot COOH + H_2O,$$

or from diethyl malonate. It boils at 154°, and resembles the normal acid very closely, but it is not miscible with water.

The *calcium salt*, $(C_4H_7O_2)_2Ca,5H_2O$, unlike that of normal butyric acid, is more soluble in hot than in cold water.

Of the four isomerides of the molecular formula, $C_5H_{10}O_2$, ***iso*valeric acid,** or iso*propylacetic acid*, $(CH_3)_2CH\cdot CH_2\cdot COOH$, and **optically active valeric acid,** or *methylethylacetic acid* (p. 295), $C_2H_5\cdot CH(CH_3)\cdot COOH$, are the more important.

These acids occur together in the plant all-heal, or valerian, and in angelica root ; the mixture of acids, obtained when the macerated plants are distilled with water, is sometimes known as valeric or valerianic acid, and is an oily liquid, boiling at about 174°.

[1] The ferment ceases to act if the solution becomes too strongly acid.

A mixture of these two acids may be prepared by oxidising commercial amyl alcohol with chromic acid.

The **hexylic acids,** $C_6H_{12}O_2$, are of little importance; all the eight isomerides theoretically possible have been prepared. The normal acid is called *caproic acid.*

Normal heptylic acid, $C_7H_{14}O_2$, or $C_6H_{13}\cdot COOH$ (*oenanthic acid*), one of the seventeen theoretically possible isomerides, of which at least fourteen are known, is prepared by oxidising castor oil, or heptaldehyde (p. 144), 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 very large quantities in combination with glycerol in animal and vegetable fats and oils (p. 251), from which they are prepared on the large scale, principally for the manufacture of stearin candles; they are wax-like substances melting at 63° and 71° respectively, and are insoluble in water, but soluble in alcohol, ether, etc. Their sodium and potassium salts are soluble in pure water, and are the principal components of soaps (p. 253), but their calcium, magnesium, and other salts are practically 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 a synthetic 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,** $CH_3\cdot COCl$, is formed, with the evolution of hydrogen chloride; this change is analogous to one of those which occur when an alcohol is treated with phosphorus pentachloride, but takes place practically quantitatively (footnote, p. 108),

$$CH_3\cdot C\langle^{O}_{OH} + PCl_5 = CH_3\cdot C\langle^{O}_{Cl} + POCl_3 + HCl,$$

$$CH_3\cdot CH_2\cdot OH + PCl_5 = CH_3\cdot CH_2Cl + POCl_3 + HCl.$$

Phosphorus trichloride and oxychloride also convert acetic acid into acetyl chloride.

Acetyl chloride is prepared in the laboratory by cautiously adding phosphorus trichloride (20 g.) from a tap-funnel to *anhydrous* acetic acid (25 g.) contained in a distillation flask connected with a condenser,

$$3CH_3\cdot COOH+PCl_3 = 3CH_3\cdot COCl+P(OH)_3.$$

Another method of preparation is to drop phosphorus oxychloride (35 g.) on to anhydrous sodium acetate (20 g.),

$$2CH_3\cdot COONa+POCl_3 = 2CH_3\cdot COCl+NaPO_3+NaCl.$$

In either case the product is then distilled from a water-bath, and collected in a receiver from which moisture is excluded.

Acetyl chloride is a mobile, pungent-smelling liquid, which boils at 51–2°, has a sp. gr. 1·104 at 20°, and fumes in moist air; it is violently decomposed by water, with the formation of acetic acid,

$$CH_3\cdot COCl+H_2O = CH_3\cdot COOH+HCl.$$

It is decomposed, not only by water and by alkalis, but also, more or less rapidly, by all those compounds which contain one or more hydroxyl groups; the interaction usually takes place in such a way that hydrogen chloride is produced, the univalent *acetyl* group, $CH_3\cdot CO$—, displacing the hydrogen of the hydroxyl group,

$$C_2H_5\cdot OH+CH_3\cdot COCl = C_2H_5\cdot O\cdot OC\cdot CH_3+HCl,$$
$$C_2H_4(OH)_2+2CH_3\cdot COCl = C_2H_4(O\cdot CO\cdot CH_3)_2+2HCl.$$

Acetyl chloride, therefore, may be employed for *detecting the presence of a hydroxyl group* in the molecule of a compound.

For this purpose the dry substance (in the state of a fine powder, if a solid) is added to an excess of acetyl chloride, the mixture or solution is heated for some time (with a reflux condenser), and the acetyl chloride is then distilled on a water-bath. The substance may be recovered unchanged, an indication 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, **Ac**—, for hydrogen; this process is called *acetylation*.

In the latter case the substance is purified and its composition is ascertained by combustion,[1] or, since acetyl derivatives are generally decomposed by boiling acids and alkalis,

$$C_2H_5\cdot O\cdot CO\cdot CH_3+KOH = C_2H_5\cdot OH+CH_3\cdot COOK,$$

[1] When the acetyl derivative has the same, or nearly the same, percentage composition as the original substance, the number of acetyl groups in the molecule is determined by the alternative method.

the quantity of acetic acid formed under these conditions, from a known weight of the substance, may be estimated. The molecular formula of the original substance being known, it is then possible to ascertain how many hydrogen atoms in the molecule have been displaced by acetyl groups ; in other words, how many hydroxyl groups were contained in the molecule of the original compound.

Example. A substance of the molecular formula, $C_2H_6O_2$, is converted by acetyl chloride into a compound which on analysis is found to have the *empirical* formula, $C_3H_5O_2$; this result points to the conclusion that the *molecular* formula of the product must be represented by $C_6H_{10}O_4$, or $C_2H_4(O \cdot CO \cdot CH_3)_2$, and that the original compound contains two hydroxyl groups. Now 0·3 g. of this product, on hydrolysis, yields 0·2466 g. of acetic acid ; one gram molecule of this acid (60 g.), therefore, is given by 73 g. of the acetyl derivative. Subtracting the gram molecular weight of the acetyl group ($CH_3 \cdot CO-$ =43) and adding 1 for the displaced hydrogen atom, it is found that the gram molecular weight of substance which contains one hydroxyl group is 31. The compound, M.W. 62, therefore, contains two hydroxyl groups, and is glycol (p. 240).

Determination of Acetyl Groups. When the acetyl derivative is that of a neutral compound it is merely boiled with a known quantity of standard alkali or acid, and the amount of acetic acid which has been formed is then estimated by titration.

In other cases, the acetyl derivative (about 0·2 g.) is mixed with about 100 c.c. of a 10% aqueous solution of benzenesulphonic acid (p. 475), and the solution is slowly distilled in a current of steam until acetic acid ceases to pass over ; the distillate is then titrated with standard alkali.

Acetyl chloride also reacts readily with most substances containing the $-NH_2$ or $>NH$ group, acetyl derivatives being formed,

$$(C_2H_5)_2NH + ClOC \cdot CH_3 = (C_2H_5)_2N \cdot OC \cdot CH_3 + HCl.$$

All the fatty acids except formic acid may be converted into *acid* or *acyl 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. *Acyl bromides*, such as $CH_3 \cdot COBr$, can be obtained in a similar manner ; *acyl iodides*, by treating the chlorides with dry hydrogen iodide.

It is often more convenient to use thionyl chloride instead of a phosphorus halide in the preparation of an acid chloride, as the products, other than the required chloride, are gaseous,

$$R \cdot CO \cdot OH + SOCl_2 = R \cdot COCl + SO_2 + HCl.$$

Anhydrides. The hydrogen atom of a carboxyl group, —COOH, as a rule, is not displaced by the acetyl group when an acid is treated 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,

$$CH_3 \cdot CO \cdot OK + ClOC \cdot CH_3 = CH_3 \cdot CO \cdot O \cdot OC \cdot CH_3 + KCl.$$

The compound obtained from an acetate in this way is the **anhydride** of acetic acid, derived from 2 mol. of the acid by the loss of 1 mol. of water, just as ethers are derived from alcohols,

$$\begin{matrix} CH_3 \cdot COOH \\ CH_3 \cdot COOH \end{matrix} = \begin{matrix} CH_3 \cdot CO \\ CH_3 \cdot CO \end{matrix} > O + H_2O,$$

$$\begin{matrix} C_2H_5 \cdot OH \\ C_2H_5 \cdot OH \end{matrix} = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O + H_2O.$$

It may also be regarded as an acetyl derivative of acetic acid.

Acetic anhydride, $(CH_3 \cdot CO)_2O$, may be prepared by treating *anhydrous* sodium acetate (20 g.) with acetyl chloride (16 g.).

The powdered alkali salt is contained in a distillation flask connected with a condenser, and, when the acetyl chloride has been cautiously added from a tap-funnel, the flask is heated in an oil-bath or over the free flame, in order to distil the acetic anhydride ; the product is collected in a receiver from which moisture is excluded and then redistilled. Yield about 17 g.

Acetic anhydride is manufactured by several processes, mainly for use in making rayon (p. 329) ; most of the methods involve the interaction of anhydrous sodium acetate and an inorganic chloride or oxychloride,

$$8CH_3 \cdot COONa + 3SCl_2 = 4(CH_3 \cdot CO)_2O + 6NaCl + Na_2SO_4 + 2S,$$
$$2CH_3 \cdot COONa + COCl_2 = (CH_3 \cdot CO)_2O + CO_2 + 2NaCl.$$

Acetic anhydride is a mobile liquid of sp. gr. 1·085 at 15°, boils at 139°, and has an unpleasant, irritating odour ; it is decomposed by alkalis, water, alcohols, and other hydroxy-derivatives, acetyl derivatives being formed,

$$\begin{matrix} CH_3 \cdot CO \\ CH_3 \cdot CO \end{matrix} > O + HO \cdot C_2H_5 = CH_3 \cdot CO \cdot O \cdot C_2H_5 + CH_3 \cdot COOH.$$

Acetic anhydride, therefore, like acetyl chloride, may be employed for the detection of hydroxyl groups and for the *acetylation* of hydroxy-compounds and amines (primary and secondary, p. 228).

The operations are carried out as described in the case of acetyl chloride, but the (undissolved) acetyl derivative is usually isolated after pouring the reaction mixture into water; the product is then examined by methods similar to those already given. The action of acetic anhydride on substances containing hydroxyl groups is often accelerated by the addition of anhydrous sodium acetate, or of a small quantity of zinc chloride or sulphuric acid.

Other fatty acids, except formic acid, may be converted into anhydrides by treating the acid chloride with an alkali salt of the acid, or by heating an excess of the alkali salt with phosphorus oxychloride. If an acid chloride is treated with a salt of a different acid, a *mixed anhydride*, corresponding with a mixed ether, is obtained. All these anhydrides resemble acetic anhydride in chemical properties.

Amides. Acetyl chloride and acetic anhydride react 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 it 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 treating ethyl acetate (p. 185) with a concentrated aqueous solution of ammonium hydroxide,

$$CH_3 \cdot CO \cdot OC_2H_5 + NH_3 = CH_3 \cdot CO \cdot NH_2 + C_2H_5 \cdot OH,$$

or by slowly distilling ammonium acetate, preferably in a stream of dry ammonia,

$$CH_3 \cdot CO \cdot ONH_4 = CH_3 \cdot CO \cdot NH_2 + H_2O.$$

In the first method ethyl acetate (20 c.c.) is left in a stoppered bottle with a concentrated ammonium hydroxide solution (60 c.c.) until it has completely dissolved, a slow process, which is hastened considerably by shaking the bottle vigorously from time to time; when the solution is then distilled slowly, the fraction, which passes over from about 200° upwards, solidifies and consists of practically pure acetamide.

In the second method, only a small proportion of the ammonium acetate is converted into acetamide, and that portion of the distillate collected above 140° is redistilled; these operations are repeated several times, and from the fractions collected above 200° the acetamide is isolated by further distillation or by recrystallisation from ether.

Acetamide crystallises in needles, melts at 82°, and boils at 222°. The pure compound has only a faint odour, but as usually prepared it has a strong smell of mice ; it is readily soluble in water and alcohol. When heated with mineral acids or alkalis, it is decomposed into acetic acid and ammonia, or their salts (footnote, p. 160),

$$CH_3 \cdot CO \cdot NH_2 + H_2O = CH_3 \cdot COOH + NH_3 ;$$

on distillation with phosphorus pentoxide it loses the elements of water, and is converted into *methyl cyanide* or *acetonitrile*,

$$CH_3 \cdot CO \cdot NH_2 = CH_3 \cdot CN + H_2O.$$

Acetamide (like other amides) is decomposed by nitrous acid, giving the corresponding acid with the evolution of nitrogen.

Formic acid and all the higher fatty acids may be converted into amides by methods similar to those given above ; *formamide*, $H \cdot CO \cdot NH_2$, a liquid b.p. 111° (20 mm.), for example, may be prepared by distilling ammonium formate. These amides closely resemble acetamide in properties, and their solubility in water diminishes as the molecular weight increases.

Halogen Substitution Products of Acetic Acid

Since acetic acid, like methyl chloride, is a mono-substitution product of methane, 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 when it is heated with chlorine in direct sunlight,

$$CH_3 \cdot COOH + Cl_2 = CH_2Cl \cdot COOH + HCl,$$
$$CH_3 \cdot COOH + 2Cl_2 = CHCl_2 \cdot COOH + 2HCl,$$
$$CH_3 \cdot COOH + 3Cl_2 = CCl_3 \cdot COOH + 3HCl.$$

Again, if the constitutions of acetic acid and of these three compounds are correctly represented by these formulae, it might be inferred 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, etc. This inference, also, is a sound one ; the three substitution products are monobasic acids, similar to acetic acid and to one another in chemical properties ; they are reconverted into acetic acid by nascent hydrogen, just as the substitution products of methane or ethane are transformed into the respective hydrocarbons.

The three chloroacetic 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 the 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 proportion of iodine being sufficient to ensure chlorination. The iodine, or rather the iodine chloride, is spoken of as a chlorine *carrier* (p. 422).

Chloroacetic acid, *monochloroacetic acid*, $CH_2Cl \cdot COOH$, melts at 62°, and boils at 189°. It is prepared commercially by agitating trichloroethylene (p. 101) with 90% sulphuric acid (p. 369),

$$CHCl{:}CCl_2 + 2H_2O = CH_2Cl \cdot COOH + 2HCl,^1$$

and isolating the product by distillation in vacuo. It is used in the synthesis of indigo.

Dichloroacetic acid, $CHCl_2 \cdot COOH$, is a liquid, and boils at 193° ; it may be prepared by heating chloral hydrate with sodium cyanide in aqueous solution,

$$CCl_3 \cdot CH(OH)_2 + NaCN = CHCl_2 \cdot COOH + HCN + NaCl.^2$$

Trichloroacetic 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 58°, boils at 196°, and is decomposed by hot alkalis into chloroform and a carbonate,

$$CCl_3 \cdot COOK + KOH = CHCl_3 + K_2CO_3.$$

The *bromoacetic* and *iodoacetic* acids resemble the corresponding chloroacetic acids in properties.

Chloroformic acid, $Cl \cdot COOH$, is unknown except in the form of its esters, which are described later (p. 262).

[1] The trichloroethylene, like other olefinic compounds, probably combines with the sulphuric acid, giving $CH_2Cl \cdot CCl_2 \cdot SO_4H$, which is then hydrolysed to $CH_2Cl \cdot C(OH)_3 \longrightarrow CH_2Cl \cdot COOH + H_2O$.

[2] $CCl_3 \cdot CHO \longrightarrow CCl_3 \cdot CH(OH) \cdot CN \longrightarrow CCl_2{:}C(OH) \cdot CN \longrightarrow CHCl_2 \cdot CO \cdot CN \longrightarrow CHCl_2 \cdot COOH$.

Many halogen substitution products of the fatty acids are known. There are, for example, two monochloro-propionic acids—namely, *α-chloro-propionic acid*, $CH_3 \cdot CHCl \cdot COOH$, and *β-chloro-propionic acid*, $CH_2Cl \cdot CH_2 \cdot COOH$—and three *dichloro-propionic acids*. For the purpose of distinguishing these isomerides, and other substitution products of acids, the carbon atoms are numbered, or more usually lettered, commencing always with that which is combined with the carboxyl group (compare p. 182),

$$\underset{\delta}{CH_3} \cdot \underset{\gamma}{CH_2} \cdot \underset{\beta}{CH_2} \cdot \underset{\alpha}{CH_2} \cdot COOH;$$

the acid of the constitution, $(CH_3)_2CBr \cdot CH_2 \cdot COOH$, for example, may be named *β-bromo*iso*propylacetic acid* or *β-bromo-β-methyl-butyric acid.*

The fatty acids (and other saturated acids) are not readily attacked by any of the halogens (except perhaps by fluorine), but the acid chlorides and bromides, and the anhydrides, are comparatively easily converted into α-substitution products.

In order, therefore, to prepare its halogen derivative, the anhydrous acid is mixed with a small quantity of red phosphorus, and dry chlorine is then passed into or over the mixture, or bromine is slowly added to it from a dropping funnel, gentle heat being afterwards applied in order to complete the interaction (*Hell-Volhard* method). Under these conditions the acid chloride or bromide is first formed, by the action of the halogen phosphorus compound, (PCl_3 or PBr_3), or the acid, if dicarboxylic (p. 271), is converted into its anhydride; substitution then takes place, the halogen displacing one hydrogen atom from the α-position; if there is no hydrogen atom in the α-position—as, for example, in trimethylacetic acid—a halogen derivative is not formed as a rule. When the reaction is at an end the product is either treated with water to convert it into the acid, or it is poured into an alcohol to convert it into an ester,

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > CBr \cdot COBr + CH_3 \cdot OH = \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > CBr \cdot COOCH_3 + HBr;$$

the second method is generally used when the substituted acid is a liquid, because the ester is more easily isolated than is the acid.

The α-halogen derivatives of many of the fatty acids may also be prepared by the following method: Diethyl malonate is converted into a mono-alkyl substitution product (p. 207), the ester is hydrolysed, and the alkylmalonic acid is treated with chlorine or bromine (X), whereby the α-hydrogen atom is easily displaced;

the product is then heated in order to convert it into a halogen derivative of a monocarboxylic acid,

$$CH_2<\begin{matrix}COOEt\\COOEt\end{matrix}\longrightarrow CHR<\begin{matrix}COOEt\\COOEt\end{matrix}\longrightarrow CHR<\begin{matrix}COOH\\COOH\end{matrix}\longrightarrow$$

$$CXR<\begin{matrix}COOH\\COOH\end{matrix}\longrightarrow CHXR\cdot COOH.$$

Derivatives containing the halogen in the α- or in other (β, γ, etc.) positions may be prepared by displacing the hydroxyl group of a hydroxy-acid by halogen, with the aid of a halogen acid or a halogen derivative of phosphorus; β, γ, etc., by the direct union of an unsaturated acid with a halogen acid or with a halogen (p. 343).

The halogen atom or atoms in a halogen substitution product of a fatty acid behave like those in the halogen derivatives of the hydrocarbons, and *not* like those in acid chlorides or bromides; examples are given later (pp. 267, 268, 342).

SUMMARY AND EXTENSION

The Fatty Acids. Carboxy-derivatives of the paraffins of the general formula, $C_nH_{2n}O_2$, or R·COOH. The more important members of this homologous series are the following, and all those mentioned after *iso*valeric acid are normal acids :

		M.p.	B.p.	Sp. gr. at 0°
Formic acid	H·COOH	+8·4°	101°	1·245
Acetic acid	$CH_3\cdot COOH$	+16·7°	118°	1·070
Propionic acid	$C_2H_5\cdot COOH$	−20°	141°	1·015
Butyric acid	$C_3H_7\cdot COOH$	−6°	163°	0·978
*Iso*butyric acid		−47°	154°	0·968
Valeric acid	$C_4H_9\cdot COOH$	−34°	186°	0·957
*Iso*valeric acid		−38°	176°	0·947
Caproic acid	$C_5H_{11}\cdot COOH$	−2°	205°	0·945
Heptylic acid	$C_6H_{13}\cdot COOH$	−10°	223°	0·933
Caprylic acid	$C_7H_{15}\cdot COOH$	+16°	237°	0·914 (20°)
Pelargonic acid	$C_8H_{17}\cdot COOH$	+12°	254°	0·910 (20°)
Capric acid	$C_9H_{19}\cdot COOH$	+31°	269°	0·895 (40°)
Undecylic acid	$C_{10}H_{21}\cdot COOH$	+30°	—	0·910 (25°)
Lauric acid	$C_{11}H_{23}\cdot COOH$	+44°	—	0·875 (m.p.)
Myristic acid	$C_{13}H_{27}\cdot COOH$	+54°	—	0·862 (m.p.)
Palmitic acid	$C_{15}H_{31}\cdot COOH$	+63°	—	0·853 (m.p.)
Stearic acid	$C_{17}H_{35}\cdot COOH$	+71°	—	0·845 (m.p.)

It is an interesting fact that lauric acid, and all the higher members named in this table, occur in nature in fats and oils, contain an even number of carbon atoms, and are all normal acids. The higher normal acids which contain an odd number of carbon atoms in their

molecules are known, but, with possible rare exceptions, they do not occur in nature.

Nomenclature. All the lower normal fatty acids have trivial names. Where isomerism occurs the terms *normal* and *iso* are used to distinguish two of the isomerides, and others may be named as derivatives of acetic acid, as shown on p. 171. The more complex acids and their derivatives are named more systematically after the *normal* paraffins from which they are derived, the terminal **e** of the suffix **ane** being changed into **oic acid**; e.g. *pentanoic acid*, $C_5H_{10}O_2$. The parent hydrocarbons themselves are in all cases the normal or straight chain compounds, as already explained (p. 60), and their chains are numbered, starting from the carboxyl group which is numbered 1. *Iso*valeric acid, $CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot COOH$, therefore, is 3-*methylbutanoic acid* (p. 171), and the acid $CH_3 \cdot CH_2 \cdot CCl(C_2H_5) \cdot COOH$ is 2-*ethyl*-2-*chlorobutanoic acid* (although it is derived from an isomeride of hexanoic acid). If the chain is lettered, instead of numbered, the 2-position is lettered α- and so on,

$$\begin{matrix} 4 & 3 & 2 & 1 \\ CH_3 \cdot & CH_2 \cdot & CH_2 \cdot & COOH. \\ \gamma & \beta & \alpha & \end{matrix}$$

Esters, however, are generally named as *carboxy*-derivatives of normal hydrocarbons; thus the ethyl ester of the chloro-acid just given would be *ethyl* 1-*chloro*-1-*ethylpropane*-1-*carboxylate*, the —COOH group being regarded as a substituent of the paraffin.

Special Methods of Preparation. Formic acid is prepared by heating oxalic acid with glycerol and from carbon monoxide and alkali; acetic acid from pyroligneous acid; butyric acid by the butyric fermentation of lactic acid; palmitic and stearic acids by the hydrolysis of glycerides occurring in fats and oils.

General Methods of Preparation. (1) Primary alcohols or aldehydes are oxidised,

$$C_2H_5 \cdot CH_2 \cdot OH + 2O = C_2H_5 \cdot COOH + H_2O,$$
$$C_6H_{13} \cdot CHO + O = C_6H_{13} \cdot COOH.$$

(2) Alkyl cyanides are heated with alkalis or mineral acids,

$$C_2H_5 \cdot CN + 2H_2O = C_2H_5 \cdot COOH + NH_3.$$

(3) Those dicarboxylic acids in which the two carboxyl groups are combined with one and the same carbon atom are decomposed by heat (p. 276),

$$CH_2(COOH)_2 = CH_3 \cdot COOH + CO_2.$$

(4) Derivatives of ethyl acetoacetate are hydrolysed (p. 202),

$$CH_3 \cdot CO \cdot CH(C_3H_7) \cdot COOC_2H_5 + 2KOH = C_3H_7 \cdot CH_2 \cdot COOK + CH_3 \cdot COOK + C_2H_5 \cdot OH.$$

(5) Dry carbon dioxide is passed into an ethereal solution of a Grignard compound,

$$C_2H_5 \cdot MgBr + CO_2 = C_2H_5 \cdot CO \cdot O \cdot MgBr,$$

and the product is decomposed with a dilute acid (p. 237).

Physical Properties. At ordinary temperatures the lower members (except acetic acid) are liquids, miscible with water, alcohol, and ether; like the alcohols, they are associated, but they are ionised to some extent in aqueous solution. As the molecular weight increases the acids become more oily in character, gradually lose their pungent smell, and become less 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. The lower members are readily volatile in steam, but the higher members, such as palmitic acid, can only be distilled in superheated steam. The first three members are specifically heavier than water, but the specific gravity decreases as the series is ascended (see table). With the exception of the very high members, they boil without decomposition, under ordinary atmospheric pressure, and the boiling points of the *normal* acids rise about 19° for every addition of $-CH_2-$ to the molecule. The melting points also rise, but not continuously; normal acids containing an odd number of carbon atoms melt at a lower temperature than the preceding normal members containing an even number of carbon atoms:

$C_{12}H_{24}O_2$	$C_{13}H_{26}O_2$	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$.
44°	43°	54°	52°	63°	62°

Chemical Properties. The fatty acids, with the exception of formic acid, are only with difficulty oxidised or converted into simpler compounds and are very stable; nevertheless, owing to the presence of the carboxyl group in their molecules, they readily undergo various double decompositions. They are all monobasic acids, but the acid character becomes less and less pronounced as the molecular weight increases; whereas formic and acetic acids readily decompose carbonates and dissolve certain metals and 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 as the series is ascended the solubility decreases, until, in the case of the higher acids, only the alkali salts (soaps) are soluble.

Fatty acids react with alcohols, forming esters and water, until equilibrium is established,

$$CH_3 \cdot COOH + C_2H_5 \cdot OH \rightleftarrows CH_3 \cdot COOC_2H_5 + H_2O.$$

When treated with phosphorus pentachloride, etc., they are converted into acid chlorides,

$$C_2H_5 \cdot COOH + PCl_5 = C_2H_5 \cdot COCl + POCl_3 + HCl.$$

These acid chlorides react readily with hydroxy-compounds, giving esters,

$$C_2H_5 \cdot COCl + CH_3 \cdot OH = C_2H_5 \cdot CO \cdot OCH_3 + HCl,$$

and, when treated with an alkali salt of a fatty acid, they yield anhydrides of the acids,

$$C_2H_5 \cdot COCl + C_2H_5 \cdot COOK = (C_2H_5 \cdot CO)_2O + KCl\ ;$$

they react readily with compounds containing the $—NH_2$ or $>NH$ group,

$$CH_3 \cdot COCl + 2NH_2 \cdot C_2H_5 = CH_3 \cdot CO \cdot NH \cdot C_2H_5 + C_2H_5 \cdot NH_2,HCl.$$

The fatty acids yield halogen substitution products from which hydroxy-, amino-, olefinic, and acetylenic acids may be prepared.

From certain salts of the fatty acids, ketones, aldehydes, and paraffins can be prepared ; and, as the aldehydes and ketones may be reduced to alcohols, and the latter may be converted into ethers and olefines, all these compounds may be obtained from the fatty acids. The esters of the fatty acids are also used for the preparation of amides, primary alcohols (p. 197), and tertiary alcohols (p. 237).

The properties of the fatty and other carboxylic acids show clearly that the behaviour of the carbonyl and hydroxyl radicals of the —COOH group, particularly the former, is quite different from that of these radicals in ketones and alcohols respectively ; an explanation of this fact is suggested later (p. 517).

Different methods by means of which a fatty acid may be converted into the next lower, or higher, homologue are described later (p. 224) ; but one method, which is based on reactions already studied, may be given here :

When the barium salt of a fatty acid (except formic) is heated with barium acetate, a ketone is formed, and the hydrocarbon radicals of the two acids become united by a carbonyl group. When this ketone is oxidised, the $CH_3 \cdot CO—$ group is converted into acetic acid, and the $—CH_2—$ group to which the carbonyl radical is united is oxidised to $—CO \cdot OH$ (p. 157). The net result of these two operations is the conversion of the higher fatty acid into its next lower homologue :

$$R \cdot CH_2 \cdot COOH \longrightarrow R \cdot CH_2 \cdot CO \cdot CH_3 \longrightarrow R \cdot CO \cdot OH.$$

This method was employed by Krafft, who started from stearic acid, ($C_{18}H_{36}O_2$), and converted it, step by step, into capric acid, ($C_{10}H_{20}O_2$), which was known to be a normal acid. He thus proved that stearic, margaric, and palmitic acids, as well as all the lower homologues which he obtained in this work, are *normal* acids ; the ketone derived from an acid such as $CH_3 \cdot [CH_2]_n \cdot CHR \cdot COOH$ could *not* yield on oxidation the next lower homologue of that acid.

CHAPTER 12

ESTERS

It has been pointed out that, in some respects, the alcohols behave like metallic hydroxides; they react with acids, forming *esters* (at one time called ethereal salts) and water,

$$C_2H_5 \cdot OH + HCl \rightleftarrows C_2H_5Cl + H_2O,$$
$$CH_3 \cdot OH + HO \cdot OC \cdot CH_3 \rightleftarrows CH_3 \cdot O \cdot OC \cdot CH_3 + H_2O.$$

These reactions, however, are *reversible*; esters are decomposed by water, with the formation of an alcohol and an acid. In the preparation of an ester, therefore, the presence of water must be avoided so far as possible, and the other conditions of the experiment must be so chosen that the reaction proceeds in the desired direction (p. 188).

Halogen esters of the monohydric alcohols are identical with the corresponding halogen mono-substitution products of the paraffins, as already explained. Esters formed from other inorganic acids resemble the alkyl halides in many respects, but they are derived from acids of such diverse characters that differences in their properties are only to be expected.

The esters of carboxylic acids, on the other hand, are derived from acids of a very similar nature and resemble one another very closely in all their reactions.

Esters of Carboxylic Acids

Ethyl acetate, $CH_3 \cdot CO \cdot OC_2H_5$, 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 ester of ethyl alcohol,

$$CH_3 \cdot COOAg + BrC_2H_5 = CH_3 \cdot COOC_2H_5 + AgBr.$$

It may be prepared by treating a mixture of alcohol and acetic acid or sodium acetate with concentrated sulphuric acid,

$$CH_3 \cdot COOH + C_2H_5 \cdot OH = CH_3 \cdot COOC_2H_5 + H_2O.$$

A mixture of equal volumes of alcohol and acetic acid is run slowly below the surface of a mixture of equal volumes of alcohol and concentrated sulphuric acid, heated at about 140° ; this process, like that by which ether is prepared, is theoretically continuous (apparatus shown in Fig. 19, p. 126) as the alcohol and sulphuric acid combine to form ethyl hydrogen sulphate, which then reacts with the acetic acid, forming ethyl acetate and sulphuric acid,

$$C_2H_5 \cdot OH + H_2SO_4 = C_2H_5 \cdot HSO_4 + H_2O,$$
$$C_2H_5 \cdot HSO_4 + CH_3 \cdot COOH = CH_3 \cdot COOC_2H_5 + H_2SO_4.$$

The distillate is shaken with a saturated solution of sodium chloride containing some sodium carbonate,[1] whereon the alcohol and acetic acid dissolve, and the ethyl acetate separates as an oil ; the ester is dried over anhydrous calcium chloride, and purified by fractional distillation.

Ethyl acetate may be manufactured by treating acetaldehyde with aluminium ethoxide (p. 111), which acts catalytically,

$$2CH_3 \cdot CHO = CH_3 \cdot COOC_2H_5.$$

Ethyl acetate is a mobile liquid of sp. gr. 0·9 at 20°, having a pleasant, fruity odour, and boiling at 77° ; it is moderately soluble in water. It is readily hydrolysed (p. 189) by alkalis, 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,

$$CH_3 \cdot COOC_2H_5 + NH_3 = CH_3 \cdot CO \cdot NH_2 + C_2H_5 \cdot OH.$$

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 the acid or an acetate may be indicated by this reaction, but there is no simple, conclusive test for ethyl acetate or acetic acid.

Methyl acetate, $CH_3 \cdot CO \cdot OCH_3$, is prepared by the same methods as those used for the ethyl ester ; it boils at 57·5°.

The esters of organic acids in general are usually prepared by the processes described later (p. 189) ; they may also be obtained by the reactions given in the case of ethyl acetate.

The first or second of these is used when it is required to convert completely a small quantity of an alcohol into its ester ; the third is useful when only a small quantity of acid is available : The acid

[1] Compare p. 73.

is converted into its silver salt, the latter is warmed with the alkyl halide (reflux condenser), and the ester, separated from the silver halide by filtration, is distilled.

Esters are usually neutral, pleasant-smelling liquids, sparingly soluble or insoluble in water ;[1] as a rule, they distil unchanged under atmospheric pressure, but those of the higher alcohols, strongly heated, may give an acid and an olefine. The hydrogen esters, such as ethyl hydrogen oxalate, may be non-volatile (760 mm.), and readily soluble in water.

All esters are hydrolysed (p. 189) by aqueous alkalis, mineral acids, and even, but more slowly, by boiling water,

$$CH_3 \cdot COOC_3H_7 + KOH = CH_3 \cdot COOK + C_3H_7 \cdot OH,$$
$$2H \cdot COOCH_3 + Ba(OH)_2 = (H \cdot COO)_2Ba + 2CH_3 \cdot OH.$$

Esters of carboxylic acids yield amides on treatment with concentrated aqueous or alcoholic ammonia,

$$C_3H_7 \cdot COOCH_3 + NH_3 = C_3H_7 \cdot CO \cdot NH_2 + CH_3OH,$$

whereas the halogen esters give amines with alcoholic ammonia (p. 214),

$$C_2H_5I + NH_3 = C_2H_5 \cdot NH_2,HI.$$

The *identification* of esters, as such, is usually impossible because they are generally liquids, and a determination of the boiling-point alone is insufficient for such a purpose ; it is necessary, therefore, to hydrolyse the ester with an excess of boiling aqueous, say 10%, alkali, using a reflux condenser, and then to separate and identify the *alcohol* and the *acid* which have been produced.

In the case of esters, derived from alcohols which are readily soluble in water, hydrolysis is complete when a homogeneous solution is obtained. The liquid is then distilled until about 5 c.c. have passed over and a portion of this distillate is warmed with dilute sulphuric acid and potassium dichromate ; the reduction of the dichromate and an odour of formaldehyde or acetaldehyde indicate the presence of methyl or ethyl alcohol, which may be further distinguished by means of the iodoform reaction (p. 112). Esters derived from alcohols, which are not readily soluble in water (amyl alcohol, for example), do not give a homogeneous solution on hydrolysis ; in such cases, after the solution has been boiled

[1] Dimethyl oxalate (p. 275) is a noteworthy exception, as it is a solid and is moderately soluble in water ; commercial samples are often acid to litmus.

during an hour or so, the undissolved oil is separated and identified by its boiling-point or in other ways.

For the identification of the acid which has been produced from the ester, the alkaline solution is concentrated and treated with an excess of dilute sulphuric acid ; the organic acid may then be precipitated as a solid or as an oil and further examined. If not, the solution is boiled and the escaping vapours are tested with litmus paper and any recognisable smell is noted ; if the acid is readily soluble in water and non-volatile, it may in many cases be extracted with ether and then identified.

The boiling-point of the ester should then be taken in order to confirm or otherwise the tentative conclusion which may have been reached.

The esters of carboxylic acids afford excellent examples of isomerism ; ethyl formate, $H \cdot COOCH_2 \cdot CH_3$, for example, is isomeric with methyl acetate, $CH_3 \cdot COOCH_3$; propyl formate, $H \cdot COOC_3H_7$, is isomeric with ethyl acetate, $CH_3 \cdot COOC_2H_5$, and with methyl propionate, $C_2H_5 \cdot COOCH_3$, and so on.

Esterification. Esters in general are formed when an alcohol is mixed with an acid ; but the change, which is a gradual one, is never complete, because the reaction is reversible. When the interaction has proceeded for a certain time, the quantity of ester which is decomposed by the water present is equal to that formed in the same time by the interaction of the acid and the alcohol ; in other words, a condition of equilibrium is established when the two changes represented by the equations,

$$CH_3 \cdot OH + CH_3 \cdot COOH = CH_3 \cdot COOCH_3 + H_2O,$$
$$CH_3 \cdot COOCH_3 + H_2O = CH_3 \cdot OH + CH_3 \cdot COOH,$$

balance one another.

This is usually expressed by

$$CH_3 \cdot OH + CH_3 \cdot COOH \rightleftarrows CH_3 \cdot COOCH_3 + H_2O,$$

and the process represented by reading the equation from left to right is called *esterification*, the reverse reaction, *hydrolysis* (p. 189).

The proportion of alcohol, which is converted into ester, depends on the nature of the alcohol and of the acid, and on their relative quantities (molecular concentrations) ; it is almost independent of the temperature, but the higher the temperature the sooner the

condition of equilibrium is attained. These facts were established by Berthelot and by Menschutkin.

Now, if the water produced during esterification could be removed, or otherwise prevented from decomposing the ester, the desired change, from left to right, should take place far more completely. This consideration led to the use of ' dehydrating agents ' in the preparation of esters, substances such as zinc chloride, hydrogen chloride, or sulphuric acid being added to the mixture of alcohol and acid to ' bind ' the water and prevent it from decomposing the ester. In practice, the results of doing this are very satisfactory, and the two methods usually employed in preparing esters of organic acids are : (*a*) By passing *dry* hydrogen chloride into a boiling mixture of the acid and alcohol contained in a flask provided with a reflux condenser ; (*b*) By warming a mixture of the acid and alcohol with concentrated sulphuric acid. In both these processes, when the object is to convert as large a proportion as possible of the acid into its ester, the alcohol is used in very considerable excess.

The action of the mineral acids during esterification is not yet thoroughly understood ; in the case of sulphuric acid, an alkyl hydrogen sulphate is doubtless formed as an intermediate product (compare p. 194), and the sulphuric acid probably combines with the water which is formed, giving a hydroxide such as $SO(OH)_4$; hydrogen chloride acts as a catalyst and probably forms some reactive additive product with the acid. By either method, with an excess of the alcohol, esterification of the acid is rapid and practically complete, and in the latter only 1–5% by weight of the catalyst, compared with that of the alcohol, is required (*Fischer-Speier* method).

The isolation of the ester is sometimes accomplished by distillation, as in the case of ethyl acetate ; as a rule, however, when esterification is at an end most of the excess of alcohol is distilled from a water-bath, the residue is poured into water, and the ester is separated with a separating-funnel or (if a solid) by filtration. It is washed with a solution of sodium carbonate, to free it from acid, and is then dried and distilled, or recrystallised.

Only a small proportion of the ester is decomposed during the comparatively rapid distillation of the alcohol.

Tertiary alcohols are only very incompletely esterified under the conditions just described.

Hydrolysis. The term *hydrolysis* was originally used to denote

the decomposition of one compound, such as a halide or other ester, into two or more, accompanied by the fixation of the elements of water as H— and —OH, or of some basic hydroxide, H— and —OM′, in the products of the reaction,

$$C_2H_5Cl+H_2O = C_2H_5\cdot OH+HCl,$$
$$CH_3\cdot COOC_2H_5+KOH = CH_3\cdot COOK+C_2H_5\cdot OH.$$

Many other classes of organic compounds, as, for example, anhydrides and amides, are thus decomposed or *hydrolysed* by water, more readily by acids and aqueous alkalis.

The term hydrolysis now includes reactions in which the addition of water does *not* involve a breaking-up or *fission* of the molecule. Such changes may occur in those hydrolyses in which a double or treble binding is involved, since one or two of the links of those bonds may remain unchanged. Methyl cyanide, for example, undergoes hydrolysis, giving acetamide ; a further hydrolysis may then occur and fission results,

$$CH_3\cdot C\vdots N+H_2O = CH_3\cdot CO\cdot NH_2,$$
$$CH_3\cdot CO\cdot NH_2+H_2O = CH_3\cdot COOH+NH_3.$$

Acetylenic compounds undergo hydrolysis giving ketones (acetylene gives acetaldehyde), without any subsequent fission taking place.

In many such examples it would seem that the elements of water are added as H_2 and O. It is probable, however, that in all cases it is H— and —OH which take part in the reaction, giving usually an unstable initial product, which then undergoes isomeric change (p. 263),

$$CH_3\cdot C\vdots N+H_2O = CH_3\cdot C(OH){:}NH\longrightarrow CH_3\cdot CO\cdot NH_2,$$
$$CH_3\cdot C\vdots H+H_2O = CH_3\cdot C(OH){:}CH_2\longrightarrow CH_3\cdot CO\cdot CH_3.$$

Esters of Nitric Acid

The esters of nitric acid are formed when the alkyl halides are heated with silver nitrate in alcoholic solution,

$$CH_3I+AgNO_3 = CH_3\cdot O\cdot NO_2+AgI\ ;$$

they are also produced, together with nitrites (see below), when the alcohols are treated with concentrated nitric acid,

$$C_3H_7\cdot OH+HNO_3 = C_3H_7\cdot O\cdot NO_2+H_2O.$$

Ethyl nitrate, $C_2H_5\cdot NO_3$, is formed when alcohol is cautiously treated with concentrated nitric acid,

$$C_2H_5\cdot OH+HNO_3 = C_2H_5\cdot NO_3+H_2O\ ;$$

but oxidation also occurs, and so much heat is developed that unless care is taken the reaction becomes almost explosive in violence ; even when the mixture is cooled, only a comparatively small quantity of ethyl nitrate is produced, as the acid oxidises some of the alcohol and is itself reduced to nitrous acid, which then reacts with the alcohol and gives ethyl nitrite. If, however, the nitric acid is previously mixed with some urea (p. 264), a substance which decomposes nitrous acid,

$$CO(NH_2)_2+2NO\cdot OH = CO_2+3H_2O+2N_2,$$

the reaction takes place quietly, and ethyl nitrate is the principal product.

Alcohol (not more than 20 g.) is gradually added to half its volume of nitric acid (sp. gr. 1·4), which has been previously shaken with, and still contains about 3 g. of urea ; 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, and the heavy oil is then run off, dried with calcium chloride, and distilled from a water-bath.

Ethyl nitrate is a mobile liquid of sp. gr. 1·11 at 15°, and boils at 87·5° ; it has a pleasant, fruity odour, and is almost insoluble in water, but readily soluble in alcohol, ether, etc. It burns with a luminous flame, and when dropped on a hot surface it sometimes explodes. It is slowly hydrolysed by boiling water, quickly by hot alkalis, yielding alcohol and nitric acid or a nitrate,

$$C_2H_5\cdot O\cdot NO_2+H_2O = C_2H_5\cdot OH+HNO_3.$$

On reduction with tin and hydrochloric acid it yields hydroxylamine,

$$C_2H_5\cdot O\cdot NO_2+6H = C_2H_5\cdot OH+NH_2\cdot OH+H_2O.$$

Methyl nitrate, $CH_3\cdot O\cdot NO_2$ (b.p. 65°), and the higher homologues closely resemble ethyl nitrate in properties.

Esters of Nitrous Acid

The esters of nitrous acid are produced by the action of nitrous acid on the alcohols,

$$C_2H_5\cdot OH+HNO_2 = C_2H_5\cdot O\cdot NO+H_2O.$$

They may be prepared by saturating the alcohols with the gas

evolved by the interaction of arsenious oxide and nitric acid,[1] or by distilling an alcohol with sodium nitrite and sulphuric acid.

Ethyl nitrite, $C_2H_5 \cdot O \cdot NO$, is prepared by adding a mixture of alcohol and dilute sulphuric acid to a solution of potassium nitrite ;[2] the product is separated, dried with calcium chloride, and distilled.

When concentrated nitric acid (3 c.c.) is dropped slowly into a cold mixture of alcohol (20 c.c.) and concentrated sulphuric acid (2 c.c.), and the solution is carefully distilled with copper turnings (about 4 g.), the distillate consists of a mixture of ethyl nitrite,[3] alcohol, and oxidation products of the latter ; when diluted with alcohol, it is employed in medicine as *sweet spirit of nitre.*

Ethyl nitrite is a liquid of sp. gr. 0·9 at 15·5° ; it boils at 17°, and has a pleasant, fruity odour like that of apples ; it is sparingly soluble in water, and is readily hydrolysed by boiling water or dilute alkalis,

$$C_2H_5 \cdot O \cdot NO + KOH = C_2H_5 \cdot OH + KNO_2.$$

Methyl nitrite, $CH_3 \cdot O \cdot NO$, is a gas (b.p. −12°) ; the higher homologues resemble ethyl nitrite. *Amyl nitrite,* $C_5H_{11} \cdot O \cdot NO$, for example, prepared by passing nitrous gases into commercial amyl alcohol, is a liquid boiling at about 96° ; it is used in medicine in cases of *angina pectoris*, and also, owing to its solubility in organic solvents, instead of an *aqueous* solution of an alkali nitrite, in preparing diazonium salts in the crystalline condition (p. 455).

Nitroparaffins

When ethyl iodide is warmed with *silver* nitrite, silver iodide is slowly formed, and when the liquid product is fractionally distilled it yields *two* substances. One of these boils at 17° and is ethyl nitrite ; the other boils at 114° and is called **nitroethane.**

Ethyl nitrite and nitroethane are *isomeric*, and the formation of both compounds may be expressed by the equation,

$$C_2H_5I + AgNO_2 = C_2H_5 \cdot NO_2 + AgI ;$$

but whereas the former is an ester of nitrous acid, $HO \cdot N{:}O$, and has the constitution, $C_2H_5 \cdot O \cdot N{:}O$, the structure of nitroethane must be represented by the formula, $C_2H_5 \cdot NO_2$.

[1] $As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$.

[2] The readiness with which the alkyl nitrites are formed in the presence of water is noteworthy : these esters are also hydrolysed very easily.

[3] $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + 2H_2O + 2HNO_2$.

Compounds, similar to nitroethane in constitution, and isomeric with the corresponding nitrites, may be obtained from other halogen esters in the above manner ; they were discovered by V. Meyer, and are termed *nitroparaffins*, because they are derived from the paraffins by the substitution of the nitro-group, $-NO_2$, for one atom of hydrogen. They may also be obtained in some cases by the direct nitration of the paraffins.

The nitroparaffins are pleasant-smelling liquids, and usually distil without decomposition, but their boiling-points are much higher than those of the corresponding nitrites, as illustrated by the case of ethyl nitrite and nitroethane. They differ entirely from the nitrites in chemical behaviour ; the nitroparaffins may dissolve in, but are *not* decomposed by, caustic alkalis, whereas the nitrites, like all other esters, undergo hydrolysis, yielding an alcohol and a nitrite.

The nitroparaffins 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,

$$C_2H_5 \cdot O \cdot N{:}O + 6H = C_2H_5 \cdot OH + NH_3 + H_2O.$$

It is on facts such as these that the structural formulae given above are based. The reactions of the alkyl nitrites show that the alkyl radical is directly united with *oxygen*, whereas those of the nitroparaffins show equally clearly that the alkyl group is directly united with nitrogen, but there is no satisfactory explanation of how both types of compounds are formed by the interaction of *silver* nitrite and an alkyl halide (compare p. 366).

All the nitroparaffins which contain the group, $-CH_2 \cdot NO_2$ or $> CH \cdot NO_2$, are converted into soluble salts by aqueous solutions of the alkali hydroxides. These salts are derived from acids which are isomeric with the corresponding nitroparaffins and which, in solution, probably exist in equilibrium with the latter. Nitroethane (I), for example, gives a sodium salt (II), which is derived from the acid (III),

$$\underset{\text{I}}{CH_3 \cdot CH_2 \cdot NO_2}, \qquad \underset{\text{II}}{CH_3 \cdot CH{:}NO \cdot ONa}, \qquad \underset{\text{III}}{CH_3 \cdot CH{:}NO \cdot OH}.$$

Although the sodium salts are stable, the corresponding acids are unstable, and cannot, as a rule, be isolated, as they undergo intramolecular or isomeric change into nitroparaffins ; compounds such

as the nitroparaffins which, although not acids themselves, are yet capable of undergoing a (reversible) change in structure and thus giving acids, are called *pseudo*-acids.

Nitromethane, $CH_3 \cdot NO_2$, is formed with the development of heat when methyl iodide is treated with silver nitrite, and the product in this case contains only a little of the isomeric nitrite. It may be prepared by heating sodium chloroacetate with sodium nitrite in aqueous solution,

$$CH_2Cl \cdot COONa + NaNO_2 = CH_2(NO_2) \cdot COONa + NaCl,$$
$$CH_2(NO_2) \cdot COONa + H_2O = CH_3 \cdot NO_2 + NaHCO_3.$$

It is a liquid (b.p. 101°), and with a solution of sodium hydroxide it gives a soluble sodium salt, analogous to that of nitroethane.

Some of the lower paraffins are now nitrated on the large scale in the vapour phase with nitrogen peroxide or nitric acid ; the products are used as solvents for cellulose acetate, nitrocellulose, etc.

Esters of Sulphuric Acid

Dibasic acids, such as sulphuric and oxalic acids, form two classes of esters—namely, alkyl hydrogen esters, corresponding with the metal hydrogen sulphates, and normal alkyl esters, corresponding with the normal metallic sulphates,

Ethyl hydrogen sulphate $C_2H_5 \cdot HSO_4$	Ethyl sulphate $(C_2H_5)_2SO_4$
Potassium hydrogen sulphate $KHSO_4$	Potassium sulphate K_2SO_4

Ethyl hydrogen sulphate or *ethylsulphuric acid*, $C_2H_5 \cdot HSO_4$, is formed when ethylene is passed into fuming sulphuric acid, or heated with ordinary sulphuric acid,

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot O \cdot SO_2 \cdot OH \text{ or } C_2H_5 \cdot HSO_4.$$

It is prepared by heating alcohol with concentrated sulphuric acid,

$$C_2H_5 \cdot OH + H_2SO_4 = C_2H_5 \cdot HSO_4 + H_2O.$$

A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated at 100° during about an hour, when some of the alcohol is converted into ethyl hydrogen sulphate. The solution is then cooled, diluted with water, and treated with a slight excess of barium carbonate, when barium sulphate and barium ethyl sulphate are formed,

$$2C_2H_5 \cdot HSO_4 + BaCO_3 = (C_2H_5 \cdot SO_4)_2Ba + CO_2 + H_2O.$$

The barium sulphate and excess of barium carbonate are separated by filtration, and the cold solution of barium ethyl sulphate is

treated with dilute sulphuric acid, so long as a precipitate is produced, and filtered again from 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 temperatures under reduced pressure, when alcohol and water pass off and impure 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. The *potassium* salt, $C_2H_5 \cdot KSO_4$, may be prepared by neutralising the acid with potassium carbonate ; also by treating a solution of the barium salt (1 mol.) with potassium carbonate (1 mol.), and then evaporating the filtered solution under reduced pressure ; it is a 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 ethyl hydrogen sulphate does not give a precipitate with barium chloride in the cold, but does so when the solution is boiled with dilute hydrochloric acid, which hydrolyses the ester.

Ethyl hydrogen sulphate is a very important substance, as it is an intermediate product in the conversion of alcohol into ethylene and into ether, and of ethylene into alcohol. It is hydrolysed by boiling water, and for this reason it cannot be obtained from its aqueous solution by evaporation 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 react with sulphuric acid, yielding *alkyl hydrogen sulphates*, corresponding with ethyl hydrogen sulphate ; these compounds closely resemble ethyl hydrogen sulphate in properties, undergo similar decompositions, and are frequently used instead of the alkyl halides in preparing other substances.

Salts of some of the higher alkyl hydrogen sulphates are used as emulsifiers and detergents (cf. p. 477).

Dimethyl sulphate or *methyl sulphate*,[1] $(CH_3)_2SO_4$, is prepared

[1] The alternative names given to this ester are used indiscriminately, and similarly in nearly all other cases of normal esters of di-, tri-, etc., basic acids.

by treating methyl alcohol with sulphur trioxide at temperatures below 0° ; the methyl hydrogen sulphate which is thus produced is afterwards heated under reduced pressure, whereon the normal ester distils,

$$2CH_3 \cdot HSO_4 = (CH_3)_2SO_4 + H_2SO_4.$$

It is an odourless, *poisonous* liquid of sp. gr. 1·33 at 15°, boiling at 188°, and it is slowly hydrolysed by cold water, giving methyl alcohol and methyl hydrogen sulphate.

When a substance which contains —OH, —NH_2, or > NH groups is treated with dimethyl sulphate and an aqueous solution of an alkali hydroxide, the hydrogen atoms of these groups are displaced by methyl groups ; hence dimethyl sulphate is often used, instead of methyl iodide, in *methylating* organic compounds (p. 484). *Its vapour must not be inhaled.*

Diethyl sulphate, $(C_2H_5)_2SO_4$, is of less importance ; it may be prepared by warming silver sulphate with ethyl iodide,

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI,$$

or, on the large scale, from ethylene and sulphuric acid, in the presence of cuprous or ferrous salts. It is a liquid, which boils at 208°, with some decomposition.

SUMMARY AND EXTENSION

Esters. Compounds derived from the alcohols by the displacement of the hydrogen atom of the hydroxyl group by an acid radical, a reaction which is reversible in the presence of water,

$$\text{Acid} + \text{Alcohol} \rightleftarrows \text{Ester} + \text{Water}.$$

Esters, therefore, may be compared with metallic salts but differ from the latter in not being electrolytes. Esters may be derived from organic or inorganic acids. Members of the former class have very similar properties, but those of the latter differ considerably according to the nature of the acid radical ; the esters of halogen acids have already been described.

Nomenclature. The name of an ester, as will have been seen, is based on those of the acid and alcohol from which the ester is derived ; where necessary the systematic names of the two parent compounds are employed.

General Methods of Preparation. (1) The acid and alcohol are

heated together in the presence of sulphuric acid, hydrogen chloride, or zinc chloride,

$$CH_3 \cdot CH_2 \cdot COOH + CH_3 \cdot OH \rightleftarrows CH_3 \cdot CH_2 \cdot COO \cdot CH_3 + H_2O,$$
$$C_5H_{11} \cdot OH + NaNO_2 + H_2SO_4 = C_5H_{11} \cdot ONO + NaHSO_4 + H_2O.$$

(2) An alkyl halide or sulphate is treated with an organic (or inorganic) salt,

$$C_2H_5I + CH_3COO \cdot Ag = CH_3COO \cdot C_2H_5 + AgI,$$
$$(CH_3)_2SO_4 + 2CH_3 \cdot COOK = 2CH_3 \cdot COO \cdot CH_3 + K_2SO_4,$$
$$C_2H_5I + AgNO_3 = C_2H_5 \cdot NO_3 + AgI.$$

(3) An alcohol or its sodium derivative is treated with an acid chloride or anhydride,

$$C_2H_5 \cdot OH + CH_3 \cdot COCl = CH_3 \cdot COO \cdot C_2H_5 + HCl,$$
$$C_2H_5 \cdot OH + (CH_3 \cdot CO)_2O = CH_3 \cdot COO \cdot C_2H_5 + CH_3 \cdot COOH.$$

(4) An acid, treated with diazomethane (p. 469), gives a methyl ester.

(5) From aldehydes with suitable catalysts (p. 158).

(6) Many esters are manufactured from an olefine and an acid; propylene, for example, with acetic acid (and sulphuric acid) at 60° under pressure gives *iso*propyl acetate,

$$CH_3 \cdot CH{:}CH_2 + CH_3 \cdot COOH = CH_3 \cdot COO \cdot CH(CH_3)_2.$$

Physical Properties. Normal esters are usually neutral, pleasant-smelling liquids, soluble in alcohol and ether, but insoluble or nearly so in water. Dimethyl oxalate is a solid, moderately soluble in water.

Hydrogen esters (of di- or poly-basic acids) are usually non-volatile liquids, soluble in water, and have acidic properties.

Chemical Properties. (1) Esters are hydrolysed by alkalis, acids, or even by water,

$$H \cdot COO \cdot C_2H_5 + NaOH = H \cdot COONa + C_2H_5 \cdot OH,$$
$$C_2H_5 \cdot ON{:}O + KOH = C_2H_5 \cdot OH + KNO_2.$$

The rapidity with which hydrolysis takes place depends on the temperature and concentration of the solution, as well as on the nature of the ester and of the hydrolysing agent; as a rule, potassium, sodium, and barium hydroxides are the most efficient hydrolysing agents. Since, however, esters are generally insoluble, or nearly so, in water, they are not attacked very quickly by aqueous alkalis or mineral acids; for this reason it is usual to employ *alcoholic* potash (in which the esters are soluble), when the only object is to bring about hydrolysis.

(2) Although as a rule carboxylic acids, like their salts and esters, are not attacked by the common reducing agents, many esters of the

higher acids, when treated with sodium and an alcohol or catalytic hydrogen, yield alcohols corresponding with those acids,

$$CH_3 \cdot [CH_2]_4 \cdot COO \cdot C_2H_5 + 4H = CH_3 \cdot [CH_2]_4 \cdot CH_2 \cdot OH + C_2H_5 \cdot OH.$$

Acids, esters, acid chlorides and anhydrides may also be reduced with an ethereal solution of lithium aluminium hydride, $LiAlH_4$ (prepared from lithium hydride and aluminium chloride), giving intermediate products which yield primary alcohols on hydrolysis,

$$4R \cdot COOH + 3LiAlH_4 = (R \cdot CH_2 \cdot O)_4LiAl + 2LiAlO_2 + 4H_2,$$
$$2R \cdot COOMe + LiAlH_4 = (R \cdot CH_2O)_2LiAl(OMe)_2.$$

Olefinic bindings are not usually attacked by this reagent and sorbic acid (p. 345), for example, gives the corresponding unsaturated alcohol.

Esters of nitric and nitrous acids, on reduction, yield an alcohol and hydroxylamine, or ammonia,

$$C_2H_5 \cdot O \cdot NO_2 + 6H = C_2H_5 \cdot OH + NH_2 \cdot OH + H_2O,$$
$$C_2H_5 \cdot O \cdot NO + 6H = C_2H_5 \cdot OH + NH_3 + H_2O.$$

(3) Esters of carboxylic acids give amides on treatment with ammonia,

$$CH_3 \cdot COO \cdot C_2H_5 + NH_3 = CH_3 \cdot CO \cdot NH_2 + C_2H_5 \cdot OH.$$

(4) When treated with sodium, many esters undergo the *Claisen condensation* (p. 199).

Occurrence and Uses. Many esters 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, etc., and for perfumes. *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 ' pineapple oil,' and iso*amyl* iso*valerate* as ' apple oil.' Many esters, such as *butyl acetate*, *ethylene diacetate*, etc., are used as solvents, especially for lacquers, and those of very high boiling-point as vacuum-pump oils.

Nitroparaffins. Derivatives of the paraffins are formed by the displacement of a hydrogen atom by the $—NO_2$ group. They are prepared (usually mixed with an isomeric nitrite) by treating an alkyl halide with silver nitrite,

$$C_2H_5I + AgNO_2 = C_2H_5 \cdot NO_2 + AgI.$$

They are pleasant-smelling liquids which are not attacked by acids or water. On reduction they yield primary amines,

$$C_2H_5 \cdot NO_2 + 6H = C_2H_5 \cdot NH_2 + 2H_2O,$$

a reaction which proves that they are *not* esters of nitrous acid.

CHAPTER 13

SYNTHESIS OF ACIDS AND KETONES WITH THE AID OF ETHYL ACETOACETATE AND DIETHYL MALONATE

IN the development of organic chemistry few compounds have been more extensively employed for synthetical purposes than ethyl acetoacetate and diethyl malonate ; one of the more important uses to which these substances have been put is the synthesis of a great number of fatty acids and ketones, many of which could have been prepared only with great difficulty by other methods.

Ethyl acetoacetate, $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$,[1] the ethyl ester of **acetoacetic acid** (*acetylacetic acid*), is formed when ethyl acetate is warmed with sodium, and the product is decomposed with dilute acids. The final result is that two molecules of ethyl acetate combine with the loss of one molecule of alcohol (*Claisen* condensation),

$$CH_3 \cdot COOC_2H_5 + HCH_2 \cdot COOC_2H_5 = CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + C_2H_5 \cdot OH.$$[2]

Sodium (30 g.), in the form of wire (prepared with the aid of a sodium press) or slices, is added to dry ethyl acetate (300 g.) contained in a flask connected with a reflux condenser. A small proportion of the sodium should be tried at first, because if the ethyl acetate has not been sufficiently purified the reaction may become too vigorous. The whole of the metal having been added, the flask is heated on a water-bath until bright particles of sodium are no longer seen after the flask has been vigorously shaken.

The thick brownish pasty product, which consists of the sodium derivative of ethyl acetoacetate (and of sodium ethoxide), is cooled and is then treated with dilute (1 : 4) hydrochloric acid, until the solution is distinctly acid to litmus paper. An equal volume of a saturated solution of salt is now added, and the oily layer is separated from the aqueous solution, dried with anhydrous calcium chloride, and fractionated. At first some unchanged ethyl acetate passes over, but the thermometer then rises rapidly to about 160° ; the fraction boiling between 175 and 185°, which consists mainly of

[1] The symbols Me, Et, etc., are used in this and in many of the following formulae instead of CH_3, C_2H_5, for the sake of clarity.

[2] The changes which occur when ethyl acetate is warmed with sodium are complex and are discussed later (Part III).

ethyl acetoacetate, and weighs 40–50 g., is collected separately. It is advisable to redistil the crude product under reduced pressure, otherwise some decomposition occurs.

Ethyl acetoacetate is a colourless liquid, boiling at 181°, and having an agreeable, fruity odour ; it is sparingly soluble in water, but miscible with alcohol and ether. Its alcoholic solution assumes a *violet-red colour* on the addition of ferric chloride.

Although neutral to litmus, the ester dissolves in dilute aqueous solutions of the alkalis, and is reprecipitated on the addition of acids, but it is practically insoluble in solutions of the alkali carbonates. Since esters of acids, R·COOH, do not dissolve chemically in cold dilute alkalis, the solubility of ethyl acetoacetate shows that its molecule contains a hydrogen atom which is displaceable by certain metals under the given conditions.

The **sodium derivative,** $CH_3 \cdot CO \cdot CHNa \cdot COOEt$,[1] may be prepared by adding a solution of sodium ethoxide (1 mol.) to ethyl acetoacetate, and then evaporating the alcohol under reduced pressure,

$$CH_3 \cdot CO \cdot CH_2 \cdot COOEt + C_2H_5 \cdot ONa = CH_3 \cdot CO \cdot CHNa \cdot COOEt + C_2H_5 \cdot OH.$$

It is crystalline and readily soluble in water and alcohol ; it rapidly decomposes when its aqueous solution is boiled. An alcoholic *solution* of the sodium derivative is almost invariably used, instead of the solid compound, in preparing derivatives of ethyl acetoacetate by the methods described below.

When shaken with a saturated solution of copper acetate, ethyl acetoacetate forms a green crystalline *copper derivative*, $(C_6H_9O_3)_2Cu$, which is readily soluble in chloroform.

The sodium derivative of ethyl acetoacetate reacts readily with alkyl halides, with the formation of a sodium halide and a *mono-alkyl derivative* of ethyl acetoacetate. Thus, methyl iodide and the sodium derivative of ethyl acetoacetate give ethyl *methyl*acetoacetate,

$$CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + \mathbf{MeI} = CH_3 \cdot CO \cdot CH\mathbf{Me} \cdot COOC_2H_5 + NaI,$$

whereas propyl bromide, or iodide, gives ethyl *propyl*acetoacetate, $CH_3 \cdot CO \cdot CH\mathbf{Pr} \cdot COOC_2H_5$, and so on.

[1] It must be clearly understood that this formula *may not* express the constitution of the sodium derivative (p. 204) ; it is used so that the final results of the action of alkyl halides on the sodium derivative may be shown in a simple manner.

All these *mono*-alkyl substitution products of ethyl acetoacetate also form sodium derivatives, on treatment with (sodium or) sodium ethoxide, and from these sodium compounds, by the action of alkyl halides, *di-alkyl derivatives* of ethyl acetoacetate are produced,

$$CH_3 \cdot CO \cdot CNaMe \cdot COOC_2H_5 + EtBr = CH_3 \cdot CO \cdot CEtMe \cdot COOC_2H_5 + NaBr,$$

Ethyl *methylethyl*acetoacetate

$$CH_3 \cdot CO \cdot CNaPr \cdot COOC_2H_5 + PrI = CH_3 \cdot CO \cdot CPrPr \cdot COOC_2H_5 + NaI.$$

Ethyl *dipropyl*acetoacetate

It is thus possible to obtain a number of *mono-* or *di-alkyl* derivatives of ethyl acetoacetate, but even when two identical groups are to be introduced into the molecule of the ester, the operation is carried out in two stages.

The synthesis of the alkyl substitution products of ethyl acetoacetate is usually carried out as follows : The theoretical quantity of sodium (1 g. atom) is dissolved in 10–12 times its weight of anhydrous alcohol, and the solution of sodium ethoxide is cooled to about 15°. The ethyl acetoacetate, or the mono-substituted ethyl acetoacetate (1 g. mol.), mixed with a slight excess of the alkyl halide (1 g. mol.), is now gradually added to the solution of the sodium ethoxide, which is kept cool during the operation. The mixture is then carefully heated on a water-bath in a flask connected with a reflux condenser until it becomes neutral to moist litmus-paper. In order to isolate the product, the alcohol is distilled from a brine-bath, the cooled residue is mixed with water to dissolve the precipitated sodium salt, and the product is extracted with ether. The ethereal solution is washed with water and dried with anhydrous calcium chloride ; the ether is then distilled, and the residual oil purified by fractional distillation.

One of the more important changes which ethyl acetoacetate and its derivatives undergo is that which takes place when they are treated with alkalis or mineral acids. Alkalis *at ordinary temperatures* merely hydrolyse the esters with the formation of the alkali salts of the corresponding acids,

$$CH_3 \cdot CO \cdot CH_2 \cdot COOEt + KOH = CH_3 \cdot CO \cdot CH_2 \cdot COOK + Et \cdot OH.$$

When *heated* with alkalis, however, ethyl acetoacetate and its derivatives are decomposed in two ways, the course of the decomposition depending to a great extent on the nature and concentration of the alkali used.

Boiling *dilute* alcoholic potash converts these substances into *ketones*, with the separation of potassium carbonate (**ketonic hydrolysis**),

$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot OEt + HOK + KOH = CH_3\cdot CO\cdot CH_3 + K_2CO_3 + Et\cdot OH,$$

$$CH_3\cdot CO\cdot CEt_2\cdot CO\cdot OEt + HOK + KOH = CH_3\cdot CO\cdot CHEt_2 + K_2CO_3 + Et\cdot OH.$$

Ketonic hydrolysis is also brought about by boiling dilute mineral acids. When, however, *concentrated* alcoholic potash is employed, the decomposition takes place in quite a different manner and the potassium salt of a fatty acid is the principal product (**acid hydrolysis**),

$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot OEt + KOH + KOH = 2CH_3\cdot COOK + Et\cdot OH,$$

$$CH_3\cdot CO\cdot CEt_2\cdot CO\cdot OEt + KOH + KOH = CH_3\cdot COOK + Et_2CH\cdot COOK + Et\cdot OH.$$

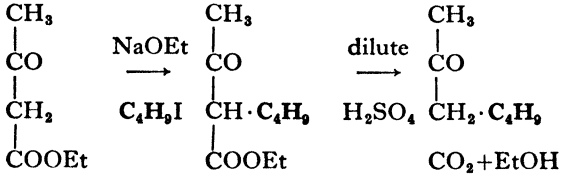
Ethyl acetoacetate, therefore, is a very important compound, as, with its aid, many fatty acids and many ketones (which contain the group, $CH_3\cdot CO\cdot CH<$) can be synthetically prepared.

Example. If an *acid* of the constitution, $(C_2H_5)(C_3H_7)CH\cdot COOH$ —namely, ethylpropylacetic acid—were required, ethyl *propyl*-acetoacetate, $CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5$, might be first prepared (p. 200); the sodium derivative of this substance would then be treated with ethyl iodide, and the ethyl *ethylpropyl*acetoacetate, $CH_3\cdot CO\cdot C(C_2H_5)(C_3H_7)\cdot COOC_2H_5$, so formed, would be heated with *strong* alcoholic potash. These stages are shown in the following scheme:

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ COOEt \end{array} \xrightarrow[PrI]{NaOEt} \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHPr \\ | \\ COOEt \end{array} \xrightarrow[EtI]{NaOEt} \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CPrEt \\ | \\ COOEt \end{array} \xrightarrow[\text{alcoholic KOH}]{\text{strong}} \begin{array}{l} CH_3 \\ | \\ COOK \\ | \\ CHPrEt \\ | \\ COOK \end{array}$$

Example. If a *ketone* of the constitution, $CH_3\cdot CO\cdot CH_2\cdot C_4H_9$ —namely, butylacetone or methylamyl ketone—were 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 ; this product would then be decomposed with boiling *dilute* alcoholic potash or dilute sulphuric acid,



The acid and the ketonic hydrolysis of ethyl acetoacetate and its derivatives always take place to some extent simultaneously, whether weak or strong alkali or acid is used. It is not easy, 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 generally produced ; nevertheless, the relative quantities of the products depend very largely on the concentration of the alkali.

Constitution of Ethyl Acetoacetate. On hydrolysis with *cold* alkalis, ethyl acetoacetate is converted into a salt of acetoacetic acid, and when this *acid* is gently warmed it is decomposed into acetone and carbon dioxide ; acetoacetic acid, therefore, seems to be represented by the formula, $CH_3 \cdot CO \cdot CH_2 \cdot COOH$, and its ester, ethyl acetoacetate, by $CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$.

That the molecule of the latter contains a ketonic group, $> CO$, seems to be proved by many facts ; it reacts with hydroxylamine and with phenylhydrazine, combines with sodium hydrogen sulphite and with hydrogen cyanide, and on reduction it is converted into *β-hydroxybutyric acid*, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot COOH$, or its ethyl ester.

On the other hand the fact that ethyl acetoacetate contains a hydrogen atom displaceable by sodium, whilst ethyl acetate does not, seems to show that the former, like ethyl alcohol, contains a *hydroxyl* group ; this view is confirmed by the knowledge that, in the vast majority of organic compounds, hydrogen *directly united with carbon* is not displaceable by metals and is supported to some extent by the behaviour of the ester towards a solution of ferric chloride. On this evidence, therefore, the structure of ethyl acetoacetate would seem to be $CH_3 \cdot C(OH):CH \cdot COOEt$.

Tautomerism. For many years after the first preparation of ethyl acetoacetate, it was not possible to decide between the alternative formulae just given, but eventually it was proved that ethyl acetoacetate is a mixture of two *different* substances, which are

easily converted one into the other. At ordinary temperatures it consists almost entirely of a compound of the constitution, $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$, but contains a small proportion of the isomeric hydroxy-compound, $CH_3 \cdot C(OH):CH \cdot COOEt$. These isomerides are in equilibrium with one another, and are readily converted one into the other in the presence of various solvents or reagents, until a new condition of equilibrium is established. On the addition of sodium ethoxide, for example, the *hydroxy*-compound is converted into its sodium derivative, $CH_3 \cdot C(ONa):CH \cdot COOEt$,[1] the equilibrium is disturbed, and the ketonic form passes into the hydroxy-isomeride, so that ultimately the whole of the ester may be converted into a sodium derivative of the above constitution. On the addition of an acid to this sodium derivative, the regenerated hydroxy- passes into the keto-compound until equilibrium is attained.

Many substances which, like ethyl acetoacetate, contain the group, $—CO \cdot CH_2 \cdot CO—$, or $—CO \cdot CHR \cdot CO—$, behave in a similar manner and readily pass into *isomeric* hydroxy-compounds, $—C(OH):CH \cdot CO—$ or $—C(OH):CR \cdot CO—$, by a reversible reaction; such isomerides differ from isomeric compounds generally in the readiness with which they are changed one into the other by heat or by the action of various chemical agents, and are termed *tautomeric* forms, *tautomerides*, or *dynamic isomerides*. The hydroxy-form is known as the *enolic* modification or *enol*; the isomeride is named the *keto* form, and the equilibrium mixture is an *allelotropic mixture*. When one of the tautomeric forms is more stable than the other under ordinary conditions, the latter is often called the *labile* modification; but, as a rule, it is difficult to say which is the more stable, as it all depends on the conditions under which the tautomerides are placed. The enolic form, as a rule, gives a violet-red colouration with ferric chloride, but the keto form does not (unless it is converted into the enol by the reagent).

Many attempts have been made to estimate the proportions of the two forms of ethyl acetoacetate by taking advantage of the differences in chemical properties of the tautomerides. Since, for example, the enol is an olefine, and combines directly with bromine, it seemed possible that titration with bromine might afford a means of estimation. Further, since the enol (only) gives a copper

[1] A suggested explanation of how such a sodium derivative gives products which have the structure, $CH_3 \cdot CO \cdot CHR \cdot COOEt$, with alkyl halides, is given later (Part III).

derivative (p. 200), this property might be employed for separating and estimating the tautomerides. All such attempts, however, gave only approximate results because of the rapidity with which the one form changes into the other in the presence of various reagents.

This rapid transformation may be demonstrated as follows: About 1 c.c. of ethyl acetoacetate is stirred with about 500 c.c. of water and a few drops of ferric chloride solution are added: the violet-red colour, characteristic of the enol, is produced, but disappears on the addition of enough bromine water, owing to the combination of the unsaturated enol with the halogen. After a few seconds, however, more enol has been produced from the keto form and the colour reappears. The experiment may be continued until all the ester has combined with bromine.

With the aid of physical methods, in the absence of all catalysts, it is possible to isolate the tautomeric forms. When carefully purified ethyl acetoacetate is diluted with alcohol, ether, or light petroleum and the solution is cooled to $-78°$, the *pure keto* form is obtained in crystals, melting at $-39°$, the enol remaining in the mother-liquor (Knorr).

When the ester is fractionated from, and collected in, ordinary glass vessels, the fractions are practically identical with the original sample, because although the enol is the more volatile it is rapidly converted into the equilibrium mixture by traces of alkali from the glass receiver. When, however, the ester is distilled from a hard glass vessel (in the presence of a trace of phthalic acid) under a pressure of 2 mm. and the distillate is collected in a *silica* receiver, a liquid containing about 88% of enol is obtained; this product, redistilled in an apparatus made entirely of silica (*aseptic distillation*) gives the *pure enol*. During the first operation in the glass vessel, the less volatile keto form is continuously changing into the equilibrium mixture in contact with the glass of the neck of the distillation flask, but when the distillation is conducted in an apparatus made entirely of silica, the enol volatilises first, and the later fractions consist of the pure keto form. The proportion of enol in the equilibrium mixture at ordinary temperatures is about 8%, as established by the results of physical measurements (refractive index, etc.) on the pure forms and on the mixture.

When, as in this case, it is known that the two tautomerides are capable of independent existence, they are further distinguished as *desmotropic* forms. A substance which behaves as if it were tautomeric, but which is actually known in one form only, is said to show *pseudomerism*; the form which has not been isolated, but of which derivatives are obtained, is the *pseudomeric* form or *pseudomer*.

Diethyl malonate, *ethyl malonate*, $CH_2(COOC_2H_5)_2$, does not belong to the same class of substances as ethyl acetoacetate, but it may be conveniently considered in this chapter on account of its employment in the synthesis of acids.

When potassium chloroacetate and potassium cyanide are heated together in aqueous solution, potassium cyanoacetate is produced,

$$CH_2Cl \cdot COOK + KCN = CH_2(CN) \cdot COOK + KCl,$$

and this salt, on hydrolysis with hydrochloric acid, yields *malonic acid* (p. 276),

$$CH_2(CN) \cdot COOK + 2HCl + 2H_2O = CH_2(COOH)_2 + KCl + NH_4Cl;$$

when, however, after evaporation, the potassium cyanoacetate is added to alcohol and the mixture is saturated with hydrogen chloride, or heated with sulphuric acid, the malonic acid which is formed is esterified and diethyl malonate is produced,

$$CH_2(CN) \cdot COOK + 2HCl + 2C_2H_5 \cdot OH = CH_2(COOC_2H_5)_2 + KCl + NH_4Cl.$$

Chloroacetic acid (50 g.) is dissolved in water (100 c.c.) and neutralised with potassium carbonate (38 g.); potassium cyanide (35 g.) is added, and the mixture is slowly heated in a large porcelain basin until a vigorous reaction commences.[1] 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 cooled solid cake of potassium chloride and cyanoacetate is powdered, transferred to a flask, and 25 c.c. of anhydrous alcohol are added. A cold mixture of 100 c.c. of alcohol and 75 c.c. of concentrated sulphuric acid is now run in slowly, while the flask is constantly shaken, and the solution is then heated on a water-bath, with reflux condenser, during two hours. When cold, the solution is poured into twice or thrice its volume of ice-cold water; the product is then extracted with ether, and the ethereal solution is washed with water and dried with calcium chloride. The crude oil, which remains after the ether has been distilled, is purified by fractional distillation; the portion boiling at 195–200° consists of practically pure diethyl malonate.

Diethyl malonate boils at 199° and has a pleasant fruity odour; like ethyl acetoacetate, it gives a sodium derivative [2] with an alcoholic solution of sodium ethoxide,

$$CH_2(COOC_2H_5)_2 + NaOEt = CHNa(COOC_2H_5)_2 + Et \cdot OH.$$

[1] These operations are carried out in a fume chamber.
[2] Compare footnote, p. 200.

Unlike ethyl acetoacetate, it does not dissolve in aqueous alkalis, because its alkali derivative is decomposed by water, giving the sparingly soluble ester ; it does not give a colouration with ferric chloride.

The sodium derivative of diethyl malonate is a solid, soluble in alcohol, but is seldom isolated ; its alcoholic solution reacts readily with alkyl halides, yielding alkyl derivatives of diethyl malonate,

$$CHNa(COOC_2H_5)_2+\mathbf{Pr}I = \underset{\text{Diethyl } \textit{propyl}\text{malonate}}{CH\mathbf{Pr}(COOC_2H_5)_2}+NaI ;$$

these mono-substitution derivatives, like those of ethyl acetoacetate, give sodium compounds, which, by further treatment with alkyl halides, yield di-substitution derivatives of diethyl malonate,

$$CH\mathbf{Pr}(COOC_2H_5)_2+NaOEt = CNa\mathbf{Pr}(COOC_2H_5)_2+Et\cdot OH,$$
$$CNa\mathbf{Pr}(COOC_2H_5)_2+\mathbf{Et}I = \underset{\text{Diethyl } \textit{ethylpropyl}\text{malonate}}{C\mathbf{PrEt}(COOC_2H_5)_2}+NaI.$$

In this way many derivatives may be obtained, and the syntheses are carried out exactly as described in the case of the substitution products of ethyl acetoacetate (p. 201).

Diethyl malonate and its derivatives are hydrolysed by boiling alcoholic potash with the formation of the potassium salts of the corresponding acids,

$$CH\mathbf{Et}(COOC_2H_5)_2+2KOH = \underset{\text{Potassium ethylmalonate}}{CH\mathbf{Et}(COOK)_2}+2C_2H_5\cdot OH,$$
$$C\mathbf{EtPr}(COOC_2H_5)_2+2KOH = \underset{\text{Potassium ethylpropylmalonate}}{C\mathbf{EtPr}(COOK)_2}+2C_2H_5\cdot OH.$$

Malonic acid and the dicarboxylic acids derived from it are rapidly and quantitatively decomposed at about 200°, with the evolution of carbon dioxide and formation of monocarboxylic acids. This behaviour is shown by *all* acids which contain two carboxyl groups directly combined with the *same* carbon atom,

$$CH_2(COOH)_2 = CH_3\cdot COOH+CO_2,$$
$$\underset{\text{Ethylpropylmalonic acid}}{C\mathbf{EtPr}(COOH)_2} = \underset{\text{Ethylpropylacetic acid}}{C\mathbf{EtPr}H\cdot COOH}+CO_2.$$

Diethyl malonate, therefore, is of great importance in the synthesis of acids, and, indeed, is more used for this purpose than ethyl acetoacetate, because, in the case of the latter, ketones are always obtained as by-products.

Example. Normal valeric acid, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$, is to be prepared synthetically. For this purpose, the sodium

derivative of diethyl malonate is heated with propyl iodide, and the resulting diethyl propylmalonate, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(COOC_2H_5)_2$, is hydrolysed with boiling alcoholic potash. The propylmalonic acid obtained from the potassium salt is heated at about 200°, or distilled, whereon it decomposes into normal valeric acid and carbon dioxide,

$$\begin{array}{l} \mathrm{COOEt} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{COOEt} \end{array} \xrightarrow[\mathrm{C_3H_7I}]{\mathrm{NaOEt}} \begin{array}{l} \mathrm{COOEt} \\ | \\ \mathrm{CH \cdot C_3H_7} \\ | \\ \mathrm{COOEt} \end{array} \longrightarrow \begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CH \cdot C_3H_7} \\ | \\ \mathrm{COOH} \end{array} \longrightarrow \begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CH_2 \cdot C_3H_7} \\ \\ \mathrm{CO_2} \end{array}$$

The examples given above show that ketones, $CH_3 \cdot CO \cdot CHRR'$, may be synthesised from ethyl acetoacetate and carboxylic acids, $RR'CH \cdot COOH$, from this ester or from diethyl malonate.

When a ketone or acid of a particular structure is required it is easy to decide which groups, R and R', in the form of alkyl halides (usually bromides or iodides) must be used for this purpose ; it is also obvious that when R or R' is hydrogen, a mono-substitution product only of the ester has to be prepared.

In the synthesis of a di-substitution derivative of either ester, when R and R' are different radicals, it is generally better to introduce first the group of higher molecular weight. This is because in the preparation of a mono-, some of the di-derivative is always formed and a part of the original ester may remain unchanged ; the greater the molecular weight of the substituent the greater the differences between the boiling-points of the components of the mixture.

All such syntheses afford good yields only when the halides of *primary* alcohols are employed.

SUMMARY AND EXTENSION

Ethyl acetoacetate is prepared by heating ethyl acetate with sodium and decomposing the resulting sodium derivative with dilute acids. The enolic product, *ethyl β-hydroxycrotonate* or *ethyl 2-hydroxy-1-propene-1-carboxylate*, $CH_3 \cdot C(OH):CH \cdot COOEt$, then passes into the tautomeride, until equilibrium is attained, and the mixture, which usually contains about 92% of the keto form, $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$, is called ethyl acetoacetate ; towards most reagents this mixture behaves as a homogeneous compound.

Acetoacetic acid, a β-ketonic acid, is obtained (mixed no doubt with its tautomeride) by hydrolysing the ester with *cold* alkali, acidi-

fying the solution, and extracting the acid with ether. This, and other *β-ketonic* acids, however, are very unstable, and decompose, in many cases at ordinary temperatures, but always when heated, yielding carbon dioxide and a ketone,

$$CH_3 \cdot CO \cdot CH_2 \cdot COOH = CH_3 \cdot CO \cdot CH_3 + CO_2,$$
$$CH_3 \cdot CO \cdot CEt_2 \cdot COOH = CH_3 \cdot CO \cdot CHEt_2 + CO_2.$$

The sodium derivative of the ester, *ethyl sodioacetoacetate*, reacts with alkyl halides yielding mono-alkyl substitution products. The latter behave like ethyl acetoacetate, and their sodium derivatives also react with alkyl halides. In this way mono- and di-substituted ethyl acetoacetates of the formula, $CH_3 \cdot CO \cdot C(RR') \cdot COOEt$, may be prepared (R and R′ = H or alkyl). On hydrolysis ethyl acetoacetate, and all its alkyl derivatives, may break down in two ways :

(*a*) With boiling dilute alcoholic potash or dilute mineral acids, *ketonic* hydrolysis occurs and a ketone is produced,

$$CH_3 \cdot CO \cdot CRR' \cdot COOEt \longrightarrow CH_3 \cdot CO \cdot CHRR'.$$

(*b*) With boiling concentrated alcoholic potash, *acid* hydrolysis takes place and an acid is formed,

$$CH_3 \cdot CO \cdot CRR' \cdot COOEt \longrightarrow CHRR' \cdot COOH.$$

The sodium derivatives of these β-ketonic esters react readily, not only with alkyl halogen esters, but also with various other types of **neutral** halogen compounds, such as the following :

(1) Aromatic halides, such as benzyl chloride, which contain a halogen in the *side chain*,

$$CH_3 \cdot CO \cdot CHNa \cdot COOEt + C_6H_5 \cdot CH_2Cl = CH_3 \cdot CO \cdot CH(CH_2 \cdot C_6H_5) \cdot COOEt + NaCl.$$

(2) Dihalides such as ethylene dibromide, etc.,

$$2CH_3 \cdot CO \cdot CHNa \cdot COOEt + \begin{vmatrix} CH_2Br \\ CH_2Br \end{vmatrix} = \begin{vmatrix} CH_2 \cdot CH(CO \cdot CH_3) \cdot COOEt \\ CH_2 \cdot CH(CO \cdot CH_3) \cdot COOEt. \end{vmatrix} + 2NaBr.$$

(3) Monohalogen derivatives of esters such as ethyl chloroacetate,

$$CH_3 \cdot CO \cdot CHNa \cdot COOEt + CH_2Cl \cdot COOEt = CH_3 \cdot CO \cdot CH(CH_2 \cdot COOEt) \cdot COOEt + NaCl.$$

(4) Monohalogen derivatives of ketones, such as bromoacetone,

$$CH_3 \cdot CO \cdot CHNa \cdot COOEt + CH_3 \cdot CO \cdot CH_2Br = CH_3 \cdot CO \cdot CH(CH_2 \cdot CO \cdot CH_3) \cdot COOEt + NaBr.$$

(5) Acid chlorides, such as acetyl chloride,

$$CH_3 \cdot CO \cdot CHNa \cdot COOEt + CH_3 \cdot COCl = CH_3 \cdot CO \cdot CH(CO \cdot CH_3) \cdot COOEt + NaCl.$$

All these reactions, (1)–(5), may also be carried out with mono-alkyl substitution products of ethyl acetoacetate and all the compounds thus obtained undergo hydrolysis in exactly the same way as the simple alkyl derivatives, so that a great many monocarboxylic acids, ketones, dicarboxylic acids, diketones, etc., all of *known constitution*, can be synthesised.

Ethyl acetoacetate and its mono-substituted derivatives are similar in chemical behaviour, and give a characteristic violet-red colouration with ferric chloride. The *di*-substituted ethyl acetoacetates, however, do *not* contain a hydrogen atom displaceable by metals, and do not give a colouration with ferric chloride.

These facts are in accordance with the view that it is only the enolic form of the ester which shows these reactions.

Pyruvic acid, $CH_3 \cdot CO \cdot COOH$ (*acetylformic acid, ketopropionic acid*), is prepared by heating tartaric acid (p. 282) with potassium hydrogen sulphate,

$$\begin{matrix} CH(OH) \cdot COOH \\ | \\ CH(OH) \cdot COOH \end{matrix} = CH_3 \cdot CO \cdot COOH + CO_2 + H_2O.$$

It boils, with decomposition, at 165–170°, and is miscible with water. It reacts with hydroxylamine, and gives with phenylhydrazine in aqueous solution a very sparingly soluble phenylhydrazone, $CH_3 \cdot C(:N \cdot NHC_6H_5) \cdot COOH$. When treated with sodium amalgam and water, pyruvic acid is reduced to lactic acid (p. 267),

$$CH_3 \cdot CO \cdot COOH + 2H = CH_3 \cdot CH(OH) \cdot COOH.$$

Laevulic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ (*β-acetylpropionic acid, γ-ketovaleric acid*), is produced when fructose, glucose, sucrose, starch, and various other carbohydrates containing 6, or a multiple of 6, carbon atoms are boiled with dilute hydrochloric acid ; it may be synthesised from ethyl acetoacetate and ethyl chloroacetate (p. 209).

It melts at 33° and boils at 245° ; it is very soluble in water, reacts readily with hydroxylamine and phenylhydrazine, and when reduced with sodium amalgam and water it yields the sodium salt of *γ-hydroxyvaleric acid*, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COOH$. Laevulic acid is isomeric with methylacetoacetic acid or α-acetylpropionic acid, $CH_3 \cdot CO \cdot CH(CH_3) \cdot COOH$; its name is derived from that of laevulose (fructose), the sugar from which it was first obtained.

α-Ketonic acids, such as pyruvic acid, and γ-ketonic acids, such as laevulic acid, show a behaviour very different from that of β-ketonic acids, such as acetoacetic acid ; they are *not* decomposed when they are heated moderately strongly, and their esters do *not* contain hydrogen displaceable by metals.

Diethyl malonate, $CH_2(COOC_2H_5)_2$, is prepared by heating cyano-

acetic acid (below) with alcohol and sulphuric acid. Its molecule contains a hydrogen atom displaceable by sodium, and the sodium derivative so formed reacts in the same way with alkyl halides as does ethyl sodioacetoacetate. The mono-substituted diethyl malonates also give sodium compounds from which di-alkyl derivatives may be obtained. The reactions (1), (2), (3), (4), and (5) given for ethyl acetoacetate (p. 209) are also shown by the sodium derivative of diethyl malonate or mono-substituted diethyl malonates. In this way substances of the constitution, $RR'C(COOEt)_2$, may be prepared, where R and R′ represent hydrogen or any of the groups indicated above (p. 209). These esters can be hydrolysed to the corresponding acids, $RR'C(COOH)_2$, which when heated give carbon dioxide and substituted acetic acids, $RR'CH \cdot COOH$. Diethyl malonate, therefore, has been extensively employed for the synthesis of many acids, and here again the structures of all the products are established by the methods of their formation.

Diethyl sodiomalonate reacts with iodine in alcoholic solution giving *tetraethyl ethanetetracarboxylate*, from which succinic acid may be obtained,

$$2CHNa(COOEt)_2 + I_2 = \begin{matrix} CH(COOEt)_2 \\ | \\ CH(COOEt)_2 \end{matrix} + 2NaI.$$

Ethyl sodioacetoacetate, in a similar manner, gives *diethyl diacetylsuccinate*, from which the diketone, *acetonylacetone* is produced by ketonic hydrolysis,

$$2CH_3 \cdot CO \cdot CHNa \cdot COOEt + I_2 = \begin{matrix} CH_3 \cdot CO \cdot CH \cdot COOEt \\ | \\ CH_3 \cdot CO \cdot CH \cdot COOEt \end{matrix} + 2NaI.$$

It is possible that the sodium derivatives of diethyl malonate and its mono-substitution products have the *enolic* constitutions,

$$EtOOC \cdot CH{:}C(ONa) \cdot OEt \quad \text{and} \quad EtOOC \cdot CR{:}C(ONa) \cdot OEt$$

respectively, but the esters themselves give no colouration with ferric chloride, and probably contain little, if any, enol.

Cyanoacetic acid, $CN \cdot CH_2 \cdot COOH$, is obtained in the form of its potassium salt in the preparation of diethyl malonate, and may be isolated by decomposing the salt with ice-cold concentrated hydrochloric acid, filtering from potassium chloride, and evaporating the filtrate under reduced pressure. It melts at 65° and decomposes at about 165°, giving methyl cyanide and carbon dioxide. **Ethyl cyanoacetate,** $CN \cdot CH_2 \cdot COOEt$ (b.p. 207°), like diethyl malonate, contains a hydrogen atom displaceable by sodium; the sodium derivative, which gives products, $CN \cdot CHR \cdot COOEt$, is often used for syntheses.

Diethyl oxaloacetate, $COOEt \cdot CH_2 \cdot CO \cdot COOEt$, or *ethyl oxaloacetate*, is prepared by adding ethyl acetate to diethyl oxalate in the presence of sodium ethoxide ; the *sodium derivative*, which is thus formed, is decomposed with dilute sulphuric acid, and the ester is fractionally distilled under reduced pressure (b.p. 131–132°, 24 mm.). It gives an intense red colouration with an alcoholic solution of ferric chloride, and resembles ethyl acetoacetate in undergoing both ketonic and acid hydrolysis ; thus, when it is heated with 10% sulphuric acid it gives pyruvic acid (p. 210), alcohol, and carbon dioxide, whereas with boiling alcoholic potash it yields alcohol and the potassium salts of acetic and oxalic acids.

Acetonedicarboxylic acid, $COOH \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH$, or *β-ketoglutaric acid*, is prepared by warming citric acid (p. 286) with anhydro-sulphuric acid,

$$\begin{array}{l} CH_2 \cdot COOH \\ \dot{C}(OH) \cdot COOH \\ \dot{C}H_2 \cdot COOH \end{array} = \begin{array}{l} CH_2 \cdot COOH \\ \dot{C}O \\ \dot{C}H_2 \cdot COOH \end{array} + CO + H_2O.$$

It melts at about 135°, decomposing into acetone and carbon dioxide,

$$COOH \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH = CH_3 \cdot CO \cdot CH_3 + 2CO_2.$$

Its ethyl ester, **diethyl acetonedicarboxylate,** forms a sodium derivative which, like that of ethyl acetoacetate, has been much used in syntheses.

CHAPTER 14

ALKYL COMPOUNDS OF NITROGEN

Amines

MANY of the compounds described in the preceding pages may be conveniently considered as derivatives of simple inorganic compounds; the alcohols and ethers, for example, as derivatives of water, the mercaptans and sulphides as derivatives of hydrogen sulphide,

$H \cdot O \cdot H$	$C_2H_5 \cdot OH$	$C_2H_5 \cdot O \cdot C_2H_5$
$H \cdot S \cdot H$	$C_2H_5 \cdot SH$	$C_2H_5 \cdot S \cdot C_2H_5$

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 basic substances, termed **amines,** may be obtained, and these compounds are distinguished 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 amines form a homologous series, $C_nH_{2n+3}N$, but it is more convenient to group them into three classes as above.

In addition to the amines, alkyl derivatives of ammonium hydroxide, such as *tetra-ethylammonium hydroxide*, $N(C_2H_5)_4 \cdot OH$, are known. The methods of formation and general characters of the amines, and of the tetra-alkylammonium derivatives, may be illustrated by a description of the ethyl compounds.

Ethylamine, $C_2H_5 \cdot NH_2$, was first obtained by heating ethyl carbimide (ethyl *iso*cyanate, p. 363) with potash (Wurtz),

$$C_2H_5 \cdot N{:}CO + 2KOH = C_2H_5 \cdot NH_2 + K_2CO_3.$$

It is produced (together with *di-* and *tri*-ethylamine and a tetra-ethylammonium derivative) 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 (or with the ammonia) forming a salt,

$$C_2H_5I + NH_3 = C_2H_5 \cdot NH_2,HI \text{ or } [C_2H_5 \cdot NH_3]I.$$

It may also be formed by cautiously mixing propionamide (1 mol.) with bromine (1 mol.), and then slowly adding a 10% solution of potassium hydroxide (1 mol.) until the colour of the bromine disappears; the solution of the *propionbromoamide* 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 slowly added to a concentrated aqueous solution of potassium hydroxide (3 mol.), whereon the bromoamide is converted into ethylamine (Hofmann) by a sequence of reactions,

$$C_2H_5 \cdot CO \cdot NHBr + 3KOH = C_2H_5 \cdot NH_2 + KBr + K_2CO_3 + H_2O.$$

The base is expelled when the solution is boiled, and the distillate, evaporated with hydrochloric acid, gives *ethylamine hydrochloride*.

Methylamine hydrochloride is obtained in a similar manner from acetamide, but is best prepared from formalin (p. 219).

Ethylamine is prepared by treating ethyl bromide with alcoholic ammonia.

Alcohol (90%, 500 c.c.) is saturated with ammonia, and ethyl bromide (120 g.) is added in eight portions at intervals of two days. At the end of about eighteen days the solution is filtered, concentrated until the remainder of the ammonium bromide has separated, again filtered, and heated at 130° until free from alcohol. The diethylamine hydrobromide and any triethylamine salt in the residue are then extracted with cold chloroform, leaving *ethylamine hydrobromide*, from which alkali liberates the base.

Ethylamine is a mobile, inflammable liquid of sp. gr. 0·706 at 4°, and boils at 16·6°; it is miscible with water, 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 when warmed, 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 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; it is very hygroscopic, and readily absorbs carbon dioxide from the air, forming with it a salt.[1]

An aqueous solution of ethylamine, or of any other amine of sufficiently low boiling-point, unless very dilute, may be readily distinguished from that of ammonia by heating it and applying a light to the escaping vapour; amines ignite at the mouth of the tube, whereas ammonia does not.

Ethylamine reacts vigorously with acid chlorides and anhydrides giving substituted amides,

$$C_2H_5\cdot NH_2+CH_3\cdot COCl = C_2H_5\cdot NH\cdot CO\cdot CH_3+HCl,$$
$$C_2H_5\cdot NH_2+(CH_3\cdot CO)_2O = C_2H_5\cdot NH\cdot CO\cdot CH_3+CH_3\cdot COOH,$$

and is therefore easily *acetylated*.

Although, speaking generally, ethylamine is very stable, it is rapidly converted into ethyl alcohol on treatment with nitrous acid [2] 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 analogous to that which occurs when ammonia and nitrous acid (ammonium nitrite) are heated together,

$$NH_4NO_2 \text{ or } NH_3+HO\cdot NO = 2H\cdot OH+N_2.$$

A solution of ethylamine hydrochloride is mixed with hydrochloric acid, and a solution of sodium nitrite is added slowly by means of a thistle funnel which passes to the bottom of the acid solution; a rapid effervescence sets in, and the gas which is evolved usually contains very little, if any, oxides of nitrogen. When the

[1] Probably a mixture of carbonate and carbamate (p. 223),

$$CO<^{NH\cdot C_2H_5}_{OH,\ C_2H_5\cdot NH_2}.$$

[2] Formed in the acid solution from a nitrite; *this is the usual procedure.* With an excess of nitrous acid some of the alcohol may be converted into the nitrite.

solution is subsequently distilled, the presence of ethyl alcohol in the distillate may be proved by the usual methods.

Ethylamine is also quickly changed when it is warmed with chloroform and alcoholic potash, giving *ethyl carbylamine* (p. 361),

$$C_2H_5 \cdot NH_2 + CHCl_3 + 3KOH = C_2H_5 \cdot NC + 3KCl + 3H_2O.$$

The intensely disagreeable smell of the product [1] is at once recognisable, and affords a sure indication of the presence of a primary amine (Hofmann's *carbylamine reaction*). The two reactions just mentioned are characteristic of all *primary amines*, and are of great practical importance; the first is employed for the conversion of the primary amines into alcohols, the second for their detection.

Ethylamine is a mono-acidic base, and, like ammonia, forms salts by direct combination; these salts are all soluble in water, and some of them, like those of ammonia, sublime readily, even at ordinary temperatures; they usually differ from ammonium salts in being soluble in alcohol, a property which is frequently made use of for separating them from mineral salts.

Ethylamine hydrochloride, $[C_2H_5 \cdot NH_3]Cl$, or $C_2H_5 \cdot NH_2,HCl$, as often written, crystallises in large plates, and is deliquescent, as is also the *normal sulphate*, $2C_2H_5 \cdot NH_2,H_2SO_4$. The halogen salts, like those of ammonia, form complex salts with many of the metallic halides; of these compounds the *platinichloride* and the *aurichloride* which correspond with the complex ammonium salts of similar composition are important,

Ethylamine platinichloride	$[C_2H_5 \cdot NH_3]_2PtCl_6$ or $(C_2H_5 \cdot NH_2)_2,H_2PtCl_6$
Ammonium platinichloride	$[NH_4]_2PtCl_6$ or $(NH_3)_2,H_2PtCl_6$
Ethylamine aurichloride	$[C_2H_5 \cdot NH_3]AuCl_4$ or $C_2H_5 \cdot NH_2,HAuCl_4$
Ammonium aurichloride	$[NH_4]AuCl_4$ or $NH_3,HAuCl_4$

Such platinichlorides and aurichlorides are usually yellow, orange, or red, and are generally much more sparingly soluble in water than the hydrochlorides; for the latter reason they are often used for detecting and isolating the amines; on ignition they give a residue of pure metal (p. 29).

Diethylamine, $(C_2H_5)_2NH$, is formed when ethyl iodide or bromide is heated with alcoholic ammonia, as described in the case

[1] Compare footnote, p. 77.

of ethylamine ; the primary base, which is first produced, combines with the alkyl halide to form a salt,

$$C_2H_5 \cdot NH_2 + C_2H_5I = (C_2H_5)_2NH,HI \text{ or } [(C_2H_5)_2NH_2]I,$$

which is partly decomposed by the excess of ammonia.

Diethylamine is a very mobile, inflammable liquid, boiling at 56° ; it is a strong base, like ethylamine, which it resembles very closely in smell, solubility, etc., and also in forming simple and complex salts. Like ethylamine it reacts with acid chlorides and anhydrides giving (di-)substituted amides,

$$(C_2H_5)NH + (CH_3 \cdot CO)_2O = (C_2H_5)_2N \cdot CO \cdot CH_3 + CH_3 \cdot COOH.$$

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 *diethylnitrosoamine*,

$$(C_2H_5)_2NH + HO \cdot NO = (C_2H_5)_2N \cdot NO + H_2O.$$

A *cold* concentrated aqueous solution of sodium nitrite is added gradually to a *cold* concentrated solution of diethylamine hydrochloride in hydrochloric acid ; the diethylnitrosoamine separates as an oil, because it is not readily soluble in water and does not form salts with acids.

All *secondary amines* behave in this way ; that is to say, on treatment with nitrous acid, they are converted into *nitrosoamines* by the substitution of the univalent nitroso-group, —NO, for the atom of hydrogen which is directly united with nitrogen.

When a nitrosoamine is mixed with phenol (p. 483) and concentrated sulphuric acid, it gives a dark-green solution which, when diluted with water, becomes red, and with an excess of alkali assumes an intense blue or green colour ; this reaction (Liebermann's *nitroso-reaction*) affords a means of detecting, not only a nitrosoamine, but also a secondary amine, as the latter is convertible into the former. The nitrosoamine (usually an oil) must be washed with water until free from nitrous acid before applying Liebermann's reaction, since nitrous acid and nitrites give the same colour changes as a nitrosoamine.

Diethylamine hydrochloride, $[(C_2H_5)_2NH_2]Cl$ or $(C_2H_5)_2NH$, HCl, is colourless, and readily soluble in water ; the *platinichloride*, $\{(C_2H_5)_2NH\}_2$, H_2PtCl_6, and *aurichloride*, $(C_2H_5)_2NH$, $HAuCl_4$, are orange, and less readily soluble.

Triethylamine, $(C_2H_5)_3N$, formed from diethylamine and ethyl bromide, is also produced when ethyl iodide or bromide is heated with alcoholic ammonia,

$$(C_2H_5)NH+C_2H_5I = (C_2H_5)_3N,HI \text{ or } [(C_2H_5)_3NH]I;$$

it boils at 89° and is more sparingly soluble in water than the primary and secondary compounds. It does *not* give the carbylamine reaction, and is *not* acted on by nitrous acid at ordinary temperatures (except to form a salt); nor by acid chlorides or anhydrides, so that it is readily distinguished from a primary or secondary amine; other *tertiary amines* resemble triethylamine in these respects. The salts of triethylamine correspond with those of the other bases.

The salts of primary, secondary, and tertiary amines are all decomposed by alkalis and by alkali carbonates; when an excess of the alkali is used, and heat is applied, the amine volatilises and, as in the case of ammonium salts, the (reversible) reaction proceeds to completion.

Quaternary Ammonium Derivatives

Triethylamine, and other tertiary amines, combine directly with one molecule of an alkyl halide, yielding salts analogous to those of ammonium,

$$N(C_2H_5)_3+C_2H_5I = N(C_2H_5)_4I,$$
$$NH_3+HI = NH_4I.$$

The bases corresponding with these salts are *non-volatile*, and therefore remain in solution when the salts are heated with aqueous alkalis; when, however, aqueous solutions of the salts are shaken with freshly precipitated silver oxide, silver halides are produced, and hydroxides, analogues of ammonium hydroxide, may be isolated by evaporating the filtered solutions,

$$(C_2H_5)_4NI+Ag\cdot OH = (C_2H_5)_4N\cdot OH+AgI.$$

The hydroxides obtained in this way are termed *quaternary ammonium bases*, or *tetra-alkylammonium hydroxides*; although they are similar in type to ammonium hydroxide, they differ from the latter in several important respects, and resemble rather the hydroxides of sodium and potassium.

Tetraethylammonium hydroxide, $(C_2H_5)_4N\cdot OH$, or $[(C_2H_5)_4N]OH$, for example, is crystalline and deliquescent; it

has a strong alkaline reaction, absorbs carbon dioxide from the air, and liberates ammonia from ammonium salts; when strongly heated it is resolved into triethylamine and ethyl alcohol (or ethylene and water),

$$(C_2H_5)_4N \cdot OH = (C_2H_5)_3N + C_2H_4 + H_2O.$$

The salts of tetraethylammonium hydroxide (such as the iodide, p. 218) may of course be obtained by treating the hydroxide with acids; they are crystalline and readily soluble in water.

The tetra-alkylammonium halogen salts undergo decomposition or dissociation when they are heated, yielding a tertiary amine and an alkyl halide, just as ammonium chloride dissociates into ammonia and hydrogen chloride,

$$N(C_2H_5)_4Cl = N(C_2H_5)_3 + C_2H_5Cl.$$

Usually the halogen ester, being more volatile than the tertiary amine, passes off before recombination takes place (see below).

In a similar manner the halogen salts of *some* tertiary amines may be converted into secondary, and those of secondary into primary, amines, with the elimination of an alkyl halide.

The three ethylamines and the tetraethylammonium compound may be taken as typical of the several classes of alkyl derivatives of ammonia; the corresponding methyl bases, and those of the higher alkyl radicals, may be prepared by methods similar to those described in the case of the ethylamine compounds, and have chemical properties so closely resembling those of the latter that a description of individual compounds is unnecessary.

Methylamine, $CH_3 \cdot NH_2$, *dimethylamine*, $(CH_3)_2NH$, and *trimethylamine*, $(CH_3)_3N$, occur in herring brine in a combined state, the last named especially in relatively large proportions; they boil at $-7°$, $7°$, and $3{\cdot}5°$ respectively. Dimethylamine and trimethylamine may be prepared on the large scale by the distillation of the waste products obtained in refining beet-sugar, and are employed for various technical purposes; trimethylamine hydrochloride may be used in the preparation of methyl chloride (p. 71, and above).

Methylamine is best prepared in the laboratory by slowly heating a solution of ammonium chloride in 35–40% formalin,

$$2H \cdot CHO + NH_4Cl = CH_3 \cdot NH_2,HCl + H \cdot COOH.$$

Dimethylamine (and trimethylamine) may be prepared in a similar manner by using a larger proportion of formalin, at a higher temperature,

$$4H \cdot CHO + NH_4Cl = (CH_3)_2NH,HCl + 2H \cdot COOH.$$

Preparation of Amines. Two important general methods which are used for the preparation of amines have already been described —namely, those which were discovered by Hofmann (p. 214). The first of these methods gives primary, secondary, and tertiary amines, as well as the tetra-alkylammonium derivatives, the composition of the product depending mainly on the proportion of the reactants and the strengths of the bases concerned.

The first additive product, $R \cdot NH_3X$, reacts with ammonia to equilibrium,

$$R \cdot NH_3X + NH_3 \rightleftarrows R \cdot NH_2 + NH_4X,$$

and the liberated primary base then gives a salt of the secondary amine, R_2NH_2X ; a new equilibrium is then reached between this salt, primary base, and ammonia, giving some free secondary base, which in its turn may afford tertiary amine, and finally a quaternary salt, by a repetition of such reactions. All these changes depend on the variable valency of nitrogen.

In order to isolate the bases, the solution is warmed gently to expel ammonia, an excess of alkali is added, the amines are distilled in steam, and the distillate is neutralised with some acid ; the mixture of salts is then submitted to fractional crystallisation. The platinichlorides and aurichlorides are often used for this purpose, or the sparingly soluble picrates (p. 486) afforded by most amines.

The solution which contains the quaternary hydroxide is neutralised with hydrochloric acid and evaporated to dryness ; the tetra-alkylammonium salt may then be separated from the alkali salts by extracting the residue with alcohol.

Hinsberg's method for the separation of amines is given later (p. 228).

Primary amines *only* may be prepared by Hofmann's second method (p. 214), namely by the decomposition of the amides with bromine and potash ; also by the following reactions :

An oxime (or a phenylhydrazone) is reduced with zinc dust and acetic acid, or with sodium and alcohol,

$$(CH_3)_2C{:}N \cdot OH + 4H = (CH_3)_2CH \cdot NH_2 + H_2O.$$

An alkyl cyanide (p. 360) is reduced with zinc and sulphuric acid, or with sodium and alcohol,

$$CH_3 \cdot CN + 4H = CH_3 \cdot CH_2 \cdot NH_2.$$

A nitroparaffin is reduced with stannous chloride and hydrochloric acid, or with zinc and an acid,

$$C_2H_5 \cdot NO_2 + 6H = C_2H_5 \cdot NH_2 + 2H_2O.$$

The last three methods are similar in that each consists in the reduction of a compound in which carbon and nitrogen are directly united.

The solution of the product is made strongly alkaline, and the liberated base is distilled in steam, and collected in hydrochloric acid ; the solution is then evaporated to dryness, and the hydrochloride is distilled with powdered caustic potash.

Secondary amines may be prepared by treating a primary base (obtained by one of the methods just given) with the theoretical quantity of an alkyl halide and gently warming the mixture if necessary ; the base is then liberated by the addition of an excess of alkali.

Tertiary amines are prepared from secondary bases in a similar manner. It is thus possible to obtain amines containing two or more different radicals and of known structure ; from the tertiary bases *quaternary salts* are formed by direct combination with an alkyl halide.

Identification of Amines. In order to find out whether a given amine is a primary, secondary, or tertiary base, Hofmann's carbylamine reaction is first tried. If this test gives no result, the base is dissolved in hydrochloric acid and a saturated aqueous solution of sodium nitrite is gradually added ; the separation of a neutral nitrosoamine (which can be further characterised by Liebermann's reaction) proves the presence of a secondary amine. A tertiary base does not give either of these reactions, and, unlike primary and secondary amines, does not react with acid chlorides.

As most amines are liquid, and a determination of the boiling-point may not afford sufficient evidence for the identification of the compound, it is generally necessary to convert the base into some crystalline derivative which can then be identified by its melting-point ; for this purpose the acetyl, benzoyl (p. 514), or *p*-toluenesulphonyl derivative (p. 228) may be employed or the platinichloride, aurichloride, or picrate (see p. 486) ; an analysis of the platinichloride or aurichloride may also be made if necessary.

Amino-Acids and their Derivatives

Two classes of compounds containing the $-NH_2$ group have already been described—namely, the amides, such as acetamide, $CH_3 \cdot CO \cdot NH_2$, and the primary amines, such as ethylamine, $C_2H_5 \cdot NH_2$. In the former, the $-NH_2$ group is easily separated

from the rest of the molecule, inasmuch as all amides are hydrolysed more or less rapidly by boiling aqueous alkalis, giving ammonia and an alkali salt of the acid; in the latter, however, the amino-group resists the action of alkalis, and can only be removed easily by the action of nitrous acid. Another important difference between these two classes of compounds is that, whereas the amines are strongly basic and form very stable salts, the amides are only very weak bases, and, although they form salts with strong acids, their salts are very unstable; for this reason and because they show a neutral reaction to litmus, amides are not generally regarded as bases.

These facts afford another good illustration of the manner in which the properties of a given group may be modified by the other atoms or groups in the molecule (compare pp. 46, 143, 164).

Now, just as the halogen atom of an alkyl halide, or an acid chloride, may be displaced by the $—NH_2$ group, so may the halogen atom of a substituted acid, such as chloroacetic acid; when, for example, chloroacetic acid (p. 179) is dissolved in concentrated ammonia at ordinary temperatures, it gives the ammonium salt of *aminoacetic acid.*

$$CH_2Cl\cdot COOH+3NH_4\cdot OH = NH_2\cdot CH_2\cdot COONH_4+NH_4Cl+3H_2O;$$

in this and similar reactions secondary compounds, etc., are not usually produced.

Glycine, *aminoacetic acid,* $CH_2(NH_2)\cdot COOH$, can be prepared from its ammonium salt as described below; it is found in certain animal secretions, usually in combination. As *hippuric acid* or *benzoylglycine,* $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$ (p. 512), it occurs in considerable quantities in the urine of the horse, and it may be obtained, together with benzoic acid, by heating hippuric acid with hydrochloric acid,

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH+H_2O+HCl = C_6H_5\cdot COOH+HCl,\ NH_2\cdot CH_2\cdot COOH.$$

Glycine crystallises from water in prisms, and melts indefinitely at *about* 256° with decomposition; it has a sweet (Gr. *glykos*) taste, is readily soluble in water, and its aqueous solution gives with ferric chloride a deep-red colouration.

Glycine contains a *carboxyl* group, and, therefore, has the properties of an acid; but it also contains an amino-group, which, like that in methylamine, confers basic properties. The result is that

glycine is *neutral* to litmus, but forms salts with bases or with acids (p. 618).

A characteristic derivative is the *copper salt*, which is obtained by boiling cupric hydroxide with a strong, aqueous solution of the acid or of its *ammonium salt*,

$$2NH_2\cdot CH_2\cdot COONH_4+Cu(OH)_2=(NH_2\cdot CH_2\cdot COO)_2Cu+2NH_3+2H_2O;$$

it crystallises in deep-blue needles. The acid is isolated by passing hydrogen sulphide into the aqueous solution of this salt, filtering from copper sulphide, and evaporating to dryness.

Glycine hydrochloride, HCl, $NH_2\cdot CH_2\cdot COOH$, also written $Cl[NH_3\cdot CH_2\cdot COOH]$, is produced by dissolving glycine in hydrochloric acid, or by decomposing hippuric acid with hydrochloric acid ; it crystallises in needles, and is readily soluble in water.

Towards nitrous acid, glycine behaves like a primary amine ; its amino-group is displaced by hydroxyl, and glycollic acid (p. 266) is formed,

$$CH_2(NH_2)\cdot COOH+HNO_2=CH_2(OH)\cdot COOH+N_2+H_2O.$$

Other *amino-acids*, such as *alanine* or α-aminopropionic acid, $CH_3\cdot CH(NH_2)\cdot COOH$, may be prepared from the corresponding halogen acids by the action of ammonia ; they are very similar to glycine in chemical properties, and when treated with nitrous acid they yield the corresponding hydroxy-acids (p. 262). The flesh of animals (apart from fat) consists almost entirely of compounds produced from amino-acids (p. 616).

Aminoformic acid or **carbamic acid,** $NH_2\cdot COOH$, is known only in the form of some of its salts and esters. Its ammonium salt, *ammonium carbamate*, $NH_2\cdot COONH_4$, is produced by the direct combination of carbon dioxide and ammonia, and is one of the components of commercial ammonium carbonate.

The esters of aminoformic acid are termed *urethanes* (because of their relation to urea) or *alkyl carbamates*.

Urethane or **ethyl carbamate,** $NH_2\cdot COOC_2H_5$, may be prepared by treating diethyl carbonate or ethyl chloroformate (p. 262) with ammonia at ordinary temperatures,

$$CO<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}+NH_3=CO<\begin{matrix}NH_2\\OC_2H_5\end{matrix}+C_2H_5\cdot OH$$

$$CO<\begin{matrix}Cl\\OC_2H_5\end{matrix}+2NH_3=CO<\begin{matrix}NH_2\\OC_2H_5\end{matrix}+NH_4Cl.$$

It is a volatile crystalline compound, melting at 50°, and when heated with ammonia it is converted into urea and alcohol,

$$CO<\begin{matrix}NH_2\\OC_2H_5\end{matrix}+NH_3 = CO<\begin{matrix}NH_2\\NH_2\end{matrix}+C_2H_5\cdot OH.$$

It is readily soluble in cold water and is decomposed by boiling alkalis giving ammonia, ethyl alcohol, and a carbonate.

Methylurethane, $CH_3\cdot NH\cdot COOEt$, obtained by treating diethyl carbonate, or ethyl chloroformate, with methylamine, boils at 170°.

The Ascent and Descent of a Homologous Series

A member of any homologous series may be transformed into the next higher or next lower homologue, a process which is commonly spoken of as ' passing up ' or ' passing down ' the series, as the case may be. As most of the reactions involved in such transformations have now been described, some examples are given below of how these changes may be accomplished.

A given fatty acid may be transformed into the next *higher* homologue in the following manner : The calcium salt of the acid is heated with calcium formate, and the resulting aldehyde is converted into the corresponding alcohol by reduction ; the alcohol is then transformed into the iodide, the latter is treated with potassium cyanide, and the resulting cyanide is hydrolysed with alkalis or mineral acids,

$$\underset{\text{Acetic acid}}{CH_3\cdot COOH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3\cdot CHO} \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Ethyl iodide}}{CH_3\cdot CH_2I} \longrightarrow \underset{\text{Ethyl cyanide}}{CH_3\cdot CH_2\cdot CN} \longrightarrow \underset{\text{Propionic acid}}{CH_3\cdot CH_2\cdot COOH.}$$

The cyanide may be converted into the acid in another way ; it is first reduced to the amine, the amine is converted into the alcohol, and the latter is oxidised through the aldehyde to the fatty acid,

$$\underset{\text{Ethyl cyanide}}{CH_3\cdot CH_2\cdot CN} \longrightarrow \underset{\text{Propylamine}}{CH_3\cdot CH_2\cdot CH_2\cdot NH_2} \longrightarrow \underset{\text{Propyl alcohol}}{CH_3\cdot CH_2\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Propionaldehyde}}{CH_3\cdot CH_2\cdot CHO} \longrightarrow \underset{\text{Propionic acid}}{CH_3\cdot CH_2\cdot COOH.}$$

Alternatively the cyanide may be reduced to the aldimine which is hydrolysed to the aldehyde, and the latter is oxidised,

$$\underset{\text{Ethyl cyanide}}{CH_3\cdot CH_2\cdot CN} \longrightarrow \underset{\text{Propionaldimine}}{CH_3\cdot CH_2\cdot CH{:}NH} \longrightarrow \underset{\text{Propionaldehyde}}{CH_3\cdot CH_2\cdot CHO} \longrightarrow \underset{\text{Propionic acid}}{CH_3\cdot CH_2\cdot COOH.}$$

In the above sequences the required additional carbon atom is obtained by substituting —CN for a halogen atom, but it may also be gained from carbon dioxide,

$$RX \longrightarrow R\cdot MgX \longrightarrow R\cdot COOMgX \longrightarrow R\cdot COOH \longrightarrow R\cdot CHO \longrightarrow R\cdot CH_2\cdot OH \longrightarrow R\cdot CH_2X.$$

The series may also be ascended in two steps at a time by treating the alkyl halide, $R\cdot CH_2X$ (obtained from the acid, $R\cdot COOH$), with the sodium derivative of diethyl malonate (or ethyl acetoacetate),

$$R\cdot CH_2X \longrightarrow R\cdot CH_2\cdot CH(COOH)_2 \longrightarrow R\cdot CH_2\cdot CH_2\cdot COOH,$$

or a Grignard reagent may be treated with ethylene oxide,

$$RX \longrightarrow R\cdot MgX \longrightarrow R\cdot CH_2\cdot CH_2\cdot OH \longrightarrow R\cdot CH_2\cdot CH_2X.$$

A given fatty acid may be transformed into the next *lower* homologue in the following manner: The acid is converted into its amide, and the amide is treated with bromine and potassium hydroxide in aqueous solution; the resulting amine is converted into the alcohol, which is then oxidised, through the aldehyde, to the fatty acid,

$$\underset{\text{Propionic acid}}{CH_3\cdot CH_2\cdot COOH} \longrightarrow \underset{\text{Propionamide}}{CH_3\cdot CH_2\cdot CO\cdot NH_2} \longrightarrow \underset{\text{Ethylamine}}{CH_3\cdot CH_2\cdot NH_2} \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3\cdot CHO} \longrightarrow \underset{\text{Acetic acid}}{CH_3\cdot COOH.}$$

Another method of passing down the series of fatty acids has already been given (p. 184).

Since the various types of compounds shown above are convertible one into the other by the reactions indicated, any homologous series may be ascended or descended by such methods. All the reactions employed in these transformations are *most important general reactions*, which should be carefully studied.

SUMMARY AND EXTENSION

Amines are derived from ammonia by the displacement of one, two, or three hydrogen atoms by alkyl groups. In this way, primary, $R\cdot NH_2$, secondary, R_2NH, and tertiary amines, R_3N, are produced. Compounds of the type NR_4R', such as *benzyltetramethyl ammonium*, $NMe_4(CH_2\cdot C_6H_5)$, have also been prepared. The tetra-alkyl or quaternary bases, $R_4N\cdot OH$, may be regarded as derived from ammonium hydroxide, and a salt of any type of amine, as derived from an ammonium salt; formulae such as

$$[R\cdot NH_3]Cl, \quad [R\cdot NH_3]_2PtCl_6, \quad [R\cdot NH_3]AuCl_4, \text{ etc.,}$$

represent their structures more accurately than $R\cdot NH_2$, HCl, etc.,

but the salts of halogen acids are still called hydrochlorides, etc., instead of chlorides, etc.

Nomenclature. The name of an amine shows each radical which is combined with the nitrogen atom and when two or more are identical this is shown by a prefix, as for example *diethylamine*, $(C_2H_5)_2NH$, *dimethylethylamine*, $(CH_3)_2(C_2H_5)N$; similarly in the case of quaternary compounds, such as *methylethylpropylbutyl ammonium hydroxide*, $(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)N \cdot OH$, and *tetramethyl ammonium hydroxide*, $(CH_3)_4N \cdot OH$. The name therefore shows the structure of the compound. The termination **ine** is used for all organic bases.

Homology and isomerism. Although the amines form a homologous series, $CH_3 \cdot NH_2$, $C_2H_5 \cdot NH_2$, $C_3H_7 \cdot NH_2$, and so on, of the general formula, $C_nH_{2n+3}N$, it is not convenient to consider them in this way, owing to the great differences in properties which may be shown by isomerides. Thus the formula of the second member of the series, C_2H_7N, would represent *ethylamine* and *dimethylamine*, and the third, C_3H_9N, would comprise all three types of amines, namely n- and iso-*propylamines*, *methylethylamine* and *trimethylamine*: isomeric members of the series, therefore, might have little in common, except their basic properties, and show a much greater diversity in their reactions than is usually met with in other cases of homologues.

Preparation. (1) Alkyl halides, usually, however, only the primary compounds, are heated with alcoholic ammonia. In this way mixtures of the three classes of amines, together with the quaternary compounds, may be obtained, and the products may be isolated by the methods given (pp. 220, 228).

(2) Compounds containing nitrogen directly united with carbon are reduced with nascent hydrogen (an appropriate reducing agent is indicated after each equation),

$$CH_3 \cdot NO_2 + 6H = CH_3 \cdot NH_2 + 2H_2O, (Zn + HCl)$$

$$CH_3 \cdot CH_2 \cdot CN + 4H = CH_3 \cdot CH_2 \cdot CH_2 \cdot NH_2, (Na + EtOH)$$

$$(CH_3)_2C{:}N \cdot OH + 4H = (CH_3)_2CH \cdot NH_2 + H_2O, \ (NaHg + CH_3 \cdot COOH)$$

$$CH_3 \cdot CH{:}N \cdot NH \cdot C_6H_5 + 4H = CH_3 \cdot CH_2 \cdot NH_2 + C_6H_5 \cdot NH_2, (NaHg + C_2H_4O_2).$$

(3) Potassium phthalimide (p. 522) is treated with an alkyl halide and the product is hydrolysed with acid or alkali (Gabriel),

$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N \cdot C_2H_5 + 2KOH = C_6H_4(COOK)_2 + C_2H_5 \cdot NH_2.$$

(4) Amides are treated with bromine and potash,

$$CH_3 \cdot CO \cdot NH_2 + Br_2 + 4KOH = CH_3 \cdot NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

(5) Acids, or anhydrides, are treated with hydrazoic acid and sulphuric acid (Curtius),

$$R \cdot COOH + N_3H = R \cdot NH_2 + CO_2 + N_2.$$

(6) Alkyl *iso*nitriles (carbylamines) are hydrolysed with dilute acid,

$$C_2H_5 \cdot NC + 2H_2O = C_2H_5 \cdot NH_2 + H \cdot COOH.$$

(7) Alkyl carbimides (*iso*cyanates) are hydrolysed with alkali,

$$CH_3 \cdot N{:}CO + 2KOH = CH_3 \cdot NH_2 + K_2CO_3,$$

or *iso*thiocyanates with acids,

$$C_2H_5 \cdot N{:}CS + 2H_2O = C_2H_5 \cdot NH_2 + CO_2 + H_2S.$$

(8) *p*-Nitroso-derivatives of tertiary aromatic amines (p. 451) are heated with alkalis,

$$NO \cdot C_6H_4 \cdot N(CH_3)_2 + KOH = NO \cdot C_6H_4 \cdot OK + (CH_3)_2NH.$$

(9) Sodium cyanamide (p. 363) is treated with an alkyl halide and the product is hydrolysed with acids or alkalis,

$$NNa_2 \cdot CN \longrightarrow NR_2 \cdot CN \longrightarrow NR_2 \cdot COOH \longrightarrow NR_2H.$$

(10) Alkali metal salts of the sulphonyl derivatives of primary amines are heated with alkyl halides and the products are hydrolysed,

$$NRNa \cdot SO_2 \cdot R' \longrightarrow NRR'' \cdot SO_2 \cdot R' \longrightarrow NHRR''.$$

Methods (2), (3), (4), (5), (6) and (7) give rise to *primary* amines only, (8), (9) and (10) to secondary amines only.

The three methylamines can be prepared from ammonium chloride and formaldehyde (p. 219); primary and secondary amines can be *methylated* with formaldehyde, dimethyl sulphate, or methyl potassium sulphate.

Physical Properties. The lower amines are gases or liquids at ordinary temperatures with a characteristic ammoniacal odour; they are inflammable and soluble in water, giving alkaline solutions. The quaternary hydroxides are usually solids and are very strong bases.

Chemical Properties. (1) In aqueous solution the amines like ammonia exist as very unstable hydroxides, $NR_3H \cdot OH$ (R = H or an alkyl radical), with acids, they form salts. With alkyl halides, primary amines give secondary bases and these give tertiary amines; the latter form tetra-alkyl ammonium salts.

(2) With chloroform and alcoholic potash primary amines (only) give carbylamines.

(3) With nitrous acid primary amines give an alcohol and nitrogen, secondary amines a nitrosoamine; tertiary amines merely form a salt.

(4) With acid chlorides (or anhydrides) primary and secondary amines form substituted amides, while tertiary amines are unchanged,

$$C_2H_5\cdot NH_2+CH_3\cdot COCl = C_2H_5\cdot NH\cdot CO\cdot CH_3+HCl,$$
$$(CH_3)_2NH+C_6H_5\cdot SO_2Cl = (CH_3)_2N\cdot SO_2\cdot C_6H_5+HCl;$$

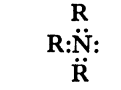
the solid amides are frequently used in the identification of (liquid) amines.

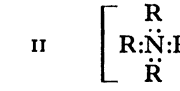
The *benzenesulphonyl* (or p-*toluenesulphonyl*) derivatives (p. 475) serve for the identification and separation of the three classes of amines (Hinsberg's method). Tertiary amines are not changed by the sulphonyl chlorides and remain soluble in dilute aqueous acid (or water), whereas primary and secondary amines give sparingly soluble sulphonyl derivatives : those of primary amines are soluble in caustic alkalis, forming salts, $NRNa\cdot SO_2\cdot R'$, but those of secondary amines are neither basic nor acidic. The two sulphonyl derivatives, therefore, are easily separated from the tertiary base and from one another, and are then hydrolysed, usually with concentrated hydrochloric acid, in order to regenerate the amines.

A tertiary base may generally be separated from a secondary base by converting the latter into its nitroso-derivative and extracting this *neutral* product from the *acid* solution with ether ; the tertiary base is then liberated with potassium hydroxide and distilled in steam, whilst the secondary base may be recovered by decomposing the nitroso-derivative with boiling hydrochloric acid,

$$(C_2H_5)N\cdot NO+H_2O = (C_2H_5)_2\cdot NH+HO\cdot NO.$$

Before the advent of the electronic theory of valency, it was assumed that the valency of nitrogen, like that of phosphorus, arsenic, etc., was three, as in ammonia and the amines, or five, as in the salts of these bases, and in the nitro-compounds ; in either case all the valencies were represented in the same way by a single line or bond. According to present views, the bases are represented by formula (I) and their salts by (II), where R is hydrogen or a univalent hydrocarbon radical. In the former all the bonds are *co-valent* ; in the latter only four of the bonds are co-valent, and the complex so formed is united to X (an acid ion or —OH) by an *electro-valency* as indicated :

I 

II 

The great difference in basic strengths between the amines and the quaternary hydroxides might be explained as follows : the latter have

structures as II (X = OH) and are strong electrolytes, whereas amines can combine with water by hydrogen bonding (p. 489),

$$R_3N \ldots H{-}O{-}H,$$

a form of union impossible in the quaternary hydroxides, but apparently preferred by the amines.

Amino-acids. Glycine, $NH_2 \cdot CH_2 \cdot COOH$ or $\overset{+}{N}H_3 \cdot CH_2 \cdot \overset{-}{C}OO$, may be prepared by heating chloroacetic acid with ammonia, by the hydrolysis of gelatin, or, best, from ammonium chloride, formaldehyde, and sodium cyanide.

$$NaCN + NH_4Cl + 2H \cdot CHO = CH_2{:}N \cdot CH_2 \cdot CN^1 + NaCl + 2H_2O.$$

The *methyleneaminoacetonitrile* [1] thus formed is then hydrolysed,

$$CH_2{:}N \cdot CH_2 \cdot CN + H_2O + H_2SO_4 = H_2SO_4, NH_2 \cdot CH_2 \cdot CN + CH_2O,$$
$$H_2SO_4, NH_2 \cdot CH_2 \cdot CN + Ba(OH)_2 = NH_2 \cdot CH_2 \cdot COOH + BaSO_4 + NH_3.$$

Glycine, and amino-acids in general, show the properties of acids and of amines (p. 617); when strongly heated with soda-lime they give amines, and when treated with nitrous acid they give hydroxy-acids.

[1] The molecular formula of methyleneaminoacetonitrile is $(CH_2{:}N \cdot CH_2 \cdot CN)_3$.

CHAPTER 15

ORGANIC COMPOUNDS OF PHOSPHORUS, ARSENIC AND SILICON AND ORGANO-METALLIC COMPOUNDS

Organic Derivatives of Phosphorus and Arsenic

THE hydrogen atoms of the hydrides of phosphorus and arsenic, like those of ammonia, may be displaced by hydrocarbon radicals. The principal alkyl compounds of these elements correspond with the *tertiary* amines, and have the compositions, PR_3 and AsR_3, respectively, but *primary* and *secondary* phosphines and arsines are also known.

Primary and secondary **phosphines** may be obtained by heating the alkyl iodides with phosphonium iodide in the presence of zinc oxide ; ethyl iodide, for example, gives salts of *ethylphosphine* and *diethylphosphine*,

$$2PH_4I+2C_2H_5I+ZnO = 2PH_2\cdot C_2H_5,HI+ZnI_2+H_2O,$$
$$PH_4I+2C_2H_5I+ZnO = PH(C_2H_5)_2,HI+ZnI_2+H_2O.$$

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. The tertiary phosphines combine with alkyl iodides, forming salts of quaternary bases, such as *tetraethylphosphonium iodide*,

$$P(C_2H_5)_3+C_2H_5I = P(C_2H_5)_4I.$$

With the exception of *methylphosphine*, $PH_2\cdot CH_3$, a gas, the phosphines are very unpleasant-smelling, feebly basic liquids which oxidise (and sometimes take fire) on exposure to the air ; tertiary phosphines are thus converted into stable oxides, such as *triethylphosphine oxide*, $P(C_2H_5)_3O$.[1] Salts of the tetra-alkylphosphonium compounds, such as *tetraethylphosphonium iodide*, $P(C_2H_5)_4I$, on treatment with moist silver oxide 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

[1] Tertiary amines give oxidation products, $R_3N(OH)_2$, on treatment with hydrogen peroxide.

carbon dioxide, and dissolve freely in water; they are, in fact, similar in properties to the hydroxides of the alkali metals, and their salts are much more stable than the phosphine salts (many of which are almost completely hydrolysed by water) just as those of the corresponding tetra-alkylammonium bases are more stable than those of the amines.

Tertiary **arsines** are obtained by treating arsenious halides with the Grignard reagents (p. 237) or zinc alkyl compounds (p. 233), or by heating the alkyl iodides with sodium arsenide,

$$AsBr_3+3CH_3\cdot MgI = As(CH_3)_3+3MgBrI,$$
$$2AsCl_3+3Zn(C_2H_5)_2 = 2As(C_2H_5)_3+3ZnCl_2,$$
$$AsNa_3+3CH_3I = As(CH_3)_3+3NaI.$$

Triethylarsine, $As(C_2H_5)_3$, is a 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 in being a *neutral* compound, and, like hydrogen arsenide, it does not form salts with acids, but it combines readily with alkyl iodides, forming salts of *quaternary arsonium hydroxides*,

$$As(C_2H_5)_3+C_2H_5I = As(C_2H_5)_4I.$$

Tetraethylarsonium iodide, $As(C_2H_5)_4I$, is crystalline, and, like other quaternary salts, it reacts with silver oxide and gives **tetraethylarsonium hydroxide,**

$$As(C_2H_5)_4I+Ag\cdot OH = As(C_2H_5)_4\cdot OH+AgI.$$

This substance is a strongly basic hydroxide, like the corresponding derivatives of nitrogen and phosphorus.

The tertiary arsines resemble the tertiary phosphines in readily undergoing oxidation on exposure to the air, with the formation of oxides, such as *triethylarsine oxide*, $As(C_2H_5)_3O$.

Some organic arsenic compounds are very important in medicine. When certain moulds are grown in solutions containing inorganic or organic arsenic compounds, alkyl arsines, as, for example, trimethylarsine, may be evolved: there have been fatalities caused by such volatile arsenic compounds evolved from wall-paper or plaster (containing arsenic), which has been attacked by moulds.

Dimethylarsine oxide, $(CH_3)_2As\cdot O\cdot As(CH_3)_2$ **(cacodyl oxide),** and its derivatives were investigated by Bunsen about 1840, and

are of historical interest. The oxide is formed by heating a mixture of equal weights of arsenious oxide and potassium acetate,

$$As_4O_6+8CH_3\cdot COOK = 2As_2(CH_3)_4O+4K_2CO_3+4CO_2.$$

It is a liquid (b.p. 150°), insoluble in water, has an intensely obnoxious smell,[1] and is extremely poisonous; the crude product obtained as above is spontaneously inflammable owing to the presence of cacodyl, but the pure compound is not. In chemical properties cacodyl oxide resembles the feebly basic oxides; it has a neutral reaction, but forms salts, such as *cacodyl chloride*, $As(CH_3)_2Cl$, and *cacodyl cyanide*, $As(CH_3)_2\cdot CN$.

When cacodyl chloride is heated with zinc in an atmosphere of carbon dioxide, it yields **cacodyl** or *tetramethyldiarsine*,

$$2As(CH_3)_2Cl+Zn = As(CH_3)_2\cdot As(CH_3)_2+ZnCl_2,$$

which, like the oxide, is a very poisonous liquid (b.p. 170°), and has an intensely disagreeable smell; it takes fire on exposure to the air.

Cacodylic acid, $(CH_3)_2AsO\cdot OH$, a crystalline, odourless substance, is formed when cacodyl oxide is oxidised with mercuric oxide,

$$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!\!>O+2HgO+H_2O = 2(CH_3)_2AsO\cdot OH+2Hg.$$

The preparation of these and other substances containing the group, $(CH_3)_2As$—, by Bunsen, was one of the very early investigations which led to the use of the term (compound) *radical*, to denote a group of atoms which remained unchanged in the course of a series of reactions.

Lewisite, $CHCl{:}CH\cdot AsCl_2$ (b.p. 190°), prepared from acetylene and arsenic trichloride in the presence of aluminium chloride, is a poison gas, as are also the compounds, methyl and ethyl arsenious dichlorides, $AsCH_3Cl_2$ and $AsC_2H_5Cl_2$.

Organic Derivatives of Silicon

Organic derivatives of silicon, which correspond with some of the more important types of carbon compounds, are known—for example, the *silicohydrocarbons*, SiR_4, the *silicyl chlorides*, SiR_3Cl, the (tertiary) *silicols*, $SiR_3\cdot OH$, and the *oxides*, $(SiR_3)_2O$. Of these related types the silicohydrocarbons are very similar to the hydrocarbons in general behaviour; but in the case of compounds in which the silicon atom is directly united to a halogen, or

[1] The name cacodyl is derived from the Greek *cacōdēs*, stinking.

to two oxygen atoms, the silicon derivative and the corresponding carbon compound differ widely in properties, and the relationship is analogous to that between silicon tetrachloride and carbon tetrachloride, or between silicic and carbonic acids, as the case may be.

Silicon tetraethyl, $Si(C_2H_5)_4$, may be obtained by treating silicon tetrachloride with ethyl magnesium bromide (p. 235), and also by heating a mixture of silicon tetrachloride and ethyl bromide, dissolved in ether, with sodium,

$$SiCl_4+4C_2H_5Br+8Na = Si(C_2H_5)_4+4NaCl+4NaBr ;$$

it boils at 153°, and so closely resembles normal nonane, C_9H_{20}, in properties, that it was formerly named *silicononane.*

Silicononane is not acted on by nitric acid or caustic alkalis, but when it is treated with chlorine it yields *silicononyl chloride*, $Si(C_2H_5)_3 \cdot C_2H_4Cl$, a liquid, boiling at 185° ; this chloride closely resembles the alkyl chlorides in properties, whereas *triethylsilicyl chloride*, $SiEt_3Cl$, like silicon tetrachloride, is rapidly and completely hydrolysed by cold water, giving *triethylsilicol*, $SiEt_3 \cdot OH$.

Certain silicon compounds are now used in the plastics industry (Part III.).

Organic Derivatives of the Metals

Many of the metals form alkyl compounds, although their hydrides are unknown. These alkyl derivatives are named ' organometallic ' compounds, but there is no sharp division between them and the alkyl derivatives of other elements, just as there is none between the metals and the non-metals. If, in fact, the alkyl compounds of elements belonging to the same natural family are considered, it will be evident that they show a *gradual* change in properties, just as do other derivatives of these elements. 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 hard to say how many of the last three should be termed organometallic compounds.

Zinc diethyl, $Zn(C_2H_5)_2$, is prepared by heating zinc with ethyl iodide in an atmosphere of carbon dioxide ; the first product is a

solid, EtZnI, but at higher temperatures a second change occurs, and zinc diethyl is formed,

$$2EtZnI = ZnEt_2 + ZnI_2.$$

This is a mobile liquid, boiling at 118°, which takes fire spontaneously on exposure to the air, burning with a luminous, greenish flame, and giving clouds of zinc oxide. It reacts vigorously with water, yielding ethane and zinc hydroxide,

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

and is also decomposed by alcohol, but not so quickly as by water,

$$Zn(C_2H_5)_2 + 2C_2H_5 \cdot OH = 2C_2H_6 + Zn(OC_2H_5)_2.$$

Its behaviour towards halogen compounds and various other substances is similar to that of a Grignard reagent (p. 235).

Zinc dimethyl, $Zn(CH_3)_2$, resembles zinc diethyl and boils at 46°.

The zinc alkyl compounds, discovered by Frankland, have been of the greatest service in the past in the synthesis of various types of organic compounds, of which some examples have already been given; except in the synthesis of ketones from acid chlorides (p. 154), their place has now been taken by the *Grignard reagents*, which are far more easily prepared and are not spontaneously inflammable.

Mercuric diethyl, $Hg(C_2H_5)_2$, is formed when mercuric chloride is treated with zinc diethyl or ethyl magnesium bromide,

$$2C_2H_5MgBr + HgCl_2 = Hg(C_2H_5)_2 + MgBr_2 + MgCl_2,$$

and when ethyl iodide is shaken with sodium amalgam,

$$HgNa_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI.$$

It is a mobile liquid, of sp. gr. 2·44, and boils at 159°; it is not spontaneously inflammable at ordinary temperatures, 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.

In addition to the di-alkyl compounds, mercury gives derivatives of the type, RHgX; with halogen acids, mercuric diethyl, for example, is converted into salts, analogous in some respects to the halogen salts of the alkali metals,

$$Hg(C_2H_5)_2 + HCl = C_2H_5HgCl + C_2H_6.$$

These salts are also formed by the direct union of mercury and

alkyl halides at ordinary temperatures, especially in sunlight. They react with moist silver oxide, and are thereby converted into *hydroxides*, $RHg \cdot OH$. These compounds 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 compounds of nitrogen, phosphorus, arsenic, etc., the substitution of alkyl groups for hydrogen (or hydroxyl) is accompanied by a marked increase in basic properties ; mercuric (hydr)oxide is a comparatively feeble base.

Lithium, *sodium*, and *potassium* also form alkyl derivatives and combine directly with various olefines (Part III.).

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 quadrivalent; stannous diethyl, $Sn(C_2H_5)_2$, corresponding with stannous chloride, is also known. Aluminium gives alkyl compounds, such as $Al(CH_3)_3$ and $Al(C_2H_5)_3$.

Lead tetraethyl, $Pb(C_2H_5)_4$, is of importance owing to its use as an anti-knock in petrol engines (p. 68) ; it is prepared commercially by heating ethyl chloride with a sodium-lead alloy under pressure. It boils at about 85° (13 mm.) and is poisonous.

As the alkyl derivatives of many metals, unlike the great majority of metallic compounds, are volatile, their molecular weights can be determined from their vapour densities, and in this way the valencies of the metals in the compounds may be established. Grignard compounds, however, cannot be volatilised.

Grignard Reagents

Ethyl magnesium bromide, $C_2H_5—Mg—Br$, or EtMgBr, may be described as an example of a Grignard reagent. It is formed, with development of heat, when ethyl bromide is added to magnesium in the presence of pure ether ; the metal gradually disappears, and when the solution is evaporated it gives a crystalline, very hygroscopic substance, which may be regarded as a compound of ethyl magnesium bromide and ether, probably of the composition, $EtMgBr, 2(C_2H_5)_2O$.

In all those reactions in which ethyl magnesium bromide (or any other Grignard reagent) is employed, it is unnecessary to isolate the crystalline compound ; an *ethereal solution* of the reagent is

used, and as the ' combined ' ether appears to play no part in the chemical change, it is not represented in the equations for the reactions.

A solution of a Grignard reagent is prepared as follows : Clean dry magnesium (1 atom) in the form of powder or turnings is placed in a flask provided with a reflux condenser, and is covered with 5–10 times its weight of pure ether ; a small quantity (1–2 c.c.) of the alkyl halide (1 mol.) is then added. If after 1–5 minutes a visible reaction sets in, it is then only necessary to continue the addition of the alkyl (or aryl, p. 414) halide at such a rate that the reaction does not become too violent ; but it is often advisable, and sometimes essential, to keep the solution at 0 to 10° during the operation. If a reaction does not set in spontaneously, the flask is gently warmed, or a small quantity of a solution of ethyl magnesium bromide, prepared in a test-tube,[1] is poured into the flask ; the reaction having been started, the addition of the requisite alkyl halide is then continued, and finally, if necessary, the flask is gently warmed until all the magnesium is dissolved.

In order to ensure success, all the reagents and the apparatus must be perfectly dry, and the condenser should be fitted with a calcium chloride tube ; the ether should have been repeatedly shaken with small quantities of alkaline potassium permanganate, dried with calcium chloride, treated with sodium, and distilled.

Ethyl magnesium iodide, EtMgI, resembles the corresponding bromide ; *methyl magnesium iodide*, MeMgI, and *propyl magnesium bromide*, PrMgBr, are also common Grignard reagents ; but in addition to those named here, many others are used, more especially those derived from aromatic halides (p. 431).

The principal reactions of the Grignard reagents are of two types : (1) Double decompositions, (2) Additions.

(1) (*a*) They are decomposed by substances containing reactive hydrogen atoms, such as water, alcohols, acids, and primary and secondary amines, giving the *hydrocarbon* derived from the Grignard reagent,

$$C_2H_5MgBr+HOH = C_2H_6+MgBr\cdot OH,$$
$$CH_3MgI+EtOH = CH_4+MgI\cdot OEt,$$
$$CH_3MgI+Et_2NH = CH_4+MgI\cdot NEt_2.$$

[1] Magnesium reacts almost immediately with ethyl bromide (and iodide). A trace of iodine may also be used to start the reaction, which, with some halides, does not commence readily.

With acetylenic hydrocarbons containing the group, —C:CH, they give new Grignard reagents,

$$C_2H_5MgBr+R\cdot C{:}CH = C_2H_6+R\cdot C{:}C\cdot MgBr,$$

which may also be used in the reactions given below.

(*b*) They react with the halides of many metals and non-metals giving alkyl (or aryl), or alkyl halogen derivatives of the elements,

$$EtMgBr+SiCl_4 = EtSiCl_3+MgClBr,$$
$$EtMgBr+EtSiCl_3 = Et_2SiCl_2+MgClBr,$$
$$4EtMgBr+SnBr_4 = Et_4Sn+4MgBr_2.$$

Compounds of this kind have been obtained from the halides of phosphorus, arsenic, antimony, silicon, tin, lead, mercury, thallium, gold, and other elements.

(*c*) They react with esters of carboxylic acids to give *ketones* (or aldehydes with formic esters),

$$RMgBr+R'\cdot COOEt = R'\cdot CO\cdot R+MgBr\cdot OEt,$$

but it is usually impossible to stop such reactions at this stage and to prepare ketones by this method, as the initial products undergo the further additive change shown below (2) (*c*) and give *tertiary alcohols*.

(2) (*a*) They absorb oxygen and the products yield *alcohols* (or phenols, p. 478) when they are hydrolysed,

$$RMgBr \xrightarrow{O_2} ROMgBr \xrightarrow{H_2O} R\cdot OH+MgBr\cdot OH.^1$$

(*b*) They also absorb carbon dioxide and the products, on hydrolysis, give *acids*,

$$RMgBr+CO_2 = R\cdot COOMgBr \xrightarrow{H_2O} R\cdot COOH+MgBr\cdot OH,$$

$$Me_3CMgCl+CO_2 = Me_3C\cdot COOMgCl \xrightarrow{H_2O} Me_3C\cdot COOH+MgCl\cdot OH.$$

The ethereal solution is saturated with pure, dry carbon dioxide, or solid carbon dioxide is added, and the ether is then distilled; the carboxylic acid is liberated with dilute sulphuric acid and distilled, or extracted with ether.

If the initial product is heated with an excess of the Grignard reagent, a tertiary alcohol may be formed; the reactions in this

[1] In this abbreviation of two equations the reagent is shown above the arrow.

case are similar to those which occur in the conversion of an ester into a tertiary alcohol.

(*c*) They give with compounds containing a carbonyl group additive products, which on hydrolysis afford *alcohols*. Formaldehyde gives *primary* alcohols,

$$RMgBr+CH_2O = R\cdot CH_2\cdot OMgBr \xrightarrow{H_2O} R\cdot CH_2\cdot OH+MgBr\cdot OH,$$

other aldehydes give *secondary* alcohols,

$$RMgBr+R'\cdot CHO = RR'CH\cdot OMgBr \xrightarrow{H_2O} RR'CH\cdot OH+MgBr\cdot OH,$$

whereas ketones give *tertiary* alcohols,

$$RMgBr+R'_2CO=R'_2CR\cdot OMgBr \xrightarrow{H_2O} R'_2RC\cdot OH+MgBr\cdot OH.$$

(*d*) They combine with oxides of olefines (p. 244) and the products yield *alcohols* on hydrolysis,

$$RMgBr+C_2H_4O = R\cdot CH_2\cdot CH_2\cdot OMgBr \xrightarrow{H_2O} R\cdot CH_2\cdot CH_2\cdot OH+MgBr\cdot OH.$$

In the addition reactions shown above the first product is hydrolysed by adding dilute acid, and the basic magnesium salt (or a mixture of magnesium salt and hydroxide) represented in the equations is therefore dissolved as a normal salt. In some cases, where the product is sensitive to acids, a solution of ammonium chloride is used to dissolve the magnesium hydroxide.

It will be seen from the above examples that the Grignard reagents are of very great importance, since, with their aid, various types of compounds, not easily obtained by other methods, may be produced with ease. Thus their value in the preparation of secondary and tertiary alcohols, and the olefines, so easily produced therefrom, and in the synthesis of alkyl and aryl derivatives from all sorts of halogen compounds, can hardly be overestimated.

A solution of methyl magnesium iodide, prepared with the aid of diamyl instead of diethyl ether, is used for the detection and estimation of —OH, —NH_2 and > NH groups (*Zerevitinoff*); for the latter purpose the volume of the liberated methane is measured.

In 1899 it was found by Barbier that when 2-methylhept-2-en-6-one, $(CH_3)_2C{:}CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, is brought into contact with methyl iodide in the presence of magnesium and ether, a reaction occurs and 2:6-dimethylhept-2-en-6-ol,

$$(CH_3)_2C{:}CH\cdot CH_2\cdot CH_2\cdot C(OH)(CH_3)_2,$$

can be isolated, after the product has been treated with an acid. These observations suggested that methyl magnesium iodide, CH_3MgI, had been formed and had subsequently reacted with the methylheptenone in the same manner as zinc dimethyl was known to react with ketones.

As it was also known that zinc dimethyl unites with anhydrous ether to form a compound, $Zn(CH_3)_2$, $(C_2H_5)_2O$, Barbier's observations led Grignard, in 1900, to investigate the action of magnesium on methyl iodide and similar compounds in the presence of ether. The alkyl magnesium halides which were thus discovered, and analogous aryl compounds, are known as the Grignard reagents.

During the preparation of these reagents other products may be formed. Magnesium and methyl iodide, for example, give hydrogen, methane, ethane, and ethylene, whereas the metal and aryl halides, RX, give considerable quantities of the hydrocarbon R·R. Atmospheric oxidation, with the formation of ROMgX may also occur.

In many cases the actual preparation of the Grignard reagent is unnecessary, and the desired synthesis may be brought about by the method employed by Barbier. It is also possible in many cases to use zinc, instead of magnesium, a method which was employed long ago by Reformatsky (p. 286) in reactions involving esters of halogen carboxylic acids.

The syntheses with the Grignard reagents are usually performed by adding the reactant, or a solution of it in ether, to the Grignard solution prepared as already described (p. 236) at such a rate that the reaction does not get out of control; when addition is complete the mixture is heated under reflux, if necessary to complete the reaction, cooled, and poured into dilute sulphuric or hydrochloric acid or ammonium chloride solution cooled by the addition of ice. The ethereal solution of the product is then treated in the usual manner. In some cases, however, the Grignard solution must be added slowly to the solution of the reactant; for example, when the latter contains two active groups only one of which is to be changed.

CHAPTER 16

DI-, TRI-, AND POLY-HYDRIC ALCOHOLS

Glycols

IT has already been shown that a very inert paraffin such as ethane may be converted into a much more reactive derivative by the substitution of an atom of chlorine for an atom of hydrogen, and that this halogen atom may in its turn be displaced by a hydroxyl group. The hydroxy-compound may then be transformed into an aldehyde, acid, or other substance by further changes in which, however, only *one* of the methyl groups of the ethane molecule is concerned,

$$\begin{array}{lllll} CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ | & | & | & | & | \\ CH_3 & CH_2Cl & CH_2\cdot OH & CHO & COOH \end{array}$$

A series of similar transformations may be brought about (often indirectly) in the other methyl group,

$$\begin{array}{lllll} CH_3 & CH_2Cl & CH_2\cdot OH & CHO & COOH \\ | & | & | & | & | \\ CH_3 & CH_2Cl & CH_2\cdot OH & CHO & COOH \end{array}$$

and it is thus possible to obtain from ethane and other paraffins di-substitution products which show, on the whole, a very close relationship with the corresponding mono-substitution compounds.

The **glycols,** or **dihydric alcohols**, discovered by Wurtz in 1856, afford an example of such compounds ; they form a homologous series of the general formula, $C_nH_{2n}(OH)_2$, and are closely related to the monohydric alcohols.

Ethylene glycol, 1:2-*dihydroxyethane*, generally called glycol, $C_2H_4(OH)_2$, is the simplest stable member of the series ; *methylene glycol*, *dihydroxymethane*, $CH_2(OH)_2$, is probably present in aqueous solutions of formaldehyde, but like other compounds which contain the group $>C(OH)_2$, it is very unstable.

Ethylene glycol is formed in small quantities when ethylene is oxidised with a cold, dilute alkaline solution of potassium permanganate,

$$C_2H_4+H_2O+O = C_2H_4(OH)_2.$$

It may be prepared in the laboratory by heating ethylene dibromide with dilute aqueous alkalis, or alkali carbonates, the change which occurs being similar to that which takes place in the formation of ethyl alcohol from ethyl bromide,

$$C_2H_4Br_2+2KOH = C_2H_4(OH)_2+2KBr.$$

For this purpose potassium carbonate (37 g.) is dissolved in water (250 c.c.), ethylene dibromide (50 g.) is added, and the mixture is boiled in a flask provided with a reflux condenser. The insoluble oily dibromide is slowly converted into ethylene glycol, which 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,[1] to expel most of the water, the semi-solid residue is extracted with alcoholic ether (which precipitates potassium bromide, but dissolves the glycol), and the glycol is isolated from the filtered solution by fractional distillation.

On the large scale glycol is obtained by the hydrolysis of ethylene dichloride or chlorohydrin (p. 243), or by heating ethylene oxide (p. 244) with water containing a trace of mineral acid.

Ethylene glycol is a hygroscopic liquid, and has a rather *sweet* taste (hence its name, p. 222); it boils at 197°, and is miscible with water and alcohol, but is only sparingly soluble in ether. It reacts with sodium at ordinary temperatures, yielding *sodium glycol*, $HO\cdot CH_2\cdot CH_2\cdot ONa$, one atom of the metal displacing one atom of hydrogen; if this product is then heated with sodium, hydrogen is again evolved, and *disodium glycol*, $NaO\cdot CH_2\cdot CH_2\cdot ONa$, is formed. These sodium derivatives are very similar to those of the monohydric alcohols; they are crystalline and hygroscopic, and are readily decomposed by water, giving glycol.

From its methods of formation and its behaviour with sodium, it seems that the molecule of glycol contains *two* hydroxyl groups. It might be expected, therefore, that glycol, like alcohol, would be attacked by the chlorides and bromides of phosphorus, giving *di*-halogen compounds; this is, in fact, the case. When glycol is treated with phosphorus pentachloride it is converted into ethylene dichloride, whereas with phosphorus pentabromide it yields the dibromide,

$$C_2H_4(OH)_2+2PBr_5 = C_2H_4Br_2+2POBr_3+2HBr.[2]$$

[1] If the solution is boiled, a considerable quantity of the glycol escapes with the steam.

[2] Compare footnote, p. 108.

Again, it has been shown that hydroxy-compounds react with acetic anhydride and with acetyl chloride, so that if glycol contains two hydroxyl groups it should be converted into a *di*-acetyl derivative ; this prediction is also confirmed, since *ethylene diacetate* (*glycol diacetate*, second footnote, p. 243) is obtained when glycol is heated with acetic anhydride,

$$C_2H_4(OH)_2+2(CH_3\cdot CO)_2O = C_2H_4(O\cdot CO\cdot CH_3)_2+2C_2H_4O_2.$$

Ethylene diacetate, b.p. 187°, is also formed when ethylene dibromide is heated with silver acetate,

$$C_2H_4Br_2+2CH_3\cdot COOAg = C_2H_4(O\cdot CO\cdot CH_3)_2+2AgBr,$$

just as ethyl acetate may be produced from ethyl bromide ; it is hydrolysed by boiling alkalis, yielding ethylene glycol, which was first obtained by Wurtz in this way.

Glycol is used as an anti-freeze in motor radiators, as a cooling liquid in aeroplane engines, for de-icing aeroplanes, and for the preparation of polyethylene glycols and other compounds (p. 368).

When nitrated, together with glycerol, glycol gives *ethylene dinitrate*, the presence of which lowers the freezing-point of the glyceryl trinitrate and makes the latter safer to handle in cold weather (low-freezing dynamite).

Polyethylene glycols. Ethylene glycol, like methylene glycol (p. 136), gives a whole series of condensation products, known as the polyethylene glycols, such as, for example, *diethylene glycol*, $HO\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot OH$, and *hexaethylene glycol*, $HO\cdot CH_2\cdot CH_2\cdot O[CH_2\cdot CH_2\cdot O]_4\cdot CH_2\cdot CH_2\cdot OH$.

These *hydroxy-ethers* are formed when glycol is heated at 115–120° with ethylene dibromide or ethylene oxide, and are commercial solvents.

Constitution of Glycol. The facts already stated show clearly that the molecule of glycol contains two hydroxyl groups, and since it is formed from ethylene dibromide, which has the constitution, $CH_2Br\cdot CH_2Br$, by a simple process of substitution, it must be represented by the formula, $HO\cdot CH_2\cdot CH_2\cdot OH$.

Very strong confirmatory evidence that the molecule of glycol consists of two $—CH_2\cdot OH$ groups is provided by its behaviour on oxidation with nitric acid ; each of these groups is changed first into —CHO and then into —COOH and the following products

can be obtained (but it is not easy to stop the reaction at an intermediate stage),

$CH_2 \cdot OH$	$CH_2 \cdot OH$	CHO	CHO	COOH
CHO	COOH	CHO	COOH	COOH
Glycollic aldehyde [1]	Glycollic acid	Glyoxal	Glyoxylic acid	Oxalic acid

The more important of these compounds are described later.

It will have been seen from the above account of glycol and a few of its derivatives that as soon as the structure of a compound has been established from some of its methods of formation and a few of its reactions, its general behaviour may be predicted.

The recognition and application of this fact are very important aids to the study of organic chemistry, because many of the radicals of known behaviour will be encountered over and over again in the compounds still to be studied and will thus afford important indications of the properties of the new compounds in which they occur. It must be emphasised, however, that chemical behaviour is governed by the structure of the molecule as a whole ; consequently it is only in the case of strictly analogous molecules that dependable conclusions can be drawn. The presence of two hydroxyl groups in the molecule of glycol, for instance, makes possible its conversion into ethylene oxide (below), a new reaction which could not have been predicted at this stage. On the other hand, the formation of propylene oxide (p. 245) might have been foretold as soon as that of ethylene oxide had been established.

Many new reactions have still to be studied before conclusions based on analogy can be accepted with confidence.

Ethylene chlorohydrin, *β-chloroethanol* (glycol chlorohydrin [2]), $CH_2Cl \cdot CH_2 \cdot OH$, is formed when hydrogen chloride is passed into glycol, heated at about 100°, and is prepared commercially by treating ethylene with chlorine water,

$$C_2H_4 + HOCl = CH_2Cl \cdot CH_2 \cdot OH,$$

or ethylene oxide with hydrogen chloride.

It boils at 129° and gives ethylene dichloride when it is heated

[1] This, the first oxidation product of glycol, is best obtained by using hydrogen peroxide in the presence of a ferrous salt (p. 248).

[2] Although still used this is an ill-chosen name.

with hydrogen chloride. It shows in other respects reactions which might be predicted from its structure, but when treated with alkalis in the cold it is converted mainly into *ethylene oxide*, an isomeride of acetaldehyde, and not into glycol as might have been predicted,

$$\begin{matrix}CH_2Cl\\ |\\ CH_2\cdot OH\end{matrix} + KOH = \begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O + KCl + H_2O.$$

Ethylene oxide, C_2H_4O, is prepared on the large scale, either from ethylene chlorohydrin, or more directly by oxidising ethylene with air in the presence of a catalyst of silver at 350–450°. It boils at 13·5°, and combines directly with many simple hydrogen compounds; in this process one of the carbon-oxygen links is broken, a hydrogen atom of the reagent unites with the oxygen atom, and the rest of the reacting molecule combines with carbon. Thus with H—OH, H—Br, H—CN, H—OEt, H—O·CO·CH_3, and H—NH_2, the following compounds, respectively, are formed:

Glycol, $\alpha\beta$-dihydroxyethane	H—O·CH_2·CH_2—OH
β-Bromoethanol, ethylene bromohydrin	H—O·CH_2·CH_2—Br
β-Cyanoethanol, ethylene cyanohydrin	H—O·CH_2·CH_2—CN
β-Hydroxyethylethyl ether	H—O·CH_2·CH_2—OEt
Monoacetylglycol, glycol monoacetate	H—O·CH_2·CH_2—OAc
β-Hydroxyethylamine, ethanolamine	H—O·CH_2·CH_2—NH_2

With ammonia, diethanolamine, $NH(CH_2\cdot CH_2\cdot OH)_2$, and triethanolamine, $N(CH_2\cdot CH_2\cdot OH)_3$, are also formed.

Some of the above are important commercially. β-Hydroxyethylethyl ether (glycolmonoethyl ether), known as *cellosolve* and diglycolmonoethyl ether (*carbitol*) are used as solvents for lacquers, etc. Ethylene oxide is used as a fumigant and insecticide.

Dioxan, $O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>O$, prepared by treating ethylene oxide with alkalis, boils at 102°, and is used as a solvent, although it is poisonous.

Homologues of glycol. **$\alpha\beta$-Propylene glycol,** 1:2-*dihydroxypropane*, $CH_3\cdot CH(OH)\cdot CH_2\cdot OH$, may be obtained by the application of suitable general reactions already studied, to propane or propylene. Thus, propane might be converted into propyl or *iso*propyl chloride, either of which would yield propylene, and from

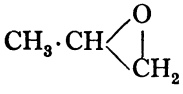
the olefine the dibromide and then $\alpha\beta$-propylene glycol could be produced,

$$CH_3 \cdot CH{:}CH_2 \longrightarrow CH_3 \cdot CHBr \cdot CH_2Br \longrightarrow CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH.$$

Such a method of preparation, however, would not actually be used in the laboratory as the chlorination of propane would be very troublesome, and the glycol could be much more easily obtained from propyl or *iso*propyl alcohol, or from acetone, by well-known reactions.

$\alpha\beta$-Propylene glycol boils at 188° and closely resembles ethylene glycol.

Propylene chlorohydrin, $CH_2Cl \cdot CH(OH) \cdot CH_3$ (*α-chloro-β-hydroxypropane*), formed by the union of propylene and hypochlorous acid, is converted by alkalis into propylene oxide,



It is evident that an isomeride of $\alpha\beta$-propylene glycol, namely, $\alpha\gamma$-propylene glycol, $CH_2(OH) \cdot CH_2 \cdot CH_2 \cdot OH$, might be obtained from propane if this paraffin could first be converted into $\alpha\gamma$-dichloropropane. As, however, four isomeric dichloropropanes (together with more highly substituted compounds) might be formed by chlorinating the hydrocarbon, such a method would hardly be attempted.

αγ-Propylene glycol may be obtained by the action of a mould on glycerol ; it boils at 214° and is usually called *trimethylene glycol.*

βγ-Butylene glycol, $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$, is obtained by a process of fermentation from sucrose. It boils at 184°.

Glycols are usually thick liquids, and as will be seen from the data given above, their boiling-points are much higher than those of the corresponding monohydroxy-derivatives.

Ethylene oxide, propylene oxide, etc., are interesting examples of simple closed chain compounds ; other instances of a similar kind are given later, pp. 261, 271, 278.

Glycerol

Just as it is possible, usually by *indirect* methods, to convert a paraffin into a dihydric alcohol, or glycol, by the substitution of hydroxyl groups for atoms of hydrogen, so those paraffins containing three or more carbon atoms may give rise to **trihydric**

alcohols, compounds which are related to the glycols as the latter to the monohydric alcohols,

Propyl alcohol, 1-Hydroxypropane $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ Propylene glycol, 1:2-Dihydroxypropane $CH_3 \cdot CH(OH) \cdot CH_2 \cdot OH$

Glycerol, 1:2:3-Trihydroxypropane $CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot OH.$

As, however, trihydric alcohols could only be obtained from paraffins or other compounds with very considerable difficulty, their study has been restricted, 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 or *glycerin*, $CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$ (*trihydroxypropane*), was first obtained by Scheele in 1779 from palm oil, in which it occurs (to some extent in the free state). It is one of the unimportant products of the alcoholic fermentation of sugar, but was prepared from this source during the war of 1914-18, as it had been found that the yield could be raised from about 3 to 20–25% by the addition of sodium sulphite or carbonate to the fermenting liquid.

Glycerol occurs in fats and oils in great abundance in the form of esters and has long been obtained from these natural sources in the manufacture of soap (p. 254). Quite recently a method has been devised for the commercial preparation of glycerol from propylene, a product of cracked petroleum. This hydrocarbon is treated with chlorine at 500°, under which drastic conditions it gives allyl chloride (p. 338) and not propylene dichloride; this compound is hydrolysed to allyl alcohol, the latter is combined with hypochlorous acid, and the chlorohydrin thus formed is hydrolysed to glycerol : [1]

$$CH_2{:}CH \cdot CH_3 \longrightarrow CH_2{:}CH \cdot CH_2Cl \longrightarrow$$
$$CH_2{:}CH \cdot CH_2 \cdot OH \longrightarrow CH_2(OH) \cdot CH(Cl) \cdot CH_2 \cdot OH \longrightarrow$$
$$CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot OH.$$

Glycerol was synthesised from acetone by Friedel and Silva as long ago as 1872 by the following series of reactions :

$$CH_3 \cdot CO \cdot CH_3 \longrightarrow CH_3 \cdot CH(OH) \cdot CH_3 \longrightarrow CH_3 \cdot CH{:}CH_2 \longrightarrow$$
$$CH_3 \cdot CHCl \cdot CH_2Cl \longrightarrow CH_2Cl \cdot CHCl \cdot CH_2Cl \longrightarrow$$
$$CH_2(OAc) \cdot CH(OAc) \cdot CH_2 \cdot OAc \longrightarrow CH_2(OH) \cdot CH(OH) \cdot CH_2OH.$$

[1] *β-Methylglycerol*, $CH_2(OH) \cdot C(CH_3)(OH) \cdot CH_2 \cdot OH$, is prepared commercially from *iso*butylene, by a similar series of reaction.

All these, or analogous reactions, except the conversion of di- into tri-chloropropane (with the aid of iodine chloride at 140°) have already been exemplified ; as acetone may be synthesised from its elements in various ways, a complete synthesis of the important natural product, glycerol, was thus accomplished. This synthesis does not by itself constitute a rigid proof of the structure of glycerol as that of the trichloropropane had not been established, but it may now be confidently assumed that each of the three hydroxyl groups is combined to a different carbon atom (below).

Glycerol (when pure) is crystalline and melts at 18–19° ; as ordinarily prepared, however, it is a thick syrup of sp. gr. 1·26 at 15°, and does not solidify readily, owing to the presence of water and traces of other impurities. It boils at 290° under atmospheric pressure, without change ; if, however, it contains even traces of salts it undergoes slight decomposition, so that it must first be distilled under reduced pressure or in superheated steam. Glycerol is very hygroscopic; it is miscible with water and alcohol, but 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 conditioned by 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.

Structure of Glycerol. That glycerol is a trihydric alcohol is proved by the fact that it may be acetylated with acetic anhydride (p. 176), with the formation of a *triacetyl* derivative (below). Now when two hydroxyl groups are attached to the same carbon atom, as in the cases of methylene glycol (p. 240) and chloral hydrate (p. 143), the complex $>C(OH)_2$ is unstable and readily loses the elements of water ; it is improbable, therefore, that glycerol, which distils unchanged at 290°, contains such a group, so that its constitution would seem to be $CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH$. This structure is fully established by a study of the whole chemical behaviour of glycerol.

Glycerol reacts with sodium but, 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 heated with acetic acid, for example,

glycerol yields the ester, *glyceryl triacetate* (*triacetin*), b.p. 260°, and water,

$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot OH \end{array} + 3CH_3\cdot COOH = \begin{array}{l} CH_2\cdot O\cdot CO\cdot CH_3 \\ | \\ CH\cdot O\cdot CO\cdot CH_3 \\ | \\ CH_2\cdot O\cdot CO\cdot CH_3 \end{array} + 3H_2O$$

It is obvious, however, that triacetin is not the only ester which may be produced by the interaction of glycerol and acetic acid, because a *trihydric* alcohol may also yield (isomeric) *monoacetins* and *diacetins*, by the displacement of only one, or of two, atoms of hydrogen,

$$C_3H_5(OH)_3+CH_3\cdot COOH = C_3H_5(OH)_2\cdot O\cdot CO\cdot CH_3+H_2O,$$
$$C_3H_5(OH)_3+2CH_3\cdot COOH = C_3H_5(OH)(O\cdot CO\cdot CH_3)_2+2H_2O.$$

Such compounds may all be obtained 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.

Glycerol, like glycol, yields various oxidation products, according to the experimental conditions ; when carefully oxidised with dilute nitric acid, it is converted into *glyceric acid*, a change analogous to the formation of glycollic acid from glycol,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH+2O=CH_2(OH)\cdot CH(OH)\cdot COOH+H_2O,$$

but a more vigorous treatment gives a mixture of glycollic, oxalic, and carbonic acids,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH+4O=CH_2(OH)\cdot COOH+CO_2+2H_2O,$$
$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH+6O=COOH\cdot COOH+CO_2+3H_2O.$$

In the presence of ferrous sulphate, glycerol is readily oxidised by an aqueous solution of hydrogen peroxide, and is converted into *glyceraldehyde*, $CH_2(OH)\cdot CH(OH)\cdot CHO$; glycol and polyhydric alcohols in general, under these conditions, are oxidised in a similar manner (footnote, p. 243).

Glyceraldehyde is also formed together with *dihydroxyacetone*, $CH_2(OH)\cdot CO\cdot CH_2\cdot OH$, by oxidising glycerol with dilute nitric acid ; the mixture is known as *glycerose*.

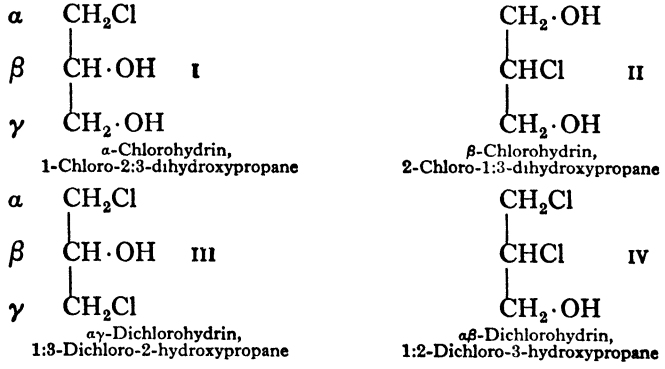
Glycerol readily undergoes decomposition into acraldehyde (p. 341) and water, a change which takes place to some extent when

impure glycerol is distilled, but much more quickly and completely when glycerol is heated with potassium hydrogen sulphate or phosphorus pentoxide. This reaction may be used as a test for glycerol, as acraldehyde has a very irritating effect on the nose.

When it is heated at about 230° with oxalic or formic acid, glycerol yields allyl alcohol (p. 340), and with phosphorus and iodine it gives allyl iodide or *iso*propyl iodide (p. 339), according to the relative quantities of the reactants.

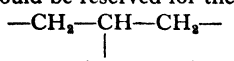
Glycerol is employed in the manufacture of nitroglycerin (p. 250) and toilet-soaps, and for lowering the freezing-point of water in motor car radiators ; it is used in smaller quantities in medicine and as an anti-putrescent in the preservation of food materials and tobacco. With phthalic anhydride it gives complex esters which are important plastics (*glyptal* or *alkyd* resins).

Glyceryl chlorohydrins. The action of concentrated hydrochloric acid on glycerol is similar to that of acetic acid. At moderate temperatures, and with relatively small proportions of the acid, one atom of chlorine is substituted for one hydroxyl group, and *glyceryl α-chlorohydrin* [1] (I) is formed, just as ethylene glycol is converted into ethylene chlorohydrin ; with an excess of hydrochloric acid, however, *glyceryl αγ-dichlorohydrin* (III) is produced.



Isomerides of (I) and (III), namely (II) and (IV) respectively, are also known ; (II) is formed with (I) from glycerol and hydrochloric

[1] The name *glyceryl*, should be reserved for the group of atoms,



which may be regarded as a tervalent radical, but it is commonly used in the names of the chlorohydroxy-derivatives.

acid, but (IV) is obtained by treating allyl alcohol (p. 340) with chlorine. The alternative names given above, which express the structures of the compounds, are based on the system of nomenclature already explained (p. 81).

Glyceryl trichloride, *αβγ-trichloropropane*, $CH_2Cl \cdot CHCl \cdot CH_2Cl$, 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 liquid which boils at 158°, and smells like chloroform.

Certain *glycerophosphates* are of great importance (p. 630).

Nitroglycerin, *glyceryl trinitrate*, $C_3H_5(O \cdot NO_2)_3$, is the glyceryl ester of 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 product is run into cold water, and the nitroglycerin, which separates as a heavy oil, is washed well with water and left to dry in the air.

It is an extremely dangerous substance, and its preparation is safe only to expert chemists; it is even more dangerous in the solid state (m.p. 13°) than in the liquid condition.

It is an odourless oil of sp. gr. 1·6 at 15°, 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 widely different from that of glycerol, a fact which shows the influence of hydroxyl groups very clearly. It explodes with great violence (detonates) when it is suddenly heated or subjected to percussion, but when ignited with a flame, in very small quantities, it burns quietly.

Nitroglycerin is readily decomposed by boiling water and by potassium carbonate solution with the formation of some glycerol and nitric acid or a nitrate,

$$C_3H_5(O \cdot NO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3,$$

but with these and other hydrolysing agents further changes occur and glyceric, oxalic and possibly formic and acetic acids, or their salts, may be produced.

It is known, however, that with potassium hydroxide solution

two molecules of potassium *nitrite* are formed from one molecule of nitroglycerin, possibly as expressed by either of the following equations,

$$C_3H_5(O\cdot NO_2)_3+5KOH = CH_3\cdot COOK+H\cdot COOK+KNO_3+2KNO_2+3H_2O,$$

$$C_3H_5(O\cdot NO_2)_3+4KOH = CH_2(OH)\cdot CH(OH)\cdot COOK+KNO_3+2KNO_2+2H_2O,$$

and this fact is made use of in the estimation of nitroglycerin in pharmaceutical preparations.

The fact that nitroglycerin, like ethyl nitrate (p. 191) can be hydrolysed, whereas nitroethane (p. 193) is stable towards alkalis, shows that the $-NO_2$ groups in the former are directly combined with oxygen and not with carbon. The name nitroglycerin, therefore, is misleading, but, being so well known, it is employed here instead of the more correct name, glyceryl trinitrate.

Nitroglycerin is extensively employed as an explosive, sometimes alone, sometimes in the form of *dynamite*, a mixture of nitroglycerin and kieselguhr ;[1] dynamite is less liable to explode, and, consequently, safer to handle and to transport than nitroglycerin alone. The presence of acids makes nitroglycerin prone to undergo spontaneous decomposition and explosion ; great care, therefore, must be taken to wash it thoroughly. Nitroglycerin is also employed, mixed with gun-cotton (p. 329), as blasting-gelatine (gelignite), and in the preparation of smokeless 'gunpowder' (cordite) ; it is used in medicine in cases of heart disease.

Glycerol undergoes condensation when it is heated (usually in the presence of some catalyst), giving mixtures of *hydroxy-ethers*, such as *di-glycerol*, ($2C_3H_8O_3—H_2O$), and *tri-glycerol*, ($3C_3H_8O_3—2H_2O$) ; these hygroscopic products are used for softening leather, and when esterified with the higher fatty acids they give emulsifying agents.

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 being cooled, and is known as *tallow*. The fat

[1] A very porous powder, consisting of the siliceous remains of small marine animals.

obtained from pig-suet, in a similar manner, is much softer, and is called *lard*.

When tallow is heated with water in closed vessels at about 200°, it undergoes decomposition into glycerol, which passes into solution, and fatty acids, which separate at the surface. In the presence of small proportions—2 to 3 %—of accelerators, such as magnesium oxide, lime, and zinc oxide, the reaction proceeds at a lower temperature (140–150°). A similar hydrolysis occurs when tallow is heated with dilute sulphuric acid, but some of the glycerol may be decomposed and charred.

All animal fats—such as lard, goose fat, bone fat, butter, etc., and the fatty vegetable oils, such as olive, linseed, rape, palm, and cotton-seed oil, which are obtained by pressing the seeds or fruit of certain plants—behave in the above manner, and when heated with dilute sulphuric acid or with water, under pressure, they are decomposed into glycerol and a mixture of acids, most of which belong to the $C_nH_{2n}O_2$ series. 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 were investigated by Chevreul, who showed them to be esters of the fatty acids derived from the trihydric alcohol, glycerol. These esters are collectively termed *glycerides*, and are named after the acids from which they are formed. The glyceride formed from acetic acid is called *triacetin*; that from palmitic acid, *tripalmitin*; that from stearic acid, *tristearin*; and that from oleic acid (p. 343), *triolein*.

Such ' simple ' glycerides, however, are found in fats and oils in small proportions only; the chief components are ' mixed ' glycerides in which two or more fatty acids are combined with glycerol. Lard, for example, contains palmitodistearin, stearodipalmitin, oleopalmitostearin, and palmitodiolein. When a fat contains in combination a relatively large proportion of palmitic or stearic acid, it is solid and comparatively hard (tallow) at ordinary temperatures; when, however, it contains a relatively large proportion of combined oleic acid, it is soft and pasty (lard), or liquid (olive oil).

These glycerides, like other esters, are decomposed by water and by dilute mineral acids at moderately high temperatures, and are

converted into glycerol and an acid ; in the case of tristearin, for example,

$$\begin{array}{l} CH_2\cdot O\cdot CO\cdot C_{17}H_{35} \\ | \\ CH\cdot O\cdot CO\cdot C_{17}H_{35} \\ | \\ CH_2\cdot O\cdot CO\cdot C_{17}H_{35} \end{array} + 3H_2O = \begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot OH \end{array} + 3C_{17}H_{35}\cdot COOH$$

Tristearin — Glycerol — Stearic acid

Since fats and oils consist of mixed glycerides, they yield mixtures of various fatty and other acids.

Soaps. When boiled with alkalis, the glycerides are decomposed much more rapidly than by water, and alkali salts of the acids are formed, together with glycerol. In manufacturing soaps, a mixture of fats or oils, such as tallow, palm oil, palm kernel oil, or coconut oil, is heated in an iron pan with a sufficient quantity of a solution of sodium hydroxide ; after some time there is formed a thick, homogeneous, frothy solution, which contains glycerol and the salts of the various acids, which were present in the glycerides—that is to say, the sodium salts of stearic, palmitic, oleic, and related acids. Some common salt is now added, whereon the sodium salts separate at the surface as a curd, because they are insoluble in salt water. After settling for some hours, the lower layer, a solution of glycerol and salt, is run off, and the curd, which contains some salt and alkali, is boiled with sufficient water to give a homogeneous liquid, after which salt is again added and the curd layer re-formed. After further treatments, involving boiling, salting, and settling, there is finally obtained a homogeneous liquid which solidifies to a *hard soap*, and (unless previously mixed with ' filling ' materials, such as salt, sodium silicate, sodium carbonate) is known as ' genuine ' soap. It consists of a mixture of the sodium salts of the fatty acids originally present as glycerides in the fats or oils, together with water, small proportions of salt and glycerol, and a little alkali.

When fats or oils are boiled with caustic potash, instead of with caustic soda, similar chemical changes take place, and the potassium salts of the acids are formed ; the homogeneous solution is allowed to cool, whereon it sets to a jelly-like mass of *soft soap*, which is a mixture of the potassium salts of the above-named acids with glycerol and a large percentage of water.

The decomposition of fats and oils in this way, in the process of soap-making, was formerly called *saponification*, and the fats and

oils were said to be *saponified*. The term saponification was then applied generally to the analogous decomposition of other esters by alkalis (in spite of the fact that the products were not soaps), but the word *hydrolysis* is now used instead.

Stearin and Glycerol. Stearin consists principally of a mixture of stearic and palmitic acids, and is manufactured by decomposing tallow and other fats or oils with water or dilute sulphuric acid (or milk of lime), under pressure. The aqueous layer is run off and treated for the recovery of glycerol, and the liberated fatty acids are purified by distillation in superheated steam. After having been cooled, the pasty mixture of acids is pressed in order to squeeze out as much of the liquid oleic acid (olein) as possible. The pressed mass is then gently warmed, and pressed again between warm plates, when a further quantity of olein is removed, together with some palmitic and stearic acids. The hard mass that remains is called *stearin*; it is employed in the manufacture of toilet preparations, and also, after admixture with paraffin to make it less brittle, in large quantities in the manufacture of candles. The liquid or pasty mass of oleic, palmitic, and stearic acids which is separated from the stearin, and known as *olein*, is employed for the preparation of soap.

Glycerol is obtained from the aqueous layer, after the fatty acids have been removed; the solution is treated with lime or baryta to neutralise the free acid, filtered and evaporated to a thick syrup. This crude glycerin is distilled under reduced pressure in superheated steam, and finally decolourised by filtration through charcoal.

The process devised by Twitchell, next to that involving the use of alkali, is probably the one most widely used at the present time for the hydrolysis of fats and oils on an industrial scale. In this process the hydrolysis is accomplished by the use of a reagent, which Twitchell originally prepared by the interaction of a mixture of oleic acid, benzene, and sulphuric acid, and which may be regarded as a *sulphobenzenestearic acid*;[1] it acts mainly as an emulsifier. The oil or fat, together with an approximately equal quantity of water, is raised to 100° and about 1% of the reagent, calculated on the fat, is added; hydrolysis is complete in about thirty hours.

Another method of hydrolysis, now little used, is carried out with the aid of an enzyme (*lipase*) which occurs in castor oil and in

[1] Instead of benzene, naphthalene is frequently used and to the reagent thus prepared, the composition, $C_{18}H_{36}O_2 \cdot C_{10}H_8 \cdot SO_3H$, has been assigned.

many other oils. The fat or oil (100 parts) is merely left in contact with water (35–40 parts) and an extract of lipase (6–7 parts); at the end of about two days, upwards of 90% of the fat has been hydrolysed, but the action of the enzyme (as in the case of many other enzymes) is reversible, and a condition of equilibrium is attained before hydrolysis is complete. The products (fatty acids, oleic acid, and glycerol) are treated as described above.

Butter. Butter, prepared from cream, is a mixture of fat (about 82·5%), water (about 14·5%), and small proportions of casein, milk-sugar, and salts. Pure butter fat consists mainly of the glycerides of palmitic and oleic acids and small proportions of the glycerides of myristic, butyric, caproic, caprylic, and other acids; it differs from other fats in containing a relatively high proportion of water-soluble acids, notably butyric, and some caproic and caprylic acids. The rancidity of butter and other fats is the result of the hydrolysis of the glycerides by enzymes (p. 331), and the atmospheric oxidation of the unsaturated acids.

Margarine consists of an emulsion prepared by churning suitable mixtures of animal and vegetable oils or fats with milk. The oils and fats used are those which are obtained naturally, like neutral lard, free from objectionable odour or taste, and oils like coconut, cotton-seed, groundnut, and palm kernel oil, which have been so obtained after a process of refining; hydrogenated oils (below) are also incorporated. The oils and fats are blended to a consistency suitable to the climate and time of the year at which they are used. The milk before use is submitted to a process of ripening by bacterial treatment with suitable cultures to produce a butter-like flavour, and the dietetic value of the margarine is improved by the addition of those vitamins (A and D) which occur in butter.

The Hardening of Oils. The solid animal fats which consist largely of the glycerides of palmitic and stearic acids are not nearly so abundant as the vegetable oils, which contain a relatively much larger proportion of the liquid glyceride of oleic acid. Moreover, the saturated acids obtained by the hydrolysis of fats are much more valuable than the liquid unsaturated acids, inasmuch as they alone can be used directly for the manufacture of stearin candles, and for many other purposes; they also give harder and better soaps than those prepared from mixtures of acids containing a large proportion of some of the liquid unsaturated acids.

Now oleic acid is known to be an olefinic derivative of normal

stearic acid (p. 173), and *linoleic acid*, $C_{18}H_{32}O_2$ (p. 345), another unsaturated acid, which occurs as glyceride in many oils, is a di-olefinic derivative of stearic acid. It is evident, therefore, that stearic acid might theoretically be produced by the reduction of these two oily unsaturated compounds ; but on a large scale this was found to be impossible practically with the aid of any ordinary reducing agents. The researches of Sabatier (p. 405) pointed to a new way of attacking this very important problem, and experiments then showed that oleic acid could be reduced to stearic acid by treating it with hydrogen, in the presence of a nickel catalyst, under suitable conditions.

Later, it was discovered by Ipatiew that, instead of the metal, an oxide of nickel could be employed with satisfactory results ; moreover, the oxide was not poisoned (p. 407) so readily as the metal, and consequently had not to be renewed so frequently ; when the oxide was used, however, it was generally necessary to work under considerable pressure, otherwise the reduction took place too slowly.

The discovery of these methods for the reduction of the unsaturated acids in the liquid state was followed by the reduction of the glycerides themselves, and the hardening of oils on the large scale is now carried out as follows :

Free acids, if present in proportions of more than 2–3%, are first neutralised by agitating the oil with lime or with a very dilute solution of sodium hydroxide. The oil is then freed from water and clarified by agitation with Fuller's earth or charcoal, followed by filtration.

The nickel catalyst is prepared by mixing pumice, kieselguhr, asbestos, charcoal, or other 'support' with a solution of nickel sulphate, then adding sodium carbonate and boiling the mixture ; the 'support,' intimately incorporated with nickel carbonate, is washed until free from soluble salts, dried, and heated at 300–400° in an atmosphere of hydrogen, whereon the carbonate is converted partly into oxide and partly into metal. The purified oil is now mixed with 0·5–1% of its weight of the catalyst, heated at about 180°, and pure hydrogen is passed into the well-agitated mixture under a pressure of 2–5 atmospheres. The progress of the hydrogenation is followed by determining the iodine value [1] of the oil,

[1] The iodine value is the weight in grams of iodine chloride, ICl, expressed in terms of iodine, which combines with 100 g. of the oil or fat; it corresponds with the proportion of unsaturated compounds present in the sample.

which falls gradually as reduction proceeds. An oil such as whale oil, which does not easily solidify, may be thus transformed into a solid fat, which can be advantageously utilised in soap-making, etc.; if this fat is then hydrolysed, the solid mixture of acids obtained from it can be used for the same purposes as those for which stearin is employed. Another advantage of hardening oils is that, as a rule, they thereby lose the very disagreeable smell, which some of them (particularly the fish-oils) possess; they may then be used, in conjunction with natural fats and oils, in the manufacture of margarine.

Drying of Oils. Some oils, such as linseed oil, which contain glycerides of unsaturated acids, possess the useful property of 'drying' when they are exposed to the air. During this change the oils are transformed into a tough resinous mass. This is due primarily to the oxidation of the unsaturated acids contained in the oil, and may be hastened by the addition of various catalysts, chiefly oxides of metals such as red-lead, which are known as 'driers.' Drying oils are used in the manufacture of paints, oil-cloth, etc.

Polyhydric Alcohols

The existence of tetra-, penta-, and hexa-hydric alcohols, which theoretically might 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, might of course be expected; nevertheless, owing to the difficulties which would have been met with in the actual synthesis of such hydroxy-derivatives from the paraffins, or from other compounds, it is not impossible that they might still have been unknown, were it not that some of them occur in nature, or may be prepared from certain 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.

Pentaerythritol, tetrahydroxytetramethylmethane, $C(CH_2\cdot OH)_4$, is formed from a mixture of acetaldehyde and formaldehyde by the action of slaked lime at 60–65°,

$$2CH_3\cdot CHO+8H\cdot CHO+Ca(OH)_2 = 2C(CH_2\cdot OH)_4+(H\cdot COO)_2Ca;$$

it melts at 250–252°, and its *tetranitrate*, $C(CH_2\cdot O\cdot NO_2)_4$, *penthrite*, is an important explosive, related to nitroglycerin.

Arabitol and *xylitol* are *optically isomeric* (p. 291) 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 sugars (aldehydes) which are obtained from various vegetable products, with sodium amalgam and water.

Hexahydric alcohols, such as *mannitol*, *sorbitol*, and *dulcitol*, also occur in nature; these three compounds are *identical* in constitution, and they are all represented by the formula,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH;$$

they are *optical isomerides*.

Mannitol 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 mannose or fructose (pp. 313, 314) with sodium amalgam and water. It is crystalline (m.p. 166°), has a 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, *fructose*.

On reduction with hydriodic acid, mannitol, sorbitol and dulcitol are converted into (secondary)[1] hexyl iodide (2-iodohexane), a derivative of the normal hydrocarbon; this is a fact of great importance, as it throws light on the constitutions not only of the hexahydric alcohols, but also on those of the monosaccharides in general (p. 315).

That the molecules of mannitol, sorbitol and dulcitol contain six hydroxyl groups is shown by the fact that they yield hexa-acetyl derivatives, $C_6H_8(O\cdot CO\cdot CH_3)_6$, and hexanitrates, $C_6H_8(O\cdot NO_2)_6$, and for reasons already given (p. 247), it must be concluded that each of the six hydroxyl groups must be combined with a different carbon atom. This conclusion is confirmed and the structures fully established by many other facts.

SUMMARY AND EXTENSION

The Glycols, or dihydric alcohols, form a homologous series of the general formula, $C_nH_{2n}(OH)_2$, and are derived from the paraffins by the substitution of two hydroxyl groups for two hydrogen atoms not

[1] The term 'secondary' distinguishes the iodide as a derivative of a secondary (hexyl) alcohol, $CH_3\cdot[CH_2]_3\cdot CH(OH)\cdot CH_3$. An isomeric iodide, $CH_3\cdot CH_2\cdot CH_2\cdot CHI\cdot CH_2\cdot CH_3$, is also produced.

attached to the same carbon atom. A few important members of the series are the following :

Name	Constitution	B.p.
Ethylene glycol	$C_2H_4(OH)_2$	197°
$\alpha\beta$-Propylene glycol	$CH_3 \cdot CH(OH) \cdot CH_2 \cdot OH$	188°
$\alpha\gamma$-Propylene (or trimethylene) glycol	$CH_2(OH) \cdot CH_2 \cdot CH_2 \cdot OH$	214°
$\beta\gamma$-Butylene glycol	$CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$	184°
$\beta\gamma$-Dimethyl-$\beta\gamma$-butylene glycol or pinacol	$(CH_3)_2C(OH) \cdot C(OH)(CH_3)_2$	172°

Nomenclature. The glycols are named as dihydroxy-derivatives of the paraffins and the positions of the HO— groups are shown by letters or numbers in the usual way. They may also be named as additive products of olefines, or of radicals, isomeric with olefines, as above, with the addition of *glycol* to denote the two hydroxyl groups. Glycols produced by the reduction of ketones or aldehydes (p. 155) are often distinguished as *pinacols*. Tri- and poly-hydric alcohols have usually trivial names ; their systematic nomenclature is based on that of the paraffins.

Preparation. (1) Alkylene halides are heated with silver acetate (and acetic acid) and the products are hydrolysed (Wurtz),

$$C_2H_4I_2+2CH_3 \cdot CO \cdot OAg = C_2H_4(O \cdot OC \cdot CH_3)_2+2AgI,$$
$$C_2H_4(O \cdot OC \cdot CH_3)_2+2KOH = C_2H_4(OH)_2+2CH_3 \cdot CO \cdot OK ;$$

some alkylene halides may be hydrolysed directly with sodium carbonate solution, but with caustic alkalis they often lose the elements of a halogen acid, and give first a substituted olefine, and then an acetylenic derivative.

(2) Olefines are oxidised with alkaline permanganate, or converted into chlorohydrins, which are then hydrolysed,

$$C_2H_4+H_2O+O = C_2H_4(OH)_2,$$
$$C_2H_4+HOCl = C_2H_4(OH)Cl \longrightarrow C_2H_4(OH)_2.$$

(3) Olefines are oxidised with perbenzoic acid and the oxides so formed are hydrolysed,

$$>C:C< \longrightarrow >C\underset{\diagdown\,O\,\diagup}{-}C< \longrightarrow >C(OH) \cdot C(OH)<$$

(4) Esters (or amides) of the *higher* dicarboxylic acids are reduced with sodium and alcohol,

$$[CH_2]_7<\begin{matrix}COOEt\\COOEt\end{matrix}+8H = [CH_2]_7<\begin{matrix}CH_2 \cdot OH\\CH_2 \cdot OH\end{matrix}+2EtOH.$$

(5) Ketones are treated with magnesium amalgam in the absence of water, and the magnesium compounds, $\begin{matrix} R_2C\cdot O \\ | \\ R_2C\cdot O \end{matrix}\!\!>\!Mg$, which are formed, are decomposed with dilute acids.

(6) Di-primary amines are treated with nitrous acid,

$$NH_2\cdot[CH_2]_n\cdot NH_2+2HNO_2 = HO\cdot[CH_2]_n\cdot OH+2N_2+2H_2O.$$

(7) Esters or ketones containing two carbonyl groups are treated with Grignard reagents and the products are decomposed with acids,

$$\begin{matrix} CH_2\cdot COOEt \\ | \\ CH_2\cdot COOEt \end{matrix} \xrightarrow{CH_3MgI} \begin{matrix} CH_2\cdot C(CH_3)_2\cdot OH \\ | \\ CH_2\cdot C(CH_3)_2\cdot OH \end{matrix}$$

Properties. The glycols are neutral, sweet, viscid liquids; the solubility in water diminishes as the hydrocarbon radical increases in molecular weight. They react with sodium, phosphorus halides, acids, etc., one or both of the hydroxyl groups taking part in the reaction. Their behaviour on oxidation is also normal.

Lead tetra-acetate is a good reagent for oxidising glycols in which the hydroxyl groups are combined with adjacent carbon atoms; ketones or mixtures of ketones and aldehydes are produced,

$$R_2C(OH)\cdot C(OH)R_2+Pb(OAc)_4 = 2R_2CO+2Ac\cdot OH+Pb(OAc)_2.$$

The **trihydric alcohols,** of which glycerol is by far the most important, have the general formula, $C_nH_{2n-1}(OH)_3$. Glycerol occurs in oils and fats, which consist for the most part of mixtures of glyceryl esters of various organic acids, the most abundant of which are palmitic, stearic, and oleic acids. It is manufactured from these esters or from propylene. Glycerol shows the properties which would be expected of a compound containing three hydroxyl groups, and gives, for example, glyceryl trinitrate with nitric acid.

When glycerol is heated with formic or oxalic acid it yields allyl alcohol; with iodine and phosphorus, allyl iodide or *iso*propyl iodide; and with potassium hydrogen sulphate, acraldehyde; in all these reactions the initial normal products undergo change. Glycerol yields various compounds by the displacement of its hydroxyl groups by chlorine.

Glyceryl *α-chlorohydrin* is obtained, together with small quantities of the β-compound, when glycerol is heated at 105–110° with hydrochloric acid; it is a thick liquid, soluble in water. Glyceryl *β-chlorohydrin* can be obtained by treating allyl alcohol with hypochlorous acid.

Glyceryl *αγ-dichlorohydrin* is produced when glycerol is heated with a solution of hydrogen chloride in glacial acetic acid ; on oxidation with chromic acid it yields symmetrical *dichloroacetone*,

$$CH_2Cl \cdot CO \cdot CH_2Cl.$$

Glyceryl *αβ-dichlorohydrin* may be obtained by treating allyl alcohol with chlorine ; on oxidation with nitric acid it gives *αβ-dichloropropionic acid*, $CH_2Cl \cdot CHCl \cdot COOH$. When treated with potash, both the αβ- and the αγ-dichlorohydrins yield epi*chlorohydrin*,

$$CH_2Cl—CH<\overset{CH_2}{\underset{O}{\cdot}},$$

a liquid b.p. 117°.

When glycerol is treated with acetyl chloride it does not yield triacetin, as might have been expected, but glyceryl *chlorohydrin diacetate*,

$$C_3H_5(OH)_3+2CH_3 \cdot COCl = C_3H_5Cl(O \cdot CO \cdot CH_3)_2+H_2O+HCl.$$

This behaviour, although apparently abnormal, is not really so ; the hydrogen chloride, produced during the earlier stages of the reaction, acts on the hydroxydiacetyl derivative, just as it does on other monohydric alcohols,

$$C_3H_5(O \cdot CO \cdot CH_3)_2 \cdot OH+HCl = C_3H_5(O \cdot CO \cdot CH_3)_2Cl+H_2O.$$

The **tetra-, penta-,** and **hexa-hydric alcohols** are important because of their close relationship to the monosaccharides (p. 310) ; all those which are obtained by the reduction of a monosaccharide are derived from *normal* paraffins.

CHAPTER 17

HYDROXY-ACIDS AND DICARBOXYLIC ACIDS

Monohydroxymonocarboxylic Acids

THE monohydroxymonocarboxylic acids are derived from the fatty acids by the displacement of one of their hydrogen atoms by a hydroxyl group, just as the alcohols are derived from the paraffins ; they therefore form a homologous series of the general formula, $C_nH_{2n}(OH)(COOH)$. They may also be regarded as oxidation products of the glycols: *glycollic acid* or *hydroxyacetic acid*, $HO \cdot CH_2 \cdot COOH$, for example, is formed by the oxidation of ethylene glycol, and higher members of the series may be obtained in a similar manner.

The first member of the series is *hydroxyformic acid*, $HO \cdot COOH$, better known as *carbonic acid*, which differs from the other members of the series in being a *dibasic*, but not a dicarboxylic, acid ; its salts are described in text books of inorganic chemistry, but a short account of some of its non-metallic derivatives is given below.

Carbonyl chloride, *phosgene*, $COCl_2$, is obtained by the direct combination of carbon monoxide and chlorine in sunlight or in the presence of a catalyst, such as charcoal. It boils at 8° and decomposes slowly in contact with water into carbon dioxide and hydrochloric acid. When it is treated with alcohol it gives ethyl chloroformate and diethyl carbonate, and with ammonia it yields urea (p. 263). It is used in the preparation of a few dyes, and was employed very largely during the war of 1914-18 as a poison gas.

Ethyl chloroformate, *ethyl chlorocarbonate*, $Cl \cdot CO \cdot OC_2H_5$, is prepared by the action of carbonyl chloride on alcohol,

$$COCl_2 + C_2H_5 \cdot OH = Cl \cdot CO \cdot OC_2H_5 + HCl ;$$

it is a pungent-smelling liquid boiling at 93°. It reacts with alcohols, phenols (p. 478), and with primary and secondary amines, yielding *carbethoxy*-derivatives,

$$R \cdot OH + Cl \cdot CO \cdot OEt = R \cdot O \cdot CO \cdot OEt + HCl,$$
$$R_2NH + Cl \cdot CO \cdot OEt = R_2N \cdot CO \cdot OEt + HCl ;$$

these reactions are usually carried out in the presence of dilute alkalis.

Diethyl carbonate, *ethyl carbonate*, $CO(OC_2H_5)_2$, is prepared by treating ethyl chloroformate with alcohol; it boils at 126°.

Xanthic acid, $S{:}C(OC_2H_5)SH$, or ethyl hydrogen dithiocarbonate, does not exist in the free state; its crystalline *potassium salt* is obtained by the action of alcoholic potash on carbon disulphide,

$$KOH+CS_2+C_2H_5\cdot OH = S{:}C(OC_2H_5)SK+H_2O.$$

Cellulose esters of xanthic acid are prepared in making artificial silk (viscose) by treating alkali cellulose with carbon disulphide (p. 330).

Urea, *carbamide*, $CO(NH_2)_2$, is a compound of very great physiological importance. It occurs in the urine of mammals and the excreta of birds and reptiles, and is one of the principal nitrogenous components of human urine, of which it forms about 3%.

It was discovered in urine in 1773 (Rouelle), and was first artificially produced in 1828 by Wöhler, who showed that it was formed, together with oxalic acid, when cyanogen was passed into an aqueous solution of ammonium hydroxide, and the solution of ammonium cyanate was then evaporated,

$$C_2N_2+2NH_4OH = NH_4CN+NH_4\cdot OCN+H_2O,$$
$$NH_4\cdot OCN \longrightarrow CO(NH_2)_2;$$

this was the first synthesis of an 'organic' compound (p. 1).

Ammonium cyanate and urea are *isomeric*, and the transformation of the one into the other is therefore called an *isomeric change* because it merely involves a rearrangement of the atoms of the molecule, the ionic structure $[NH_4]OCN$ being transformed into $NH_2\cdot CO\cdot NH_2$; the reaction is reversible and at the equilibrium point the solution contains only about 5% of the ammonium salt.

Urea may be obtained by evaporating urine to a small bulk and adding strong nitric acid. The precipitate of crude *urea nitrate* (p. 265) 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 in the laboratory by mixing a solution of potassium cyanate (16 g.) with an equivalent quantity of ammonium sulphate (13 g.), evaporating the solution to dryness, extracting the residue with alcohol, and concentrating the filtered extract.

Urea may also be obtained synthetically by treating diethyl carbonate, or 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 is manufactured by hydrolysing cyanamide (p. 363) with a weak acid,

$$NH_2\cdot CN+H_2O = NH_2\cdot CO\cdot NH_2,$$

or by heating together ammonia and carbon dioxide under pressure,

$$2NH_3+CO_2 = NH_2\cdot COONH_4,$$
$$NH_2\cdot COONH_4 = NH_2\cdot CO\cdot NH_2+H_2O.$$

It crystallises in needles, melts at 132°, and is readily soluble in cold water and alcohol, but almost insoluble in ether; unlike an ammonium salt, urea is *not* immediately decomposed by a cold solution of sodium carbonate, but is rapidly hydrolysed when it is heated with aqueous alkalis, with the evolution of ammonia. When heated alone at about 155°, it melts and then decomposes, giving ammonia, *biuret*, *cyanuric acid*, and other compounds; the first products are ammonia and cyanic acid (p. 362) and the latter combines with urea, giving biuret,

$$NH_2\cdot CO\cdot NH_2+HNCO = NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

but some polymerises to *cyanuric acid* (p. 366) and *cyamelide* (p. 362). An aqueous solution of the residue gives with a few drops of copper sulphate solution, and a few drops of dilute potash, a violet or pink colouration (*biuret reaction*).

Urea is decomposed by nitrous acid, giving nitrogen, carbon dioxide, and water, both the NH_2— being displaced by HO— groups,

$$CO(NH_2)_2+2HNO_2 = CO(OH)_2\{CO_2+H_2O\}+2N_2+2H_2O;$$

a similar change takes place when urea is treated with alkaline solutions of hypochlorites or hypobromites,

$$CO(NH_2)_2+3NaOCl+2NaOH = Na_2CO_3+3NaCl+N_2+3H_2O;$$

from the volume of nitrogen obtained in the latter reaction, under particular conditions, the quantity of urea in a solution can be approximately estimated.

Urea is converted into ammonium carbonate by an enzyme,

urease, which is present in most soils, and also in soya- and Jack-beans,

$$CO(NH_2)_2+2H_2O = (NH_4)_2CO_3;$$

the most accurate method for the estimation of urea is based on this reaction, the resulting ammonium carbonate being titrated with an acid.

Urea is basic and combines with *one* equivalent of an acid to form salts, most of which are readily soluble in water. *Urea nitrate*, $CO(NH_2)_2,HNO_3$, crystallises in plates, and is sparingly soluble in nitric acid; with cold concentrated sulphuric acid it gives *nitrourea*, $NH_2\cdot CO\cdot NH\cdot NO_2$. *Urea oxalate*, $\{CO(NH_2)_2\}_2,H_2C_2O_4$, crystallises in prisms and is sparingly soluble in water; these and other salts of urea give a vigorous effervescence with sodium carbonate and might be easily mistaken for organic acids.

Urea is used as a fertiliser in agriculture; also for the manufacture of synthetic resins and various drugs.

Constitution. The formation of urea from diethyl carbonate and from the chloride of carbonic acid (carbonyl chloride) are reactions analogous to those which take place in the formation of acetamide from ethyl acetate and acetyl chloride respectively; urea, therefore, may be represented by the formula, $NH_2\cdot CO\cdot NH_2$, and regarded as the di-amide of carbonic acid—hence the name *carbamide*. Carbonyl chloride, $Cl\cdot COCl$, may also be regarded as the acid chloride of chloroformic acid, $Cl\cdot COOH$, and urea as the *amide* of *aminoformic acid*. The *urethanes* (p. 223) are closely related both to aminoformic acid and to urea.

Compounds derived from a tautomeric form of urea, called *iso-urea*, $HN{:}C(OH)\cdot NH_2$, are known.

Guanidine, '*iminourea*,' $NH_2\cdot C(:NH)\cdot NH_2$, was first prepared by Strecker in 1861 by the oxidation of *guanine*, a product of animal origin. It may be synthesised by treating cyanogen iodide (p. 354) with ammonia, cyanamide (p. 363) being formed as an intermediate product,

$$NH_2\cdot C{\vdots}N+H\cdot NH_2 = NH_2\cdot C(:NH)\cdot NH_2.$$

It is conveniently prepared by heating ammonium thiocyanate at 170–200°, whereon the thiourea (p. 364), which is first produced, reacts with unchanged ammonium thiocyanate, yielding guanidine thiocyanate,

$$NH_2\cdot CS\cdot NH_2+NH_2,HS\cdot CN = NH_2\cdot C(:NH)\cdot NH_2,HS\cdot CN+H_2S.$$

Guanidine forms deliquescent crystals, and is readily soluble in water; it is a strong mono-acidic base, and of its salts the nitrate, $NH_2 \cdot C(:NH) \cdot NH_2, HNO_3$, like urea nitrate, is sparingly soluble in water. The base is decomposed by a boiling solution of barium hydroxide, giving urea and ammonia.

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 *amino-guanidine*, $NH_2 \cdot C(:NH) \cdot NH \cdot NH_2$. When the latter is warmed with acids, it yields *semicarbazide*,

$$NH_2 \cdot C(:NH) \cdot NH \cdot NH_2 + H_2O = NH_2 \cdot CO \cdot NH \cdot NH_2 + NH_3,$$

which may be further hydrolysed into ammonia, carbon dioxide, and *hydrazine*,

$$NH_2 \cdot CO \cdot NH \cdot NH_2 + H_2O = NH_3 + CO_2 + NH_2 \cdot NH_2.$$

Semicarbazide, *aminourea*, $NH_2 \cdot CO \cdot NH \cdot NH_2$, may be obtained from hydrazine sulphate and potassium cyanate, just as urea may be obtained from ammonium sulphate and potassium cyanate,

$$NH_2 \cdot NH_3 \cdot CNO \longrightarrow NH_2 \cdot CO \cdot NH \cdot NH_2,$$

but it is usually prepared by reducing nitrourea. It melts at 96°, is basic, and is an important reagent for aldehydes and ketones.

Glycollic acid, *hydroxyacetic acid*, $HO \cdot CH_2 \cdot COOH$, the second member of the series, $C_nH_{2n}(OH) \cdot COOH$, may be produced by the oxidation of glycol, just as acetic acid may be obtained by the oxidation of alcohol,

$$\begin{matrix} CH_2 \cdot OH \\ | \\ CH_2 \cdot OH \end{matrix} + 2O = \begin{matrix} CH_2 \cdot OH \\ | \\ COOH \end{matrix} + H_2O,$$

but as several oxidation products are formed, the isolation of the acid might be very troublesome. It is also formed when amino-acetic acid (glycine, p. 222) is treated with nitrous acid, a reaction exactly analogous to the conversion of ethylamine into ethyl alcohol,

$$\begin{matrix} CH_2 \cdot NH_2 \\ | \\ COOH \end{matrix} + HO \cdot NO = \begin{matrix} CH_2 \cdot OH \\ | \\ COOH \end{matrix} + H_2O + N_2.$$

Glycollic acid is prepared by boiling the potassium salt of chloro-acetic acid with water, whereon the hydroxyl group is substituted for

the atom of chlorine, just as in the formation of alcohol from ethyl chloride,

$$\begin{matrix}CH_2Cl \\ | \\ COOK\end{matrix} + H_2O = \begin{matrix}CH_2\cdot OH \\ | \\ COOH\end{matrix} + KCl.$$

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.

Since its constitution is established by its methods of formation it is almost unnecessary to describe at length the chemical behaviour of glycollic acid, because this is summarised in its structural formula. Its molecule contains one carboxyl group ; therefore, like the fatty acids, it is a monobasic acid and forms salts with metallic hydroxides and esters 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 first glyoxylic acid and then oxalic acid, just as alcohol gives acetaldehyde and acetic acid,

$$\begin{matrix}CH_2\cdot OH \\ | \\ COOH\end{matrix} \longrightarrow \begin{matrix}CHO \\ | \\ COOH\end{matrix} \longrightarrow \begin{matrix}COOH \\ | \\ COOH\end{matrix}$$

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 an alkali metal and by the acetyl group ; *ethyl glycollate*, for example, is readily converted into an acetyl derivative on treatment with acetyl chloride,

$$\begin{matrix}CH_2\cdot OH \\ | \\ COOC_2H_5\end{matrix} + CH_3\cdot COCl = \begin{matrix}CH_2\cdot O\cdot CO\cdot CH_3 \\ | \\ COOC_2H_5\end{matrix} + HCl.$$

Lactic acid, *α-hydroxypropionic acid*, $CH_3\cdot CH(OH)\cdot COOH$, is formed during the lactic fermentation of sugars, starch, and other substances, and is present in sour milk (Scheele, 1780).

It can be obtained by methods analogous to those given in the case of glycollic acid—namely, by oxidising *αβ*-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, dilute aqueous alkalis, or moist silver oxide,

$$CH_3 \cdot CHBr \cdot COOH + H_2O = CH_3 \cdot CH(OH) \cdot COOH + HBr,$$

and by treating α-aminopropionic acid (*alanine*) 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 can also be synthesised from acetaldehyde as described later (p. 270).

It is prepared by the lactic fermentation of sugar (p. 172).

Lactic acid, as usually obtained, is a thick, sour liquid, miscible with water, alcohol, and ether ; when pure it is crystalline and melts at 18°. It cannot be distilled under atmospheric pressure, as it undergoes decomposition into acetaldehyde, water, carbon monoxide, and other products. When heated with dilute sulphuric acid it is decomposed into acetaldehyde 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 salts and esters.

Calcium lactate, $(C_3H_5O_3)_2Ca$, $5H_2O$, and *zinc lactate*, $(C_3H_5O_3)_2Zn$, $3H_2O$, are crystalline ; the latter is sparingly soluble in cold water. *Ethyl lactate*, $CH_3 \cdot CH(OH) \cdot COOC_2H_5$, is prepared commercially from acetaldehyde cyanohydrin, which is heated with alcohol and sulphuric acid,

$$CH_3 \cdot CH(OH) \cdot CN + C_2H_5 \cdot OH + H_2SO_4 + H_2O = CH_3 \cdot CH(OH) \cdot COOC_2H_5 + NH_4HSO_4 ;$$

it is a neutral liquid, but, since it contains a $>CH(OH)$ group, it yields metallic derivatives with potassium and sodium, and, like other hydroxy-compounds, it reacts with acetyl chloride, giving *ethyl acetyllactate*, $CH_3 \cdot CH(O \cdot CO \cdot CH_3) \cdot COOC_2H_5$, an ester of acetyllactic acid, $CH_3 \cdot CH(OAc) \cdot COOH$. It is used as a solvent.

Lactic acid also contains the group, $>CH \cdot OH$, and shows, therefore, the reactions of an alcohol. When, for example, it is heated with concentrated hydrobromic acid, it is converted into α-bromo-propionic acid,

$$CH_3 \cdot CH(OH) \cdot COOH + HBr = CH_3 \cdot CHBr \cdot COOH + H_2O ;$$

with concentrated hydriodic acid, however, it may yield propionic

acid, because the α-iodopropionic acid which is first produced is readily reduced by an excess of hydrogen iodide,

$$CH_3 \cdot CHI \cdot COOH + HI = CH_3 \cdot CH_2 \cdot COOH + I_2.$$

On oxidation with potassium permanganate, lactic acid behaves like a *secondary* alcohol, and is converted into *pyruvic acid*, just as *iso*-propyl alcohol gives acetone,

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

Lactic acid and its salts are largely used in dyeing, tanning, and calico printing.

Sarcolactic acid, or *paralactic acid*, $C_3H_6O_3$, occurs in animals, more especially in the muscle juices, and may be isolated from extract of meat. It has the same constitution as lactic acid, but it differs from ordinary (*dl*-)lactic acid in being optically active (dextro-rotatory, p. 294).

Hydracrylic acid, $CH_2(OH) \cdot CH_2 \cdot COOH$, or *β-hydroxy-propionic acid*, an isomeride of lactic acid, may be obtained by reactions similar to those which give the corresponding α-acid—namely, by oxidising αγ-propylene glycol, and by boiling β-chloro-, bromo-, or iodo-propionic acid, $CH_2X \cdot CH_2 \cdot COOH$, with silver oxide and water. It is best prepared by the hydrolysis of ethylene cyano-hydrin (p. 270).

It is a thick, sour syrup, and when heated alone or with moderately dilute sulphuric acid, it is converted into acrylic acid (p. 342), with the 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 many respects hydracrylic behaves like lactic acid ; it is a monocarboxylic acid, and also contains a $-CH_2 \cdot OH$ group, so that it shows 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 Monohydroxypropionic Acids. The methods of formation and the chemical behaviour of lactic acid and of hydracrylic acid show that both compounds are monohydroxy-

monocarboxylic acids of the molecular composition, $C_3H_6O_3$; as only two such structural isomerides—namely,

$$\underset{\text{I}}{CH_3\cdot CH(OH)\cdot COOH} \text{ and } \underset{\text{II}}{CH_2(OH)\cdot CH_2\cdot COOH},$$

are theoretically possible, all that is necessary is to determine which of these formulae represents the one, and which the other, acid. This, of course, is already settled if the constitutions of the chloropropionic or aminopropionic acids, or those of the oxidation products of the hydroxy-acids are known; if, however, this were not the case, the following syntheses of the hydroxy-acids establish their constitutions.

When acetaldehyde is treated with hydrocyanic acid direct combination occurs, and the product is converted into lactic acid when it is heated 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, ethylene chlorohydrin is formed; this compound reacts with potassium cyanide in dilute alcoholic solution, giving ethylene 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, acetaldehyde and ethylene may be prepared from their elements, this is also true as regards the two hydroxypropionic acids.

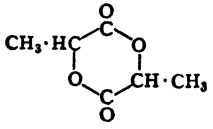
These two examples again show that when the structure or constitution of a compound has been ascertained from a study of some of its reactions, it is often possible to devise and carry out operations, based on general methods, by which the compound may be obtained from simpler substances; its *molecule* is thus built up, step by step, from a known foundation by known processes, and a successful synthesis thus affords very strong and generally conclusive evidence of the structure of the compound.

Lactides. Since lactic acid is an alcohol, as well as an acid, two molecules of lactic acid may react with one another to form an ester-like compound of the constitution,

$$CH_3 \cdot CH(COOH)O \cdot CO \cdot CH(OH) \cdot CH_3,$$

and this product, in an analogous manner, may give a substance of the constitution (I). Both these compounds are formed when lactic acid is heated; the former is called *lactyllactic acid*; the latter, *lactide*.

Other α-hydroxy-acids may give rise to similar compounds, and those which correspond with lactide in structure are classed as *lactides*; glycollic acid, for example, may be transformed into a lactide (II), which is distinguished as *diglycollide*.



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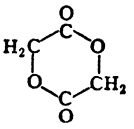


II

Dicarboxylic Acids

Just as ethyl alcohol gives acetic acid on oxidation, so ethylene glycol gives rise to a dicarboxylic acid, oxalic acid, HOOC·COOH. As, moreover, other glycols, such as αγ-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 by this and many different methods 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 first few members of this homologous series are :

Oxalic acid	$C_2H_2O_4$	or	$\begin{matrix}COOH\\ \vert \\ COOH\end{matrix}$
Malonic acid	$C_3H_4O_4$	or	$CH_2 < \begin{matrix}COOH\\ COOH\end{matrix}$
Succinic acid	$C_4H_6O_4$	or	$\begin{matrix}CH_2 \cdot COOH\\ \vert \\ CH_2 \cdot COOH\end{matrix}$
*Iso*succinic acid	$C_4H_6O_4$	or	$CH_3 \cdot CH < \begin{matrix}COOH\\ COOH\end{matrix}$

Oxalic acid, HOOC·COOH, 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; when sorrel is ground up with water, the filtered solution gives with calcium chloride a precipitate of calcium oxalate. Oxalic acid is formed when alcohol, glycol, sucrose, 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 instructive:

Its sodium salt is formed when sodium is heated at about 350° in an atmosphere of carbon dioxide,

$$2CO_2+2Na = C_2O_4Na_2,$$

and when sodium formate is heated at about 440°; it is also produced (in the form of its ammonium salt), together with several other compounds, when an aqueous solution of cyanogen (p. 353) is kept for some time, a change which is analogous to the conversion of methyl cyanide into acetic acid,

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4H_2O = \begin{matrix} CO\cdot ONH_4 \\ | \\ CO\cdot ONH_4 \end{matrix}$$

Each of these three reactions affords a means of synthesising oxalic acid from its elements, since carbon dioxide, formic acid, and cyanogen may be obtained from their elements.

Oxalic acid may be prepared in the laboratory by gently warming sucrose (cane-sugar) with about six times its weight of concentrated nitric acid (sp. gr. 1·3).

The operation is performed in a good draught-cupboard, and as soon as brown fumes appear the heating is temporarily discontinued, in spite of which oxidation proceeds very vigorously; after some time the solution is evaporated, a little more nitric acid being added, if necessary, to ensure complete oxidation. The syrupy product, when practically free from nitric acid, is dissolved in a little water, and the crystals which separate are purified by recrystallisation from water; further quantities may be obtained by evaporating the mother-liquor.

Oxalic acid is manufactured by heating sodium formate with sodium carbonate at about 360°,

$$\begin{matrix} H\cdot COONa \\ H\cdot COONa \end{matrix} = \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2;$$

the sodium oxalate so formed is boiled with milk of lime and the precipitated calcium oxalate is 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.

Oxalic acid, until recently, was manufactured from sawdust, which consists of organic compounds (cellulose, lignin, etc.) closely related to sucrose ; when heated with alkalis, these compounds undergo decomposition giving oxalic acid.

The sawdust was made into a paste with a concentrated solution of the hydroxides of sodium and potassium, and then heated in iron pans at about 240° ; afterwards the mass was extracted with water, the solution of potassium and sodium oxalates was boiled with lime, and the oxalic acid was isolated as just described.

The formation of oxalic acid from sawdust and from sucrose involves complex changes, during which molecules containing —CH(OH)·CH(OH)— groups undergo both decomposition (scission) and oxidation.

Oxalic acid crystallises from water in hydrated prisms, $C_2H_2O_4,2H_2O$; it is freely soluble in alcohol and moderately so in water, but is only sparingly soluble in ether. When quickly heated, it melts at about 100° and loses its water of hydration ; the anhydrous acid sublimes at about 150°, but if heated more strongly, it decomposes into carbon dioxide and formic acid (p. 161) or its decomposition products,

$$HOOC\cdot COOH \longrightarrow H\cdot COOH+CO_2 \longrightarrow H_2O+CO+CO_2 ;$$

the anhydrous acid, best prepared by boiling the hydrated crystals with carbon tetrachloride [1] in a distillation flask, is very hygroscopic, and is sometimes used as a dehydrating agent.

Oxalic acid is decomposed by concentrated sulphuric acid, but only when the mixture is heated above about 95° (distinction from formic acid),

$$HOOC\cdot COOH = CO_2+CO+H_2O ;$$

it is a feeble reducing agent, precipitates gold from its solutions, and is readily oxidised by *warm* acidified permanganate (or chlorine

[1] The water vapour passes over with the tetrachloride.

water) by which it is converted into carbon dioxide and water; this reaction is employed for the volumetric estimation of oxalic acid and also in standardising permanganate solutions,

$$HOOC \cdot COOH + O = 2CO_2 + H_2O.$$

Oxalic acid is acid to litmus, decomposes carbonates, and attacks certain metallic oxides; it is dibasic. Most of its salts except some of those of the alkalis and ammonia are almost insoluble in water; even sodium oxalate is only sparingly soluble in the cold.

Ammonium oxalate, $C_2O_4(NH_4)_2,H_2O$, is decomposed, giving oxamide, when it is carefully heated, just as ammonium acetate yields acetamide,

$$\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} = \begin{matrix} CO \cdot NH_2 \\ | \\ CO \cdot NH_2 \end{matrix} + 2H_2O;$$

when heated with phosphorus pentoxide it gives cyanogen (p. 353).

Potassium oxalate, $C_2O_4K_2,H_2O$, is readily soluble in cold water, but *potassium hydrogen oxalate*, C_2O_4KH, which occurs in many plants, is more sparingly soluble; the latter forms with oxalic acid a crystalline compound, $C_2O_4KH,C_2O_4H_2,2H_2O$, which is known as 'salts of sorrel,' or *potassium quadroxalate*; this salt is used in removing iron-mould and ink-stains, as it converts the iron compounds into soluble iron potassium oxalate.

Silver oxalate, $C_2O_4Ag_2$, is obtained in crystals when silver nitrate is added to a neutral solution of an oxalate; it is only sparingly soluble in water, and the dry salt explodes when it is quickly heated.

Calcium oxalate, C_2O_4Ca,H_2O, occurs in crystals in the cells of various plants, and is precipitated when a solution of a calcium salt is added to a neutral or ammoniacal solution of an oxalate; it is insoluble in water, and also in *acetic acid*.

Oxalic acid and its salts are used to a considerable extent in dyeing, in photography (as developers), and in analytical chemistry. The metallic salts are all decomposed when they are heated with concentrated sulphuric acid, giving carbon dioxide, carbon monoxide, water, and a sulphate; they are also decomposed when they are heated alone, but in neither case is there any appreciable charring. 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 substance when it is heated alone or with

sulphuric acid ; (*b*) the behaviour of the neutral solution with calcium chloride, and the insolubility of the precipitate in acetic acid.

The *constitution* of oxalic acid is established by its formation from glycol, glycollic acid, and formates ; it is a dicarboxylic acid.

Oxalic acid, like other compounds which are very rich in oxygen, is comparatively unstable ; its *anhydride* is unknown, but when treated wtih phosphorus pentachloride it is converted into the chloride, $COCl \cdot COCl$, a liquid (b.p. 64°), which is readily decomposed by water, giving hydrogen chloride and the oxides of carbon.

Dimethyl oxalate, $CH_3OOC \cdot COOCH_3$, is a crystalline compound, melting at 54°, and is prepared by heating anhydrous oxalic acid with methyl alcohol and then distilling the product ; it is hydrolysed by boiling water, and is sometimes employed in the preparation of pure methyl alcohol.

Diethyl oxalate, $C_2H_5OOC \cdot COOC_2H_5$, can be obtained in a similar manner, or by heating the hydrated acid with alcohol and carbon tetrachloride ; it boils at 186°, and is sparingly soluble in water. It may be noted that the methyl esters of organic acids are often crystalline, even when the ethyl, propyl, butyl, etc. esters are liquid at ordinary temperatures.

Oxamide, $NH_2 \cdot CO \cdot CO \cdot NH_2$, is formed as an intermediate product in the conversion of cyanogen into ammonium oxalate (p. 353) ; also when ammonium oxalate is heated. It is very easily prepared by shaking dimethyl or diethyl oxalate with concentrated ammonia, a general method for the preparation of amides from esters,

$$C_2H_5OOC \cdot COOC_2H_5 + 2NH_3 = NH_2 \cdot CO \cdot CO \cdot NH_2 + 2C_2H_5 \cdot OH.$$

It is crystalline, sublimes when heated, and is practically insoluble in water ; by boiling alkalis, it is slowly converted into an oxalate, just as acetamide gives an acetate,

$$NH_2 \cdot CO \cdot CO \cdot NH_2 + 2NaOH = NaOOC \cdot COONa + 2NH_3.$$

Glyoxal, $CHO \cdot CHO$, the dialdehyde which corresponds with oxalic acid, is produced by the oxidation of glycol, or alcohol, with nitric acid under particular conditions, and by passing pure acetylene through an aqueous solution of auric chloride at 70–80° ; this last reaction is also a process of oxidation,

$$CH \vdots CH + O_2 + 2H_2O \longrightarrow (HO)_2CH \cdot CH(OH)_2 \longrightarrow CHO \cdot CHO + 2H_2O.$$

It reduces ammoniacal silver oxide and combines with sodium hydrogen sulphite (2 mol.).

Glyoxal is prepared by oxidising acetaldehyde with selenium dioxide or by hydrolysing with water the compound,

$$SO_2<^{O}_{O}>CH\cdot CH<^{O}_{O}>SO_2,$$

which is formed by the action of fuming sulphuric acid on tetrachloroethane.

Its aqueous solution gives on evaporation a colourless polymeride, *paraglyoxal* $(C_2H_2O_2)_n$; when this substance is distilled with phosphorus pentoxide it affords a green vapour, which condenses to yellow crystals, melting at about 15°.

Malonic acid, $CH_2(COOH)_2$, the next homologue of oxalic acid, has already been mentioned, and the preparation of its diethyl ester from chloroacetic acid has been described (p. 206).

If, instead of the diethyl ester, the free acid is required, the product of the action of potassium cyanide on potassium chloroacetate is mixed with about twice its volume of concentrated hydrochloric acid, and the solution is 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 with ether.

Malonic acid was first prepared by oxidising malic acid (p. 280); hence its name. It occurs in sugar-beet, is crystalline and readily soluble in cold water; it melts at 136°, and at higher temperatures decomposes into acetic acid and carbon dioxide,

$$CH_2(COOH)_2 = CH_3\cdot COOH + CO_2.$$

All other dicarboxylic acids, in which *both* the carboxyl groups are united to *one and the same* carbon atom, are decomposed in a similar manner when they are heated alone or in aqueous solution (at 100–200°); this is a very important general reaction.

When malonic acid (or diethyl malonate) is heated with phosphorus pentoxide it gives *carbon suboxide*, CO:C:CO, a gas, which combines with water to form malonic acid.

Succinic acid, $HOOC\cdot CH_2\cdot CH_2\cdot COOH$, was first obtained by the destructive distillation of amber (Lat. *succinum*); it occurs also in small quantities in lignite (fossil wood), in many plants, and in certain animal secretions. It is formed during the alcoholic fer-

mentation of sugar, and in several other fermentation processes; also when fats are oxidised with nitric acid.

It can be synthesised from its elements in the following manner: acetylene is successively converted into acetaldehyde, alcohol, ethylene, and ethylene dibromide, and the last-named compound is boiled with potassium cyanide in aqueous alcoholic solution; the *ethylene dicyanide* which is thus formed,

$$C_2H_4Br_2+2KCN = C_2H_4(CN)_2+2KBr,$$

is decomposed by boiling alkalis or mineral acids, giving succinic acid and ammonia (footnote, p. 160).

Succinic acid may also be prepared synthetically from diethyl sodiomalonate and iodine (p. 211) or from ethyl acetoacetate (or diethyl malonate) and ethyl chloroacetate,

$$CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + CH_2Cl\cdot COOC_2H_5 = CH_3\cdot CO\cdot CH(COOC_2H_5)\cdot CH_2\cdot COOC_2H_5 + NaCl$$

$$CH_3\cdot CO\cdot CH(COOC_2H_5)\cdot CH_2\cdot COOC_2H_5 + 3KOH =$$

(Acid hydrolysis, p. 202)

$$CH_3\cdot COOK + CH_2(COOK)\cdot CH_2\cdot COOK + 2C_2H_5\cdot OH.$$

Succinic acid is usually prepared commercially by reducing maleic acid (p. 347).

It crystallises in prisms, melts at 185°, 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 alkalis, are sparingly soluble or insoluble in water.

The *constitution* of succinic acid is established not only by its synthesis from ethylene dibromide, diethyl malonate, and other compounds, but also, by the fact that the only alternative formula for a dicarboxylic acid, $C_4H_6O_4$, must be assigned to *iso*succinic acid (p. 279).

Succinic anhydride, $C_4H_4O_3$, is formed when succinic acid is distilled, but a large proportion of the acid passes over unchanged. It is prepared by heating the acid with phosphorus oxychloride and then isolating the product by distillation; the oxychloride combines with the water which is produced, and thus prevents 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 crystalline, and melts at 120° ; it resembles the anhydrides of the monocarboxylic acids in chemical properties, and when boiled with water or alkalis it is reconverted into succinic acid or a succinate.

In the formation of succinic anhydride *one* molecule of the acid loses one molecule of water, whereas in the case of the anhydride of a fatty acid *two* molecules of the acid take part in the formation of the product,

$$\begin{matrix} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{matrix} = \begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{matrix}\!\!>\!O + H_2O$$

$$\begin{matrix} CH_3\cdot COOH \\ CH_3\cdot COOH \end{matrix} = \begin{matrix} CH_3\cdot CO \\ CH_3\cdot CO \end{matrix}\!\!>\!O + H_2O.$$

Many other dicarboxylic acids give anhydrides, which are of the same type as succinic anhydride, and which are called *inner* anhydrides ; as a rule, however, this reaction is restricted to those acids in which the two carboxyl groups are separated by two or three carbon atoms only.

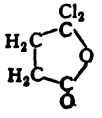
Succinyl chloride, $Cl\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot Cl$,[1] is formed when succinic acid is treated with phosphorus pentachloride, the interaction recalling that which occurs in the formation of acetyl chloride,

$$\begin{matrix} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{matrix} + 2PCl_5 = \begin{matrix} CH_2\cdot COCl \\ | \\ CH_2\cdot COCl \end{matrix} + 2POCl_3 + 2HCl.$$

It melts at 16°, boils at 193°, and is decomposed by alkalis, yielding a succinate.

Succinamide, $NH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, is prepared by shaking diethyl succinate with concentrated ammonia ; it is crystalline, decomposes at about 200° into ammonia and *succinimide*, and is only very sparingly soluble in cold water. When heated with

[1] It is difficult to decide from its reactions whether succinyl chloride should be represented by this formula or by

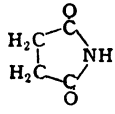


water it is slowly converted into ammonium succinate, just as oxamide is converted into ammonium oxalate,

$$\begin{matrix}CH_2\cdot CO\cdot NH_2\\ |\\ CH_2\cdot CO\cdot NH_2\end{matrix} + 2H_2O = \begin{matrix}CH_2\cdot COONH_4\\ |\\ CH_2\cdot COONH_4\end{matrix}$$

Succinamide cannot be obtained by distilling ammonium succinate, although oxamide and acetamide are produced by the distillation of the corresponding ammonium salts; this is merely because when succinamide is heated, it is converted into succinimide.

Succinimide, $C_4H_5O_2N$, is also formed when succinic anhydride is heated in a stream of dry ammonia; it melts at 126° and is readily soluble in water, from which it crystallises with one molecule of solvent. When boiled with water, mineral acids, or alkalis, it is converted into succinic acid or a succinate,



$$+ 2H_2O = \begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} + NH_3.$$

The constitution of succinimide, shown above, is based principally on its relation to succinamide; 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 bivalent *succinyl* group, $-CO\cdot CH_2\cdot CH_2\cdot CO-$, just as an amide is a mono-substitution product of ammonia. Many other dicarboxylic acids yield *imides* similar in constitution to succinimide (p. 521).

***Iso*succinic acid,** $CH_3\cdot CH(COOH)_2$, is isomeric with succinic acid; it may be prepared by treating diethyl sodiomalonate with methyl iodide and hydrolysing the product, a synthesis which shows that *iso*succinic acid is *methylmalonic acid*,

$$CHNa(COOC_2H_5)_2 + CH_3I = CH_3\cdot CH(COOC_2H_5)_2 + NaI.$$

It is crystalline, sublimes readily, and melts at 130° with decomposition; 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,

$$CH_3\cdot CH(COOH)_2 = CH_3\cdot CH_2\cdot COOH + CO_2.$$

Hydroxydicarboxylic Acids

With the exception of oxalic acid, dicarboxylic acids in general are capable of yielding substitution products in exactly the same

way as are the fatty acids; malonic acid, for example, may be converted into chloromalonic acid, $CHCl(COOH)_2$, hydroxymalonic acid, $HO \cdot CH(COOH)_2$, etc.; succinic acid, into bromosuccinic acid, $COOH \cdot CHBr \cdot CH_2 \cdot COOH$, dibromosuccinic acid, $COOH \cdot CHBr \cdot CHBr \cdot COOH$, or the corresponding mono- and dihydroxysuccinic acids, 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, $HOOC \cdot CH(OH) \cdot CH_2 \cdot COOH$ (*monohydroxysuccinic acid*), occurs not only in the free state, but also in the form of salts, in many plants, more especially 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 oxide, a reaction exactly analogous to the formation of lactic acid from α-bromopropionic acid,

$$\begin{matrix} CHBr \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + Ag \cdot OH = \begin{matrix} CH(OH) \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + AgBr.$$

As, therefore, bromosuccinic acid may be prepared by brominating succinic acid, and succinic acid may be synthesised in the manner already described, it is possible to obtain malic acid from its elements.

Malic acid may be produced by treating *aminosuccinic* or *aspartic acid* (a compound which may be obtained indirectly from asparagus[1]) with nitrous acid, just as lactic acid may be prepared from α-aminopropionic acid,

$$\begin{matrix} CH(NH_2) \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + HO \cdot NO = \begin{matrix} CH(OH) \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + N_2 + H_2O.$$

Malic acid is prepared commercially by heating maleic acid (p. 347) with steam under pressure, or from the juice of unripe berries of the mountain-ash.

Malic acid melts at 100° and is readily soluble in water and alcohol, but only sparingly so in ether. Its metallic salts and esters are of little importance.

[1] *Asparagine*, $COOH \cdot CH(NH_2) \cdot CH_2 \cdot CO \cdot NH_2$, the amide of aspartic acid, occurs in asparagus; when it is boiled with acids or alkalis it is converted into aspartic acid, $COOH \cdot CH(NH)_2 \cdot CH_2 \cdot COOH$ (aminosuccinic acid, p. 624).

Many of the reactions of malic acid may be foretold from a consideration of its constitution, which is fully established by its methods of formation. Since, for example, it is a hydroxy-derivative of succinic acid, it might be expected that, on reduction with hydriodic acid at a high temperature, it would be converted into succinic acid, just as lactic acid is converted into propionic acid ; also that, when heated with hydrobromic acid, it would yield bromosuccinic acid, a change which would be analogous to the conversion of lactic into bromopropionic acid. Both these changes actually take place,

$$\mathrm{COOH\cdot CH(OH)\cdot CH_2\cdot COOH + 2HI = COOH\cdot CH_2\cdot CH_2\cdot COOH + H_2O + I_2},$$

$$\mathrm{COOH\cdot CH(OH)\cdot CH_2\cdot COOH + HBr = COOH\cdot CHBr\cdot CH_2\cdot COOH + H_2O}.$$

When malic acid is heated, 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 (p. 347),

$$\begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{matrix} = \begin{matrix}\mathrm{CH\cdot COOH}\\ \|\\ \mathrm{CH\cdot COOH}\end{matrix} + \mathrm{H_2O}.$$

Although the malic acid obtained from plants undergoes exactly the same chemical changes as that prepared from bromosuccinic acid or maleic acid, the two acids are not identical in all respects ; they differ principally in their action on polarised light, the naturally occurring acid being optically active (p. 295).

Tartaric acid, $\mathrm{HOOC\cdot CH(OH)\cdot CH(OH)\cdot COOH}$ (*dihydroxy-succinic acid*), is one of the more commonly occurring vegetable acids, and is contained in grapes, in the berries of the mountain-ash, and in other fruits ; during the later stages of the fermentation of grape-juice, a considerable quantity of *argol*, impure potassium hydrogen tartrate, is deposited, and it is from this salt that the tartaric acid of commerce is prepared.

The crude, coloured deposit is boiled with hydrochloric acid and the solution is then nearly neutralised with milk of lime, whereby insoluble calcium tartrate is precipitated and normal potassium tartrate and chloride remain in solution,

$$2\mathrm{C_4H_5O_6K} + \mathrm{Ca(OH)_2} = \mathrm{C_4H_4O_6Ca} + \mathrm{C_4H_4O_6K_2} + 2\mathrm{H_2O} ;$$

the calcium salt is separated, and the solution is treated with calcium chloride when a further quantity of calcium tartrate is precipitated,

$$\mathrm{C_4H_4O_6K_2} + \mathrm{CaCl_2} = \mathrm{C_4H_4O_6Ca} + 2\mathrm{KCl}.$$

The calcium tartrate from these two operations is washed with water, and decomposed with dilute sulphuric acid; finally, the filtered solution of the tartaric acid is evaporated to crystallisation.

Other non-volatile acids, which cannot be extracted from their impure aqueous solutions with organic solvents, are isolated by methods similar to those used for tartaric and citric acids (p. 284)

The acid obtained from argol is distinguished as *d*-tartaric acid; other tartaric acids or dihydroxy-succinic acids can be obtained from succinic acid, and, therefore, from their elements, by reactions corresponding with those employed in the synthesis of malic acid. Dibromosuccinic acid is first prepared by treating succinic acid with bromine and red phosphorus (p. 180), 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 oxide,

$$\begin{matrix}\mathrm{CHBr\cdot COOH}\\ |\\ \mathrm{CHBr\cdot COOH}\end{matrix} + 2\mathrm{Ag\cdot OH} = \begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 2\mathrm{AgBr};$$

the product is a mixture of racemic and *meso*tartaric acids (p. 302).

A similar mixture of tartaric acids may also be obtained synthetically from glyoxal (p. 275), which, like other aldehydes, combines directly with hydrogen cyanide,

$$\begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{matrix} + 2\mathrm{HCN} = \begin{matrix}\mathrm{CH(OH)\cdot CN}\\ |\\ \mathrm{CH(OH)\cdot CN}\end{matrix}$$

the dicyanohydrin thus produced is decomposed by mineral acids, giving tartaric acids, just as ethylene dicyanide yields succinic acid,

$$\begin{matrix}\mathrm{CH(OH)\cdot CN}\\ |\\ \mathrm{CH(OH)\cdot CN}\end{matrix} + 4\mathrm{H_2O} = \begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 2\mathrm{NH_3}.$$

d-tartaric acid (obtained from argol) forms large transparent crystals, and is readily soluble in water and alcohol, but insoluble in ether; it melts at about 167°, but not sharply, as some decomposition takes place.

When heated for a long time with water at about 175°, it is converted into racemic and *meso*tartaric acids (p. 302), but when strongly heated alone it chars and yields a variety of products, among others, pyruvic acid and pyrotartaric acid (p. 288).

Tartaric acid, like other dicarboxylic acids, forms both normal and hydrogen salts, some of which are of considerable importance.

Normal *potassium tartrate*, $C_4H_4O_6K_2,\frac{1}{2}H_2O$, 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 [1] when an *excess* of a very concentrated solution of tartaric acid is added to a concentrated neutral solution of a potassium salt (test for potassium), and also when a concentrated aqueous solution of normal potassium tartrate is treated with a mineral acid,

$$C_4H_4O_6K_2+HCl = C_4H_5O_6K+KCl\,;$$

purified argol is known in commerce as cream of tartar.

Potassium sodium tartrate, $C_4H_4O_6KNa,4H_2O$ (Rochelle salt), is obtained when a solution of 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. 312).

Calcium tartrate, $C_4H_4O_6Ca,4H_2O$, is precipitated when a solution of a calcium salt is added to a neutral solution of a tartrate ; it is readily soluble in potash, but is precipitated when the solution is boiled.

Tartar emetic, $C_4H_4O_6K(SbO),\frac{1}{2}H_2O$ (potassium antimonyl tartrate), is prepared by heating potassium hydrogen tartrate with antimonious oxide and water ; it is readily soluble in water, and is used as an emetic and as a mordant.

The detection of tartaric acid or of a tartrate is based (*a*) 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 oxides of carbon being evolved ; (*b*) on the behaviour of the neutral solution with an ammoniacal solution of silver oxide, from which a mirror of silver is deposited when the mixture is warmed ; (*c*) on the behaviour of the neutral solution with calcium chloride (in the cold), and that of the precipitated calcium salt (above) ; (*d*) on the reaction of the acid with a solution of a potassium salt (above).

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 that compound.

[1] The precipitation is hastened by rubbing the inner wall of the containing vessel with a glass rod.

On reduction with hydriodic acid, tartaric acid is converted first into malic, then into succinic acid,

$$\begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{array} + 2\mathrm{HI} = \begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{array} + \mathrm{H_2O} + \mathrm{I_2},$$

$$\begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{array} + 4\mathrm{HI} = \begin{array}{l}\mathrm{CH_2\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{array} + 2\mathrm{H_2O} + 2\mathrm{I_2};$$

whereas, when heated with concentrated hydrobromic acid, it yields dibromosuccinic acid, as was to be expected,

$$\begin{array}{l}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{array} + 2\mathrm{HBr} = \begin{array}{l}\mathrm{CHBr\cdot COOH}\\ |\\ \mathrm{CHBr\cdot COOH}\end{array} + 2\mathrm{H_2O}.$$

Four dihydroxysuccinic acids are known—namely, dextrotartaric acid (the compound obtained from argol), laevotartaric acid, racemic acid, and *meso*tartaric acid. These four compounds have the *same constitution*, and are all represented by the formula,

$$\mathrm{COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH};$$

they differ, however, in certain *physical* properties, as, for example, in their crystalline form, but more especially in their behaviour towards polarised light; the relationship between these physically different modifications is discussed in the next chapter.

Citric acid, $\mathrm{C_6H_8O_7}$, is a hydroxy-tricarboxylic acid of considerable importance; like tartaric acid, it occurs in the free state in the juices of many fruits and is found in comparatively large proportions in lemons, in smaller ones in unripe currants, gooseberries, raspberries, and other fruit.

It is prepared on the large scale from lemon-juice, which is first boiled, in order to coagulate and precipitate protein-like 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 is evaporated to crystallisation.

It is also now made by the action of certain moulds, Penicillium and Aspergillus, on molasses.

Citric acid forms large transparent crystals, which contain one molecule of water and liquefy at 100°, whereas the anhydrous acid

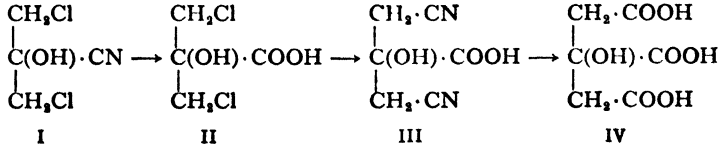
melts at 153° ; it is readily soluble in water and fairly so in alcohol, but insoluble in ether. Like tartaric acid, and several other hydroxy-acids, it has the property of preventing the precipitation of certain metallic hydroxides from solutions of their salts. Solutions of ferric chloride and of copper sulphate, for example, do not give a precipitate with potassium or ammonium hydroxide if citric acid is present ; on account of this property, citric acid and tartaric acid are employed in analytical chemistry and in calico-printing.

Since citric acid is a tricarboxylic acid, it forms, like phosphoric acid, 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 when a solution of a calcium salt is added to a neutral, dilute solution of a citrate, because it is readily soluble in cold water ; on the application of heat, 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 caustic 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 immediately char when it is gently heated with concentrated sulphuric acid.

Citric acid may be obtained synthetically by a series of reactions, which show it to be a hydroxytricarboxylic acid of the constitution (IV) :

Symmetrical dichloroacetone, $CH_2Cl \cdot CO \cdot CH_2Cl$, which may be obtained by oxidising glyceryl $\alpha\gamma$-dichlorohydrin with chromic acid, combines with hydrogen cyanide, forming the cyanohydrin (I); this product, like other compounds containing the —CN group, is converted into a carboxylic acid (II), by boiling mineral acids. The two atoms of chlorine in this acid may now be displaced by —CN groups, by heating the potassium salt of the acid with potassium cyanide in aqueous solution, and this dicyano-derivative (III) may then be converted into citric acid (IV) by boiling it with hydrochloric acid,



When heated alone at 175°, citric acid is converted into *aconitic acid*, just as malic is converted into fumaric acid,

$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} = \begin{array}{l} CH\cdot COOH \\ \| \\ C\cdot COOH + H_2O\,; \\ | \\ CH_2\cdot COOH \end{array}$$

when carefully warmed with sulphuric acid, it yields *acetonedicarboxylic* acid (p. 212), and on reduction with hydriodic acid it is converted into *tricarballylic acid* (propane-1:2:3-tricarboxylic acid), $COOH\cdot CH_2\cdot CH(COOH)\cdot CH_2\cdot COOH$.

SUMMARY AND EXTENSION

The **monohydroxymonocarboxylic acids** form a homologous series, $C_nH_{2n}(OH)\cdot COOH$ ($n=0$ in the case of carbonic or hydroxyformic acid); there are two structural (α-, β-) isomerides, $C_3H_6O_3$, whereas five acids of the molecular formula, $C_4H_8O_3$, are theoretically possible, of which three (α-, β-, γ-) are derived from butyric acid and two (α-, β-) from *iso*butyric acid.

Nomenclature. The names of these compounds are those of the parent fatty acids, with the prefix hydroxy and a letter or numeral (usually the former) to show the position of the substituent.

General Methods of Preparation. (1) Monohalogen derivatives of the fatty acids are hydrolysed with silver (hydr)oxide or with dilute aqueous alkalis.

(2) Amino-acids are treated with nitrous acid,

$$CH_3\cdot CH(NH_2)\cdot COOH + HO\cdot NO = CH_3\cdot CH(OH)\cdot COOH + N_2 + H_2O.$$

(3) Aldehydes or ketones are combined with hydrogen cyanide and the cyanohydrins are hydrolysed with concentrated hydrochloric acid (not with an alkali),

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C(OH)\cdot CN \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C(OH)\cdot COOH\,;$$

although only α-hydroxy-acids are thus obtained, this method is of great importance particularly in the study of the monosaccharides (p. 320).

(4) Aldehydes or ketones are treated with an α-bromo-derivative of an ester in the presence of zinc (Reformatsky reaction),

$$>CO + CHRBr\cdot COOEt + Zn = >C(OZnBr)\cdot CHR\cdot COOEt\,;$$

the products, decomposed with a mineral acid, give β-hydroxy-acids.

(5) Ketonic acids are reduced with sodium amalgam and water, etc.,

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH + 2H = CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COOH.$$

Since many ketonic acids containing the group, $CH_3 \cdot CO—$, can be obtained from ethyl acetoacetate, many hydroxy-acids may be synthesised in this way without difficulty.

Properties. Most of the simpler acids are solids of low melting-point, readily soluble in water and not volatile in steam. They combine the properties of monohydric alcohols and of acids, but they differ from one another in certain important respects because of the difference in the position of the HO— relatively to the —COOH group

α-Acids, e.g. *α-hydroxybutyric acid*, $CH_3 \cdot CH_2 \cdot CH(OH) \cdot COOH$ (obtained by treating an aqueous solution of α-bromobutyric acid with silver oxide), are generally converted into lactides (p. 271) when they are heated alone. The β-acids, such as *β-hydroxybutyric acid* (p. 203), behave like hydracrylic acid, and when heated alone they give αβ-unsaturated acids, of which crotonic acid is an example. The γ-acids, e.g. *γ-hydroxyvaleric acid*, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COOH$ (prepared by reducing laevulic acid), undergo yet a different type of change and pass spontaneously into ester-like compounds, which are classed as **lactones**; γ-hydroxyvaleric acid, for example, gives *γ-valerolactone*,

$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COOH = \begin{array}{l} CH_3 \cdot HC \overset{O}{\diagdown\!\diagup} CO \\ \quad\quad H_2C \diagup\!\diagdown CH_2 \end{array} + H_2O.$$

δ-Hydroxy-acids behave in a similar manner, and give δ-lactones.

The lactones are usually liquids, which may be distilled under atmospheric pressure; they are neutral and resemble esters in some respects. They are very slowly hydrolysed by water (until a condition of equilibrium is reached); but they are readily and completely hydrolysed by alkali hydroxides, giving alkali salts of the hydroxy-acids. The lactones of acids derived from the aldoses (p. 319) are very important.

Dicarboxylic Acids. Carbonic acid is not a dicarboxylic acid, but a hydroxymonocarboxylic acid; as, however, both the HO— groups are combined with $>CO$ the acid is dibasic.

The dicarboxylic acids form a homologous series, $C_nH_{2n}(COOH)_2$

($n = 0$ in the case of oxalic acid); there are two acids, $C_4H_6O_4$, and the following four having the formula, $C_5H_8O_4$:

$CH_2<\begin{matrix}CH_2\cdot COOH\\CH_2\cdot COOH\end{matrix}$

Glutaric acid
(Propane-1:3-dicarboxylic acid)

$CH_3\cdot CH(CH_2\cdot COOH)\cdot COOH$

Pyrotartaric or methylsuccinic acid
(Propane-1:2-dicarboxylic acid)

$CH_3\cdot CH_2\cdot CH<\begin{matrix}COOH\\COOH\end{matrix}$

Ethylmalonic acid
(Propane-1:1-dicarboxylic acid)

$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}COOH\\COOH\end{matrix}$

Dimethylmalonic acid
(Propane-2:2-dicarboxylic acid)

As the series is ascended the numbers of the isomerides rapidly increase, but only the *normal* higher acids are of much importance, namely:

Glutaric acid	$HOOC\cdot[CH_2]_3\cdot COOH$
Adipic acid	$HOOC\cdot[CH_2]_4\cdot COOH$
Pimelic acid	$HOOC\cdot[CH_2]_5\cdot COOH$
Suberic acid	$HOOC\cdot[CH_2]_6\cdot COOH$
Azelaic acid	$HOOC\cdot[CH_2]_7\cdot COOH$
Sebacic acid	$HOOC\cdot[CH_2]_8\cdot COOH$

Nomenclature. It will be seen that all the above *normal* acids have common names, which are also often used in describing their alkyl substitution products. All the acids, however, may be named systematically as derivatives of the paraffins, as shown above.

Preparation. (1) Glycols which contain two $-CH_2\cdot OH$ groups are oxidised (p. 243).

(2) Dicyanides, usually prepared from dibromides, are hydrolysed with mineral acids (p. 277).

(3) Halogen derivatives of monocarboxylic acids are converted into the cyano-compounds, which are then hydrolysed,

$$CH_2Cl\cdot COOH \longrightarrow CH_2(CN)\cdot COOH \longrightarrow CH_2(COOH)_2.$$

(4) Diethyl sodiomalonate is treated with an alkyl halide and the ester thus produced is hydrolysed; all the acids thus obtained contain the group, $>C(COOH)_2$, and give monocarboxylic acids when they are heated.

(5) Halogen derivatives of the monocarboxylic acids are treated with precipitated silver,

$$2CH_2I\cdot CH_2\cdot COOH + 2Ag = COOH\cdot[CH_2]_4\cdot COOH + 2AgI.$$

(6) Potassium salts of hydrogen esters of dicarboxylic acids are submitted to electrolysis (Crum Brown and Walker),

$$\begin{matrix}\mathrm{KOOC\cdot CH_2\cdot COOEt}\\ \mathrm{KOOC\cdot CH_2\cdot COOEt}\end{matrix} + 2\mathrm{H_2O} = \begin{matrix}\mathrm{CH_2\cdot COOEt}\\ \mathrm{CH_2\cdot COOEt}\end{matrix} + 2\mathrm{KHCO_3} + \mathrm{H_2}.$$

(7) *Esters* of some of the members of the series may be reduced to glycols with sodium and alcohol, and the products may then be converted into higher homologues by the usual methods of passing up a series (p. 224).

$$\mathrm{C_nH_{2n}}\begin{matrix}\mathrm{COOEt}\\ \mathrm{COOEt}\end{matrix} \longrightarrow \mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2\cdot OH}\\ \mathrm{CH_2\cdot OH}\end{matrix} \longrightarrow \mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{CH_2Br}\end{matrix} \longrightarrow$$

$$\mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2\cdot CN}\\ \mathrm{CH_2\cdot CN}\end{matrix} \longrightarrow \mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2\cdot COOH}\\ \mathrm{CH_2\cdot COOH}\end{matrix}$$

The dibromides may also be treated with diethyl sodiomalonate, etc.,

$$\mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{CH_2Br}\end{matrix} \longrightarrow \mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2\cdot CH(COOH)_2}\\ \mathrm{CH_2\cdot CH(COOH)_2}\end{matrix} \longrightarrow$$

$$\mathrm{C_nH_{2n}}\begin{matrix}\mathrm{CH_2\cdot CH_2\cdot COOH}\\ \mathrm{CH_2\cdot CH_2\cdot COOH}\end{matrix}$$

In addition to these general methods there are particular reactions by which a given dibasic acid may often be more easily prepared. Thus glutaric acid may be obtained, not only from trimethylene glycol, through the dibromide and the dicyanide, but also by the condensation of diethyl malonate with formaldehyde in the presence of diethylamine : the product is hydrolysed and heated,

$$2\,\mathrm{CH_2(COOEt)_2} + \mathrm{H\cdot CHO} \longrightarrow \mathrm{CH_2\{CH(COOEt)_2\}_2} \longrightarrow \mathrm{CH_2(CH_2\cdot COOH)_2}.$$

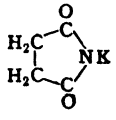
Adipic acid is most easily prepared by the oxidation of *cyclo*hexanone (p. 401) and pimelic acid from trimethylene dibromide and diethyl malonate or from salicylic acid (p. 533). Suberic acid is obtained by the oxidation of cork or castor oil, azelaic acid by the oxidation of oleic acid and sebacic acid by heating castor oil with caustic soda.

Properties. The dicarboxylic acids are usually crystalline ; the lower members are readily soluble in water but are not volatile in steam ; as the molecular weight rises the solubility in water diminishes, whereas the solubility in ether increases. With the exception of oxalic acid, they are stable towards oxidising agents.

The calcium and other salts of the higher members give cyclic ketones when they are heated (Part III).

Succinic and glutaric acids, and other members in which the two carboxyl groups are separated from one another by *two* or by *three* carbon atoms, give inner anhydrides ; such acids also give *imides*, of which succinimide may be taken as a typical example.

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* (I), is produced; this compound reacts with silver nitrate, giving *silver succinimide* (II), and the latter, on treatment with ethyl iodide, yields *ethyl succinimide* (III), which, on hydrolysis, gives ethylamine:



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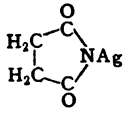

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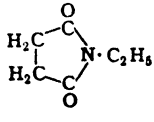


III

It has been pointed out that a hydrogen atom in the group, —CO·CH_2·CO—, is displaceable by certain metals, as in the cases of ethyl acetoacetate and diethyl malonate. The behaviour of succinimide, and of other imides, shows that the hydrogen atom of an *imido*-group, —CO·NH·CO—, is also displaceable by metals. In both types of compounds the metallic derivatives may be regarded as substitution products of the tautomeric enolic forms, —C(OH):CH— and —C(OH):N—, respectively (p. 204).

Many di-, tri- and poly-hydroxy-derivatives of mono- and di-carboxylic acids are well-known compounds, obtained from polyhydric alcohols and aldehydes which occur in nature, and are described later.

CHAPTER 18

OPTICAL ISOMERISM

THERE should be little need at this stage to iterate and emphasise the importance of determining the constitution or structure of an organic compound. When this has been done, all the results of the study of the properties of the molecule can be expressed by an assembly of symbols and lines, as suggested by Kekulé in 1858, which shows the various groups or radicals of which the molecule is constituted and also indicates their relationship to one another. Such structural formulae play an indispensable role in the study of organic chemistry; without their aid progress would have been hampered beyond measure.

Structural formulae, as already shown, not only afford a summary of the known properties of compounds, but also allow of the prediction of others, which may not have been actually observed; they also serve as a guide to methods by which a compound so represented may be built up bit by bit from its constituent groups or even from its elements. Without their use there would be no simple explanation of the existence of homologous series and the relations of the members to one another, and the phenomena of isomerism, tautomerism and polymerisation would remain obscure.

But in spite of all the advantages of their use, structural formulae have their limitations: (1) They give no indication of the stability or otherwise of the molecules which they represent. The same symbol may be used for a bond which is broken by cold water or for one which resists the action of the strongest reagents; this limitation, however, becomes of continually decreasing importance as more and more groupings become familiar and then serve as guides to the behaviour of analogous structures in new compounds. (2) They do not, as hitherto interpreted, afford any information as to the distribution in space of the atoms of the molecule (p. 45.)

At this juncture it is desirable to consider the last-mentioned problem, namely that of molecular architecture, in order to explain the existence of the different forms of lactic, malic, and tartaric acids described in the last chapter and their behaviour towards polarised light.

It had long been known that quartz and certain other minerals rotate the plane of polarised light, some crystals turning the plane to the right, others to the left, when in 1815 Biot discovered that this property was also possessed by oil of turpentine and *solutions* of various organic compounds isolated from vegetable or animal products. As he pointed out, this fact proved that the property in question is due, in the case of the liquids and solutions, to some action of the *molecules* of the compound and not to some particular arrangement of these molecules in a crystal, as in the solid substances.

It was not until 1848, however, that any progress was made with this problem of molecular architecture ; in that year Pasteur announced the results of his classic investigation of the crystalline forms of salts of tartaric and racemic acids.

Tartaric acid (p. 281), is an *optically active* compound : its solution rotates the plane of polarisation of polarised light, but that of racemic acid (*racemus*, the grape), which also occurs in argol, has no such action and is optically inactive. The two acids have the same structural formula, and except for the difference in behaviour just mentioned, they, as likewise their salts, are identical in chemical properties ; their existence could not be explained.

From each of these acids Pasteur prepared the sodium ammonium salts, $C_4H_4O_6NaNH_4,4H_2O$, which form large glass-like crystals, and were thought to be identical except that the salt of tartaric acid was optically active in aqueous solution, that of racemic acid optically inactive. He then observed that in fact these salts showed a very remarkable difference in crystalline form inasmuch as *all* the perfect or well-grown crystals of the salt obtained from tartaric acid had certain small faces or facets (*a*, *b*) arranged in one particular manner, as shown in the crystal D (Fig. 20), in which these particular faces are darkened ; the crystals of the salt obtained from racemic acid, on the other hand, were of *two kinds*, the one being identical with those of the salt of tartaric acid, the other having the particular faces (*a*, *b*) arranged as shown in the crystal L (Fig. 20).

The two kinds of crystals obtained from racemic acid were, in fact, found to be related to one another as an object, such as the hand, is related to its mirror-image ; a left hand, held before a mirror, gives an image which is a right hand, and *vice versa* ; similarly, a D crystal (Fig. 20), if held before a mirror, gives an image identical with the L crystal viewed directly.

Having observed the existence of two kinds of crystals of the salt

of racemic acid, Pasteur picked out a number of each from the mixture, dissolved the two kinds separately in water, and examined the solutions in the polarimeter (p. 308). One solution was *dextrorotatory*—that is, rotated the plane of polarisation of polarised light to the right—the other was *laevorotatory*.

This highly important discovery was carefully followed up and it was next found that one of the sodium ammonium salts (the dextrorotatory one) gave an acid identical with ordinary tartaric acid in every respect, whereas the other salt—namely, the laevorotatory one—gave an acid identical with ordinary tartaric acid, except that its solution rotated the plane of polarisation of polarised

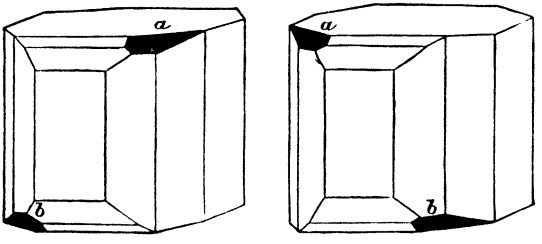


Fig. 20

light to the *left*, to exactly the same extent as a solution of tartaric acid of the same concentration rotated it to the *right*. When aqueous solutions of equal quantities of these two acids were mixed, the solution was optically inactive and, on evaporation, gave crystals of racemic acid, which could not be sorted into two kinds.

From these results Pasteur concluded that molecules could be classed into two groups: (*a*) those which were identical with their mirror-images; (*b*) those which were *not* identical with their mirror-images and could not be superposed on the latter.[1] Molecules of the first group (*a*) have a symmetrical, whereas those of the second group (*b*) have a dissymmetrical[2] structure which determines their

[1] One molecule can be superposed on another when, in imagination, it can be so placed on (or over) the other that it fits exactly into the space occupied by the latter; two right-hand gloves of identical pairs are superposable, but neither can be superposed on a left-hand glove.

[2] The term '*dissymmetric*' (*dis-symmetric*) signifies that the structure may have *some* elements (axes) of symmetry, but is not superposable on its mirror image. '*Asymmetric*' (*a-symmetric*) denotes a lack of any kind of symmetry.

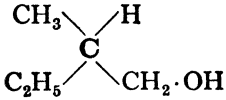
optical activity. He suggested that the atoms in the dissymmetrical molecules might be arranged in the form of a right- or left-handed spiral, or at the corners of an irregular tetrahedron, or in some other dissymmetrical manner, but there was insufficient evidence on which to found any conclusion.

This matter may perhaps be made clear by considering ordinary solid objects, which may be divided into two classes. (*a*) Those such as cubes, tea-cups, wheel-barrows, and most common objects each of which is identical with its image in a mirror and may be bisected by at least one plane into halves which are either identical or mirror-images of one another. Such a plane is called a *plane of symmetry*. (*b*) Those such as gloves or hands, shoes, golf-clubs, and motor-cars, which are not identical with their mirror-images, have no plane or centre [1] of symmetry, and can be made in two forms, related to one another as an object to its mirror-image.

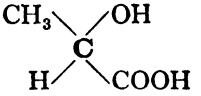
A molecule may be considered in the same way. When it has a plane of symmetry it exists in one form only ; when it has no plane or centre of symmetry, two forms are possible, related to one another as an object to its mirror-image.

It was not until much later that any notable advance was made in the study of optically active compounds. In 1874 van't Hoff and Le Bel showed, independently, that there was a definite relation between the optical activity and the structure or constitution of an organic compound; that a substance was optically active in *solution* only when its molecule contained at least one carbon atom which was directly united with *four different* atoms or groups. Such an atom was termed an **asymmetric** carbon atom.

When the following graphic formulae of various optically active compounds are examined, it will be seen that in every case there is (at least) one carbon atom in the molecule—namely, that printed in heavy type—which is thus directly united with four different atoms or groups ; any molecule which contains one such atom is optically active.

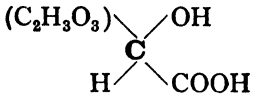


Active amyl alcohol

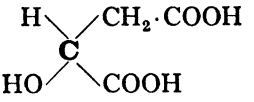


Lactic acid

[1] A centre of symmetry is a point within a molecule from which a line, drawn to any atom or group, meets an identical atom or group at an equal distance from this centre if extended in the opposite direction.



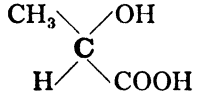
Tartaric acid



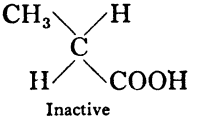
Malic acid

That this property of rotating the plane of polarisation of polarised light is due to such an arrangement of the atoms in the molecule is now fully established; if by any means the structure of the molecule is so changed that it no longer contains an asymmetric carbon atom, the power of rotating the plane of polarisation also disappears.

Lactic acid (p. 269), for example, is optically active, but when it is reduced with hydrogen iodide it yields propionic acid, which is inactive, because it does not contain a carbon atom united with four different atoms or groups,

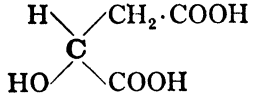


Active

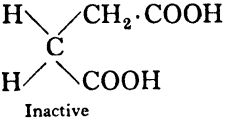


Inactive

Malic acid, again, is optically active, but on reduction inactive succinic acid is formed,

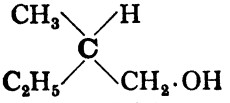


Active

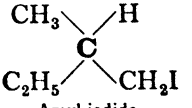


Inactive

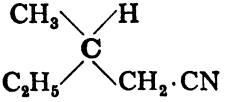
A still more instructive case is afforded by active amyl alcohol (p. 120), and the following derivatives of this alcohol,



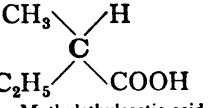
Amyl alcohol



Amyl iodide



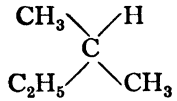
Amyl cyanide



Methylethylacetic acid

These substances, prepared from active amyl alcohol by the usual series of reactions, are themselves optically active, because

each still contains an asymmetric carbon atom ; when, however, the iodide is reduced to the hydrocarbon,

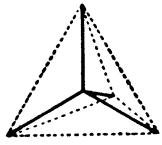


Dimethylethylmethane

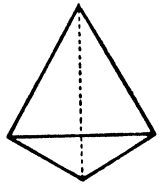
two groups become identical, and the product is optically inactive.

The proved relation between the constitution of the molecule and the property of rotating the plane of polarisation of polarised light, and van't Hoff and Le Bel's theory concerning the *arrangement in space* of the four atoms or groups united to an asymmetric carbon atom may now be considered more fully.

According to this theory, each of the four atoms or groups, with which a carbon atom is united, is situated at some point on one of four lines, which start from the carbon atom and are symmetrically arranged in the space around it. It may be supposed, therefore, that the carbon atom is situated at the centre of an imaginary regular tetrahedron, and that its four valencies (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 (I). It is more convenient, however,



I



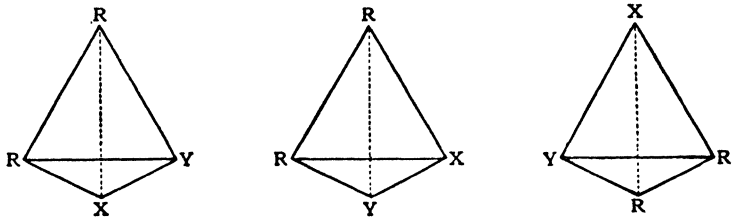
II

to omit the four heavy lines altogether and to indicate merely the tetrahedral arrangement of the four atoms or groups at the corners of the tetrahedron as in (II).

With the aid of such figures, the study of the application of van't Hoff and Le Bel's theory is greatly facilitated and the following well-established facts are easily explained :

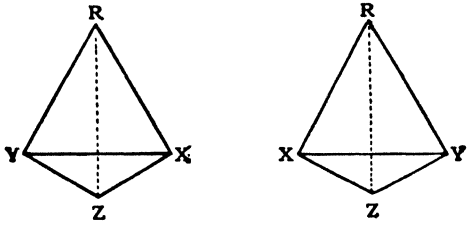
(1) A compound of the type, CR_3X (where R and X represent any atom or group)—as, for example, CH_3Cl, $CHCl_3$, $CH_3 \cdot OH$, $CH_3 \cdot COOH$, etc.—can exist in *one* form only, because whichever corner of the tetrahedron is occupied by X, the result is the same.

(2) A compound of the type, CR_2XY (that is to say, one in which any two atoms or groups are identical)—as, for example, CH_2ClBr, CH_2Cl_2, $(CH_3)_2CH \cdot OH$—can also exist in *one* form only ; arrangements at the corners of the tetrahedron such as the following,



which may appear to be different as printed, are in reality identical.

(3) A compound of the type, CRXYZ—in which the carbon atom is united with four different atoms or groups—can exist in *two*, but only two, different forms, which may be represented by the following figures :



Points such as these are most clearly understood by actually handling models of the structures concerned ; [1] it will then be seen that whatever attempts are made to vary the positions of the different atoms in CR_3X or CR_2XY, only one arrangement is possible, but that a compound CRXYZ may exist in the two forms already shown.

When the models are used, four differently coloured balls are first attached to each of two black carbon balls, in such a way as to produce identical arrangements ; any two of the coloured balls in

[1] In order to facilitate the study of stereochemistry, sets of black and coloured wooden balls and flexible metallic rods, with which models of molecules may be constructed, can be purchased ; the black balls, representing the carbon atoms, are so pierced with four holes, that when the rods are fitted into the holes, they are directed towards the corners of an imaginary tetrahedron. Models may also be easily made with plasticine and matches.

one of the models are then interchanged. The two arrangements of CRXYZ which are thus obtained are different, as shown in the last figure (p. 297).

These two arrangements, moreover, 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 positions of X, Y, and Z in relation to R, in the mirror-image, will be identical with those in the other model viewed directly ; for the sake of convenience, one of these arrangements may be distinguished by + or *d*, the other by − or *l*, the actual choice being immaterial.

In accordance with theory it is now known that the simplest optically active substances—namely, those containing *only one* asymmetric carbon-group [1]—invariably exist in two optically active forms, one of which is dextrorotatory (*d* or +), the other laevorotatory (*l* or −), to exactly the same extent. These two forms, which may be represented by the figures just given, are called *optical* (physical, or *stereochemical*) *isomerides*. The two optical isomerides have the same chemical properties and the same constitution or structure, and their molecules differ only in *configuration*, that is to say, as regards the arrangement of their atoms in space. They have also the same melting-point and boiling-point, and are *identical* in all other physical properties, except that, if solids, they usually differ in crystalline form and the crystals of the one, if sufficiently well-defined, are found to be related to those of the other as an object to its mirror-image, just as in the case of the sodium ammonium salts already referred to. Such crystals are said to be *enantiomorphous* or *hemihedral*, and the *d*- and *l*-molecules which form these crystals are said to be *enantiomorphously related* to one another or to be *antimeric*.

When any substance containing *one* asymmetric carbon-group is prepared synthetically, the product is found to be optically *inactive*. When, for example, lactic acid is produced from acetaldehyde, or bromosuccinic acid from succinic acid, 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. By merely dis-

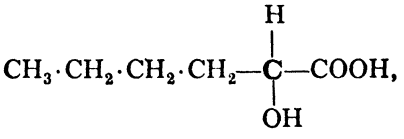
[1] The term ' asymmetric carbon-group ' is used henceforth instead of ' asymmetric carbon atom,' since it is the molecule as a whole which lacks symmetry.

solving together equal quantities of the *d*- and *l*-forms, and then evaporating the solution, an inactive product, identical with that produced synthetically, is obtained.

Products of this kind, which consist of equal quantities of the *d*- and *l*-forms are called *dl*-, or *externally compensated* substances.

When a *dl*-substance is a solid, *all* its crystals may differ entirely from those of the active isomerides in crystalline form, melting-point, solubility, density, etc. If so, every crystal, no matter how small, consists of equal numbers of molecules of the *d*- and *l*-isomerides. Such a crystallographic combination of the *d*- and *l*-forms is termed a *racemic* [1] compound. Sometimes, however, the *d*- and *l*-forms when crystallised from the same solution do not give a racemic compound, and the deposit is just a mixture; when, for example, a solution containing the sodium ammonium salts of both *d*- and *l*-tartaric acids is evaporated at temperatures below 28°, the crystals of the two salts are deposited separately, side by side; every crystal, no matter how large, consists *only* of *d*- or of *l*-molecules. Such a product is termed a *dl*-mixture or a *dl*-conglomerate. Above 28° all the crystals are those of the racemic salt.

In the case of compounds containing only *one* asymmetric carbon-group, no matter how many carbon atoms the molecule may contain, or what the nature of the other atoms may be, so 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 *dl*-; a substance of the constitution,



for example, would not form a larger number of optical isomerides than a simple substance such as lactic acid.

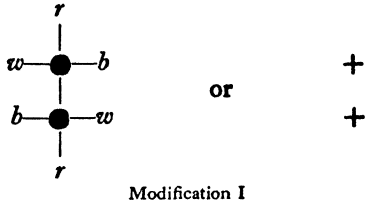
When, however, a compound contains *two* asymmetric carbon-groups, a larger number of modifications may exist, as will be seen by constructing models in the following manner:

I. Make two *identical* asymmetric carbon-groups, **C**, *r*, *b*, *w*, *y*,[2]

[1] The term racemic is derived from racemic acid—*dl*-tartaric acid—itself an externally compensated and racemic compound.

[2] The letters *r*, *b*, *w*, and *y* refer respectively to the red, blue, white, and yellow balls usually found in the sets of models.

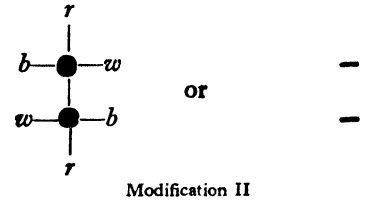
each of which, for convenience, may be designated + ; now remove *y*, with its rod, from both models, join the latter with a single rod, and lay the model on the table, so that the two red balls point upwards. This is one possible modification, a plane figure of which may be obtained by pressing the red balls outwards on the table, when the model 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-group asymmetric ; in other words, each is now combined with the four different groups (*r*), (*b*), (*w*), and (C, *r*,*b*,*w*), instead of with (*r*), (*b*), (*w*), and (*y*).

II. Repeat the above operations, but start with two *identical* asymmetric carbon-groups, C, *r*, *b*, *y*, *w*, which are the mirror-images of those taken in (I), and which may, therefore, be marked − ; the plane projection of this model will be,

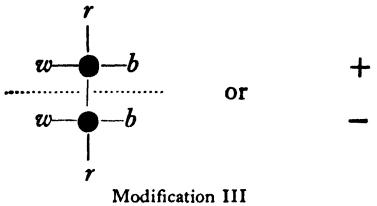


Modification II

This form is quite different from (I), and cannot possibly be made to coincide with it in any position ; if, for example, (II) is turned over, although the positions of *b* and *w* will correspond with those in (I), *r* and *r* will now point downwards in (II), whereas they pointed upwards in (I) ; if, in fact, this model (II) is 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-groups, C, *r*, *b*, *w*, *y*, and C, *r*, *b*, *y*, *w*, or + and −, are 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 form different from one of these three can be made. It is evident, then, that a compound containing *two* such asymmetric carbon-groups may exist in *three* distinct modifications. One of these, say, (I), will be dextrorotatory, and contain two *identical* (+) asymmetric carbon-groups; the other (II) will be laevorotatory to exactly the same extent, and contain two *identical* (−) asymmetric carbon-groups; as may be seen from the models, neither (I) nor (II) has a plane of symmetry. The form (III), on the other hand, will be optically inactive because the molecule has a plane of symmetry (indicated by the dotted line) and is identical with its mirror-image. This form (III) represents a molecule which contains two *different* asymmetric carbon-groups, one + and the other − but otherwise identical. Since it might be supposed that each of these groups is optically active but that the dextrorotatory action of the one is exactly counterbalanced by the laevorotatory action of the other: in other words, that the rotatory power of one *part* of this molecule is balanced or neutralised by that of the other part, compounds of the form (III) were once regarded as *internally compensated* or inactive by *internal compensation*. It is clear, however, that such a molecule is identical with its mirror-image, and substances which are inactive in this way are now called *meso*-compounds.

There is, however, a further possibility 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 the solution, either a racemic substance or a *dl*-conglomerate is obtained, just as in the case of compounds which contain only one asymmetric carbon-group (p. 299).

In order to decide which two of the above three models represent the active (*d*- and *l*-) modifications of the substance, it is only necessary to determine which two are related to each other as object

to mirror-image. This will be found to be the case with the forms (I) and (II).

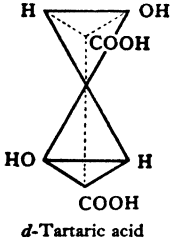
Optical Isomerism of the Tartaric Acids

The best known example of optical isomerism in substances containing two asymmetric carbon-groups is that of the tartaric acids, investigated by Pasteur. Tartaric acid,

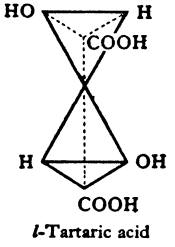
$$COOH \cdot \mathbf{C}H(OH) \cdot \mathbf{C}H(OH) \cdot COOH,$$

contains two carbon atoms, each of which is united with four different atoms or groups—namely, {COOH}, {H}, {OH}, and {CH(OH)·COOH}, and consequently, as just shown, there should be *three* optically isomeric forms of this acid, or four, if a racemic modification exists.

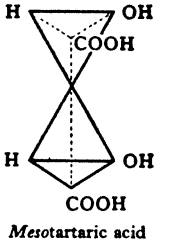
Four modifications—namely, dextrotartaric, laevotartaric, *meso*-tartaric, and racemic acid—are, in fact, known and the first three compounds may be represented as follows :



d-Tartaric acid

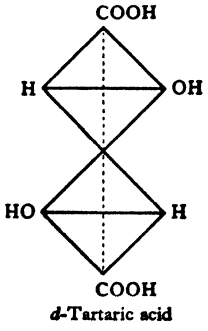


l-Tartaric acid

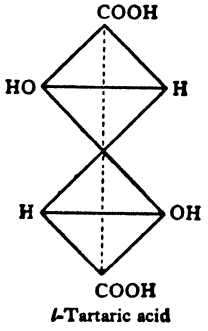


*Meso*tartaric acid

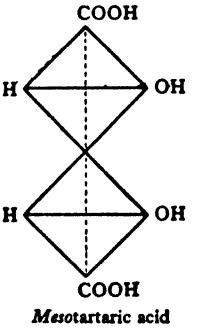
Alternative representations from a slightly different viewpoint are given below and it can be seen that the two diagrams of each isomeride are identical,



d-Tartaric acid

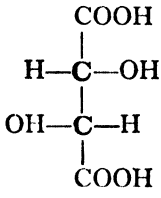


l-Tartaric acid

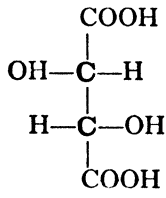


*Meso*tartaric acid

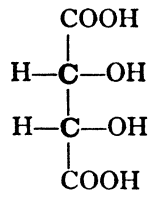
For ordinary purposes the *configurations* shown above may be more conveniently symbolised by using their projections,



d-Tartaric acid [1]



l-Tartaric acid [1]



*Meso*tartaric acid

Dextrotartaric acid and laevotartaric acid are the two optically active forms. The one rotates the plane of polarisation to the right, whereas the other rotates it to the left; but in all other respects they are identical, except for the differences in crystalline form already mentioned. They possess the same melting-point and the same solubility in a given solvent; their metallic salts have the same composition when they are crystallised under the same conditions. Their esters boil at the same temperature; all their salts, like the acids themselves, are optically active, and corresponding salts have equal, but opposite, rotations.

Meso*tartaric acid* is the optically inactive form of tartaric acid; it is inactive because its molecule has a plane of symmetry although it contains two asymmetric carbon-groups.

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 a totally 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. *Meso*tartaric acid *cannot be resolved into two optically active modifications*, because all the molecules of which it is composed are identical.

Racemic acid, or *dl*-tartaric acid, is simply a crystallographic union of equal quantities of dextro- and laevo-tartaric acids, and is inactive in solution because that solution contains equal numbers of molecules of the two different forms. It is obtained when a solution of equal quantities of the two active modifications is evaporated, and it *can be separated again into these two forms* by

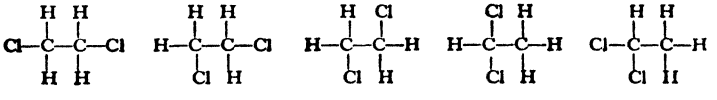
[1] The letters *d*- and *l*- here refer merely to the sign of rotation of the acids (p. 335).

certain methods given below. Nevertheless, racemic acid, in the *solid* state, is physically a distinct substance and not a mixture.

Racemic acid or *dl*-tartaric acid is obtained, together with *meso*-tartaric acid, when ' tartaric acid ' (dihydroxysuccinic acid) is prepared by any synthetical process ; also when *d*- or *l*-tartaric acid is heated with water at 175°. Many optically active compounds are more or less readily converted into the corresponding *dl*-substances when they are heated alone, or in solution, or treated with various reagents. This change is termed *racemisation*, and is due to the transformation of some of the *d*- and *l*-groups into the optically isomeric arrangements.

It will be seen from the above examples that the existence of optical 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 also perfect.

The view that the atoms or groups united to carbon are not arranged in one plane (as represented in ordinary structural formulae) is very strongly supported by considerations based on the phenomenon of structural isomerism, because a planar arrangement of the atoms or groups would render possible the existence of isomerides, in cases where experience has shown that isomerism does not occur ; in the case of the compound, $C_2H_4Cl_2$, for example, two structural isomerides—namely, $CH_3 \cdot CHCl_2$ and $CH_2Cl \cdot CH_2Cl$ —are known, in accordance with theory ; were all the atoms arranged in one plane, the following *five* isomeric compounds might be capable of existence,



As the number of asymmetric carbon-groups in the molecule of any compound increases, the number of optical isomerides becomes larger ; a substance such as saccharic acid (p. 312), for example,

$$COOH \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot COOH,$$

which contains four asymmetric groups, is capable of existing in ten optically isomeric forms. Many other examples of optical isomerism occur among the polyhydric alcohols, the carbohydrates and their derivatives (p. 310), and many other types of compounds.

An examination of the models of substances containing two asymmetric carbon-groups—or, in fact, of those of *any* compounds containing two (or more) carbon atoms united by single bonds—might lead to the supposition that such substances might exist in many modifications.

If one of the tetrahedra were slowly rotated about the common axis, the model would pass through an infinite number of forms, all of which would be different, because they would represent different relative positions in space of the atoms constituting the molecule.

This difficulty, however, is only apparent. In any compound the atoms or groups united with one of the carbon atoms exert attraction or repulsion on those united with the other ; if then, the carbon atoms are capable of *free rotation* about an axis, a certain position of equilibrium, which is the resultant of all the forces, will be attained, or the molecule will be in continuous motion. In either case the compound exists in one form only, unless, of course, it contains one or more asymmetric carbon-groups. For the purpose of determining whether a molecule is dissymmetric or not its model should be considered in its least unsymmetrical position : such a position will always be attained at some time during the rotation of the groups.

It is now possible to add another example of the use of structural formulae to those already given. The inspection of such a formula, with the aid of a model if necessary, will show whether the compound so represented can exist in an optically active form or not. In most cases all that is required is to look for the presence of an asymmetric carbon-group : if only one such group forms a part of the molecule, then the latter is dissymmetric, the compound is a *dl*-substance and it should be possible to resolve it by one or other of the methods used for this purpose. If the molecule contains two asymmetric groups of identical constitution it may be a *meso*-compound.

Resolution of dl-*Substances*

The *dl*-form of tartaric acid and the corresponding varieties of other dissymmetric substances—namely, those which are inactive because they are composed of equal quantities of the *d*- and *l*-forms —may generally be ***resolved*** into their optically active (enantiomorphously related) components by various processes.

One method, discovered by Pasteur, and even now by far the most important one, consists in fractionally crystallising the salt formed from an externally compensated or *dl*-acid, or base, with

an optically *active* substance. This method depends on the fact that the *d*- and *l*-components of the externally compensated compound give, with one and the same optically active substance, salts which are no longer enantiomorphously related and may *differ in solubility* ; such salts, therefore, may often be separated by fractional crystallisation in the ordinary way. When, for example, racemic acid is combined with the optically active base, *d*-cinchonine (p. 608), the product consists of two salts, which may be represented by (*d*-acid, *d*-base) and (*l*-acid, *d*-base) respectively ; these two salts may be separated from one another, and one at least—namely, that which is the less soluble—obtained in a pure state ; the pure acid (*d*- or *l*-) may then be prepared from the salt. In a similar manner the inactive modification of coniine (p. 598) may be *resolved* into its components by the fractional crystallisation of the salt which it forms with *d*-tartaric acid.

Another method, also discovered by Pasteur, has already been described (p. 293) : if a solution of the sodium ammonium salt, prepared from racemic (*dl*-tartaric) acid, is left to crystallise very slowly at a temperature below 28°, enantiomorphous crystals (right- and left-handed, as shown in the fig., p. 293) are deposited, and if the crystals are sufficiently large and well-formed they may be distinguished and sorted from one another. This method of separation, however, is seldom applicable, because the two active components may form a racemic substance, or, if deposited separately, their crystals may not be sufficiently well-defined to be distinguishable. Racemic acid itself cannot be resolved by this method.

A third method which is also due to Pasteur depends on the fact that when certain organisms, such as yeast or *Penicillium glaucum*, are grown in a solution of a *dl*-substance, they may bring about the decomposition of *one* of the optical isomerides, the result being that, after a time, the solution contains the other modification only.

SUMMARY AND EXTENSION

Optical isomerism. The theory originated simultaneously, but independently, by van't Hoff and Le Bel accounted satisfactorily for certain cases of isomerism met with in organic compounds, notably that of the tartaric acids, investigated by Pasteur. In its original form the theory postulated that the four valencies of a carbon atom were directed in space with equal angles between them and showed how optical isomerism was connected with the presence in the molecule of

asymmetric arrangements of carbon atoms united with four different atoms or groups.

A compound containing one asymmetric group exists in two forms, dextro (*d*-) and laevo (*l*-), which give rise to a *dl*- or externally compensated substance ; the latter, if a solid, may be racemic or a mere mixture. With *n structurally different* asymmetric groups the number of *active* forms is 2^n. In the case of a compound, such as tartaric acid, with two *structurally identical* groups the number of *active* forms is only two, because two of the four active isomerides of a compound containing two *different* asymmetric groups become identical and optically inactive, and give rise to the *meso*-isomeride. Since the original conception of Le Bel and van't Hoff was advanced the theory has been very much extended, and compounds, in the molecules of which there is no carbon atom united to four different atoms or groups, have been resolved into optically active isomerides; in these cases the structure of the molecule, regarded as a whole, is dissymmetric.

The dextro- and laevo-enantiomorphously related isomerides of any compound are identical in chemical properties and in all physical properties except those already mentioned, namely crystalline form and action (in solution) on polarised light.

A *dl*- and a *meso*-form usually differ from one another, and from the active forms, in most physical properties, but show identical chemical reactions. They also differ from one another in that the former can usually be resolved, by suitable methods, into its optically active components, whereas the latter is unresolvable.

The most usual method of resolution is by crystallising a salt formed from the externally compensated base (or acid) with an optically active acid (or base). The two salts (*d*A*d*B and *d*A*l*B or *l*A*d*B and *l*A*l*B, as the case may be) may then differ so much in solubility, that their separation can be effected. In many cases, however, the two compounds crystallise together from a given solvent and the product is then known as a *partially racemic salt* : nevertheless a separation might still be accomplished by using another solvent or crystallising at a different temperature.

Primary *dl*-bases may sometimes be resolved by condensing them with an optically active aldehyde ; the *anils*, $R \cdot N{:}CH \cdot R'$, which are thus formed may be separated by fractional crystallisation, and then reconverted into the amines by hydrolysis with acids.

dl-Alcohols, such as methylethyl carbinol, $CHMeEt \cdot OH$, may be resolved into their optically active components by the following method : the *dl*-alcohol is converted into a hydrogen ester with the aid of a dicarboxylic acid, such as phthalic acid (p. 520) ; the hydrogen ester, $CHMeEt \cdot O \cdot CO \cdot C_6H_4 \cdot COOH$, is then combined with an

alkaloid, or some other optically active base, and the two components of the salt are separated by fractional crystallisation, as described above. The *d*- and *l*-acid esters are separately regenerated from the salts and the *d*- and *l*-alcohols are finally obtained by hydrolysing the esters.

dl-Aldehydes and *dl*-ketones may be resolved with the aid of an optically active derivative of hydrazine, or other optically active primary base. The *dl*-compound gives two different hydrazones, which may be separable by fractional crystallisation.

Optically active derivatives of nitrogen, phosphorus, sulphur, selenium, silicon and many other elements, including some metals, have also been prepared. In the case of nitrogen, tetra-alkylammonium salts of the type $NR_1R_2R_3R_4X$ (where R_1, R_2, R_3, and R_4 represent *different* hydrocarbon radicals, and X a halogen atom) are treated in aqueous solution with the silver salt of an optically active acid. The product, like that formed from a *dl*-acid and an optically active base, consists of two components, which may be separable by fractional crystallisation ; if so, the halogen salts, regenerated from these components, are optically active and enantiomorphously related, unless they have racemised (p. 304).

Polarimetry

The nature of polarised light, and the instrument (the *polarimeter*) which is employed in the examination of optically active compounds, are described in text-books on physics ; but for those who are unacquainted with the use of a polarimeter the following note may be useful.

When the monochromatic light, obtained from a sodium or mercury vapour lamp, is examined with a polarimeter, and the scale of the instrument is set at the zero, an illuminated disc, divided by a vertical line, is observed,[1] and the two halves of this disc are equally bright ; if the vertical line is not sharply defined, the focus must be adjusted with the aid of the eye-piece. When now a polarimeter tube filled with a solution of an optically active substance is placed in the instrument (in the hollow bed) and the focus is adjusted, one-half of the illuminated disc becomes darker than the other. With the aid of the milled screw-head (which is usually placed horizontally) the movable graduated circle, to which the eye-piece is fixed, is turned either to the right or to the left, according as the substance is dextro- or laevo-rotatory, until a point is reached at which the two halves of the disc again become equally illuminated. The angle, through which the graduated circle has been turned from the zero, is read from the scale,

[1] This is the two-field instrument.

and is the angle of rotation, α_D (+ or −).[1] Satisfactory observations can be made only when the solution is perfectly clear and the light is good ; 5–10 observations are made, and the average result is taken : the zero of the instrument should be similarly checked.

The *specific rotation* of a liquid is the angular rotation (α), which is produced by a column of the substance 1 decimetre in length, divided by the specific gravity of the substance, and is represented by $[\alpha]_D$; hence $[\alpha]_D = \frac{\alpha_D}{l \times \text{sp. gr.}}$, where l is the length, in *decimetres*, of the column in the polarimeter tube (usually 2 decimetres).

In the case of solids the specific rotation has to be determined in solution ; observations are made with a solution of known concentration, and the rotation which would be produced by a solution containing 1 gram of the substance in 1 c.c. of the solution is then calculated. For this purpose a weighed quantity (usually about 0·5 g.) of the solid is washed into a 20 or 25 c.c. flask, with the aid of the solvent, the flask is filled to the graduation mark, the contents are thoroughly mixed, and the polarimeter tube is then filled. The specific rotation is calculated from the formula (I), where p is the weight of the substance in 100 c.c. of the solution.[2] The specific rotation varies not only with the wave-length of the light but also with the solvent, the concentration of the solution, and the temperature.

The *molecular rotation*, $[M]_D$, of a substance is given by (II) ; the division by 100 is merely for convenience.

$$[\alpha]_D = \frac{\alpha_D \times 100}{l \times p}, \qquad \text{I}$$

$$\frac{[\alpha]_D \times \text{M. Wt.}}{100}. \qquad \text{II}$$

[1] The letter D refers to the principal bright line in the spectrum of sodium. If a different line is used this is indicated by giving its wave-length, as, for example, α_{5461}.

[2] The sp. gr. of the solution is not considered as it depends almost entirely on that of the solvent which is used.

CHAPTER 19

CARBOHYDRATES

THE term *carbohydrate* was originally used to denote certain naturally occurring substances, composed of carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen was the same as in water, because such compounds might be represented as composed of carbon and water in different proportions; the formula of glucose, $C_6H_{12}O_6$, for example, might be written $6C+6H_2O$, a mode of expression which, if employed now, would be both useless and misleading.

In the course of time many derivatives of these natural products, and many other compounds more or less closely related to them, have been obtained from natural sources, or prepared in the laboratory, and have been classed with the carbohydrates; the term, therefore, can hardly be defined, as it embraces compounds which differ considerably in constitution.

The carbohydrate group is one of the more important in organic chemistry, as it includes some of the principal components of plants. 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: (*c*) The *celluloses*, substances of which the cell membranes and tissues of plants are principally composed, and which in the form of cotton, artificial silk, paper, wood, etc., are of the greatest importance in daily life.

SUGARS

The *sugars* described in the following pages may be classed into two groups: I. The *monosaccharides*, the more important of which have the molecular formula, $C_6H_{12}O_6$: II. The *disaccharides*, $C_{12}H_{22}O_{11}$. The former are not decomposed by very dilute acids, but the latter readily undergo hydrolysis, yielding two molecules of the same or of different monosaccharides.

Monosaccharides

Glucose, $C_6H_{12}O_6$, also called **dextrose,** is found in large quantities in grapes—hence the name **grape-sugar,** by which it

was formerly known ; when the grapes are dried in the sun, in the preparation of raisins, the glucose in the juice is deposited in hard, brownish-coloured nodules. It is more frequently met with associated with fructose, and mixtures of these sugars occur in the juices of a great many sweet fruits, in the roots and leaves of many plants, and in honey. Glucose may be prepared by decomposing *sucrose* (cane-sugar) with dilute acids (p. 323) and recrystallising the product (*invert sugar*) from alcohol, when the more readily soluble fructose remains in solution.

A mixture of 90% alcohol (200 c.c.) and concentrated hydrochloric acid (8 c.c.) is heated at about 50°, and powdered sucrose (75 g.) is added in small portions, the liquid being well stirred during the operation. The mixture is kept at 50° during two hours, then allowed to cool, and crystallisation is promoted by stirring the solution, or better, by adding to it a crystal of glucose. After the lapse of some days the crystals are collected and purified by recrystallisation from 80% alcohol.

Glucose is prepared commercially by the hydrolysis of starch with dilute sulphuric or hydrochloric acid under pressure (p. 327).

It crystallises with water (1 mol.) in warty masses, which liquefy at 86°, the anhydrous substance melting at 146° ; it is almost insoluble in anhydrous alcohol, but it dissolves in about its own weight of water at ordinary temperatures. It is not so sweet as sucrose. It is not carbonised when it is gently warmed with sulphuric acid (distinction from sucrose).

It reacts with certain metallic hydroxides, forming *glucosates* as, for example, *calcium glucosate*, $C_6H_{11}O_6 \cdot CaOH$, and *barium glucosate*, $C_6H_{11}O_6 \cdot BaOH$; these compounds are readily soluble in water and are decomposed even by carbonic acid, with the regeneration of glucose.

A solution of glucose gives a deposit of silver, usually as a mirror, when it is warmed with an ammoniacal solution of silver oxide ; it also precipitates gold and platinum from warm solutions of their salts. When a solution of glucose, to which potassium hydroxide has been added, is mixed with a solution of copper sulphate, a deep-blue liquid is obtained ; but when this mixture is boiled, a bright-red precipitate of cuprous oxide is deposited, and the solution becomes colourless when sufficient glucose is present ; as, moreover, a given quantity (1 molecule) of glucose always reduces exactly the same quantity (approximately 5 molecules) of cupric to cuprous

oxide, this behaviour affords a method of *estimating* glucose by titration.

The *standard* solution used for this purpose is known as *Fehling's solution*, and, as it is rather unstable, it is best prepared, as required, by mixing equal volumes of the following solutions : (1) 34·6 g. of hydrated copper sulphate, made up to 500 c.c. with water ; (2) 173 g. of Rochelle salt (p. 283) and 60 g. of sodium hydroxide, made up to 500 c.c. with water. 10 c.c. of the deep-blue solution thus obtained are completely decolourised by 0·05 g. of glucose, or by 0·0475 g. of sucrose (after inversion). In the estimation of a sugar, the solution of the latter is slowly added to a known volume of the Fehling's solution, which is kept at about 100°, until the blue colour is discharged.

A solution of *d*-glucose is dextrorotatory, hence the name dextrose, and the quantity of the dissolved sugar can be determined by finding the specific rotation (p. 309) of the solution as, within certain limits, the rotation is proportional to the concentration.[1]

Glucose ferments readily with yeast in dilute aqueous solution at a temperature of about 20–30°, yielding principally alcohol and carbon dioxide (p. 330),

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

but at the same time small quantities of glycerol, succinic acid, and other substances are formed.

It is used for preserving fruit, making syrups, caramel, etc., and for the production of alcohol.

On reduction with sodium amalgam and water, glucose is converted into a hexahydric alcohol, *sorbitol*, $C_6H_{14}O_6$ (p. 258), by the addition of two atoms of hydrogen, and on oxidation with bromine water it yields *gluconic acid*, $C_6H_{12}O_7$, by the addition of one atom of oxygen. These changes prove that glucose is an aldehyde, and as sorbitol contains six hydroxyl groups, one of which was produced from the —CHO group of glucose, five must have been already present in the glucose molecule : glucose is therefore a pentahydroxyaldehyde, $C_5H_6(OH)_5 \cdot CHO$. On oxidation with dilute nitric acid gluconic acid gives a dicarboxylic acid, *saccharic acid*, $C_6H_{10}O_8$, by the change of a $—CH_2 \cdot OH$ into a —COOH group.

Glucose is slowly transformed into a penta-acetyl derivative, $C_6H_7O(O \cdot CO \cdot CH_3)_5$, when it is warmed with acetic anhydride and

[1] For $C_6H_{12}O_6$, $[\alpha]_D$ is 52·6° in 10% aqueous solution.

a little zinc chloride. With hydroxylamine it gives an oxime, and with phenylhydrazine it forms a phenylhydrazone just as do other aldehydes.

Mannose, $C_6H_{12}O_6$, is obtained by oxidising mannitol (p. 258) with nitric acid, and by hydrolysing *seminin* (contained in various vegetable products, such as ivory-nuts) with dilute sulphuric acid. It melts at 136° and ferments with yeast.

Galactose, $C_6H_{12}O_6$, is formed by the hydrolysis of lactose, together with glucose, from which it may be separated by crystallisation from water. It is also formed by boiling certain gums with dilute sulphuric acid. It crystallises in prisms, melts at 168°, and ferments with yeast.

Mannose and galactose are both optically active and structurally *identical* with glucose, with which they are *optically isomeric*; all three compounds, therefore, show the same chemical behaviour. Thus mannose, on reduction, gives *mannitol*, $C_6H_{14}O_6$, and, on oxidation, *mannonic acid*, $C_6H_{12}O_7$; in a similar manner galactose gives *dulcitol*, $C_6H_{14}O_6$, and *galactonic acid*, $C_6H_{12}O_7$.

The dibasic acid obtained by the oxidation of mannonic acid is called *mannosaccharic acid* and, like saccharic acid, is optically active; that obtained by the oxidation of galactonic acid is called *mucic acid* and is optically inactive, just as is *meso*tartaric acid.

Fructose, $C_6H_{12}O_6$, also called **laevulose**, because it is laevorotatory,[1] occurs, together with glucose, in most sweet fruits and in honey; it may be prepared from invert sugar (p. 323) by taking advantage of the fact that it forms with calcium hydroxide a compound (*fructosate*) which is sparingly soluble in water, whereas that of glucose (p. 311) is readily soluble.

Invert sugar (10 g.) is dissolved in water (50 c.c.), the solution is well cooled with ice, and slaked lime (6 g.) is stirred into the solution in small quantities at a time. The sparingly soluble lime compound of fructose is collected on a filter, washed with a little water, well pressed, and then suspended in water and decomposed with carbon dioxide; the filtrate, on evaporation, yields nearly pure fructose as a transparent syrup.

Fructose is also prepared by heating an aqueous solution of inulin (p. 327) on a water-bath during one hour, with a few drops of sulphuric acid,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

[1] $[\alpha]_D - 93°$ in 10% aqueous solution.

The sulphuric acid is then removed by precipitation with barium hydroxide, and the solution is evaporated at 80°. On the addition of a crystal of fructose, the syrup slowly solidifies, and the crystals may then be purified by recrystallisation from alcohol.

Fructose separates from alcohol in crystals, and melts at 95°; it is more soluble in water and in alcohol than is glucose, and its taste is just about as sweet as that of the latter; it reduces Fehling's solution more rapidly than, although to exactly the same extent as, glucose, and may therefore be estimated by the same method as that used for the latter.

Fructose ferments with yeast, yielding the same products as glucose, and in the form of invert sugar is used for the manufacture of alcohol.

On reduction with sodium amalgam and water fructose is converted into two optically isomeric hexahydric alcohols, $C_6H_{14}O_6$, *mannitol* and *sorbitol*;[1] but when it is oxidised with dilute nitric acid or bromine water, instead of giving an acid, $C_6H_{12}O_7$, corresponding with gluconic acid, its molecule is broken down and a mixture of tartaric acid, $C_4H_6O_6$, and glycollic acid, $C_2H_4O_3$, is produced. In boiling aqueous solution it is also oxidised by mercuric oxide, giving *$\alpha\beta\gamma$-trihydroxybutyric acid*, $C_4H_8O_5$, and glycollic acid. It is thus proved that fructose is not an aldehyde, but a pentahydroxyketone, $C_6H_7O(OH)_5$, and as a ketone may undergo oxidation in at least two ways (p. 157); all that is proved so far is that the $>CO$ group must form the second or the third link in the carbon chain.

Fructose, just like glucose, gives a penta-acetyl derivative, $C_6H_7O(O\cdot CO\cdot CH_3)_5$, when it is warmed with acetic anhydride and zinc chloride, and it also reacts with hydroxylamine giving an oxime, and with phenylhydrazine giving a phenylhydrazone.

Except for the important difference in their behaviour on oxidation, glucose and fructose are not easily distinguished, except with the aid of a polarimeter.

Constitutions of the Monosaccharides

Although it has already been shown that glucose is a pentahydroxyaldehyde and fructose is a pentahydroxyketone, much more is needed before the complete formulae of the sugars can be given.

A most important advance towards this end was made by the

[1] The production of *two* optically isomeric alcohols is due to the fact that when the group $>CO$ becomes $>CH\cdot OH$, the two forms (+ and −) of a new asymmetric group are generated.

classical work of Kiliani: Each of these sugars combines directly with hydrogen cyanide, just like the simple aldehydes and ketones, forming cyanohydrins, which on hydrolysis with a mineral acid are converted into hexahydric acids,

$$^{1}\ M\cdot CH(OH)\cdot CHO \longrightarrow M\cdot CH(OH)\cdot CH(OH)\cdot CN \longrightarrow M\cdot CH(OH)\cdot CH(OH)\cdot COOH,$$

$$M\cdot CO\cdot CH_2\cdot OH \longrightarrow M\cdot C(OH)(CN)\cdot CH_2\cdot OH \longrightarrow M\cdot C(OH)(COOH)\cdot CH_2\cdot OH.$$

When these hexahydric acids are heated strongly with an excess of hydriodic acid and a little red phosphorus, every alcoholic hydroxyl group is displaced by a hydrogen atom and unsubstituted fatty acids are obtained.

The polyhydric acid obtained from glucose gave *n*-heptylic acid, whereas that from fructose gave methyl-*n*-butylacetic acid, $CH_3(C_4H_9)CH\cdot COOH$, the structures of both of which acids were known.

It was thus conclusively proved that both glucose and fructose are *straight chain* molecules based on normal hexane: in glucose one end of the chain of six atoms is —CHO and in fructose the second link is $>CO$. In addition to this evidence, the fact that the hexahydric alcohols obtained from glucose and fructose are both converted into normal secondary hexyl iodide when they are reduced with hydriodic acid and red phosphorus (p. 258) proves that these two compounds are derivatives of normal hexane.[2]

If now it is assumed that no carbon atom in either of the sugars is directly combined with more than one hydroxyl group, the structures of the two compounds could be represented respectively,

Glucose	Fructose
CHO	$CH_2\cdot OH$
$\dot{C}H\cdot OH$	$\dot{C}O$
$\dot{C}H\cdot OH$	$\dot{C}H\cdot OH$
$\dot{C}H\cdot OH$	$\dot{C}H\cdot OH$
$\dot{C}H\cdot OH$	$\dot{C}H\cdot OH$
$\dot{C}H_2\cdot OH$	$\dot{C}H_2\cdot OH$

[1] The group $CH_2(OH)\cdot CH(OH)\cdot CH(CH)\cdot CH(OH)$— is represented by M.

[2] The sugars themselves cannot be directly reduced in this way as they are charred.

The assumption just made, based on evidence accumulated during many years, is fully established by a great many independent facts; (1) Although hydroxy-acids such as glycollic, tartaric and trihydroxybutyric acids have been obtained from the two sugars by oxidation, no decomposition products containing the $>C(OH)_2$ group have been isolated; (2) In the step by step ascent or descent of the sugar series (p. 320) each complete stage results in the addition or loss of a $>CH(OH)$ group, never $>CH_2$ or $>C(OH)_2$; (3) The results of the study of the optical isomerism of each of the two sugars are in complete agreement with those demanded by the given formulae.

It was not so very long before it became necessary to modify the formulae given above in order to account for new facts.

When *d*-glucose is dissolved in methyl alcohol, and hydrogen chloride is passed into the hot solution, two optically isomeric (α- and β-) *methylglucosides* of the composition, $C_6H_{11}O_6 \cdot CH_3$, are gradually formed. These compounds do not reduce Fehling's solution, and do not react with phenylhydrazine, so that their molecules do not contain an aldehyde group. Only one methyl group can thus be introduced into the molecule of the sugar, and although the glucosides are stable towards alkalis, they are hydrolysed by dilute mineral acids giving glucose.

These facts can be explained by assuming that the —CHO group of the sugar combines with methyl alcohol to form —CH(OH)·OMe, of which there will be two optically isomeric forms, *d*- and *l*-, and that each of these forms then reacts with an —OH group of the same sugar molecule, with the elimination of the elements of water. In this way a ring compound will be produced and the stereoisomeric methyl glucosides are now known to be represented by the following structure:

$$CH_2(OH)\cdot CH(O)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot OCH_3.$$

Later, it was found that solid glucose exists in two stereoisomeric forms, each of which corresponds with one of the methyl glucosides, but that, unlike the glucosides, the two sugars are convertible one into the other by crystallisation under specified conditions. It was concluded therefore that in *solution*, the molecule of glucose may exist as $R\cdot CHO$ or $R\cdot CH(OH)_2$ or as an oxide form (α- or β-) derived from the latter by the loss of a molecule of water as indicated above.

Other aldoses (and ketoses) also exist in two optically isomeric *glycosidic* forms (which are polyhydric oxides) and give two optically isomeric methyl- (ethyl-, propyl-, etc.) glycosides.

The term *glucoside* is now reserved for such derivatives of *glucose* which, with similar derivatives of other sugars, are classed as *glycosides*.

Action of Phenylhydrazine on Glucose and Fructose

When glucose and fructose are treated with phenylhydrazine (1 mol.), they yield phenylhydrazones, just as do other aldehydes and ketones (p. 150),

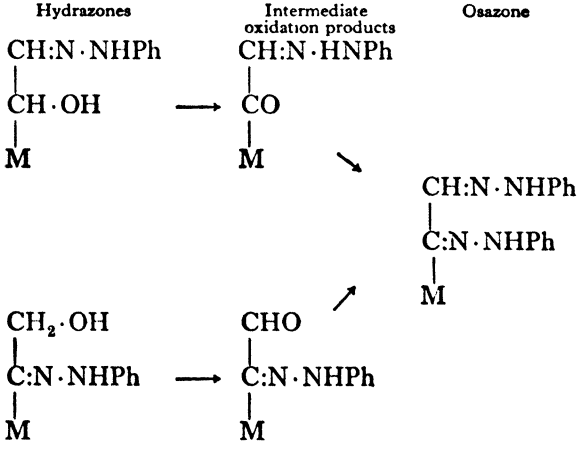
[1] $\underset{\text{Glucose}}{M\cdot CH(OH)\cdot CHO}+NH_2\cdot NHPh = \underset{\text{Glucosephenylhydrazone}}{M\cdot CH(OH)\cdot CH{:}N\cdot NHPh}+H_2O,$

$\underset{\text{Fructose}}{M\cdot CO\cdot CH_2\cdot OH}+NH_2\cdot NHPh = \underset{\text{Fructosephenylhydrazone}}{M\cdot C(:N\cdot NHPh)\cdot CH_2\cdot OH}+H_2O.$

These phenylhydrazones, when heated with an excess of phenylhydrazine, undergo some unknown changes whereby two more molecules of phenylhydrazine react to form an *osazone* (*phenylosazone*). The simplest, although possibly not the correct, explanation of osazone formation, is that the $>CH(OH)$ group adjacent to the phenylhydrazine residue of the glucose phenylhydrazone is oxidised to $>CO$ and the $—CH_2\cdot OH$ group of the fructose compound is similarly oxidised to —CHO, with the reduction of some of the phenylhydrazine to aniline and ammonia,

$$C_6H_5\cdot NH\cdot NH_2+2H = C_6H_5\cdot NH_2+NH_3.$$

The ketone or aldehyde thus formed then reacts with another molecule of phenylhydrazine, with the formation of an osazone,[2]



[1] 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 clarity, and the group $C_6H_5—$ by Ph.

[2] The practical details of the preparation of an osazone are given later (p. 461).

Although the phenylhydrazones of glucose and fructose are quite distinct substances, *they yield one and the same osazone* (m.p. 204°); this fact proves that the two sugars differ in constitution only as regards the two groups which take part in the formation of the osazone.

Other sugars, as well as other types of compounds which contain a group —CH(OH)·CHO or —CH(OH)·CO— or $CH_2(OH)\cdot CO$—, yield hydrazones or osazones according as 1 mol., or an excess, of phenylhydrazine is employed. The phenylhydrazones of the sugars are usually readily soluble in water, but the osazones are only sparingly soluble; the latter, therefore, are of the greatest service, not only in the detection and identification of a sugar, but also in the isolation of a sugar from an aqueous solution containing saline matter, etc.

When treated with strong hydrochloric acid, the osazones are decomposed with the separation of phenylhydrazine hydrochloride, and the formation of *osones*, substances which contain the group, —CO·CHO, and are therefore *both* ketones *and* aldehydes,

$$\begin{array}{lll} \text{CH:N·NHPh} & & \text{CHO} \\ \text{C:N·NHPh} & +2H_2O+2HCl = & \text{CO}+2PhNH\cdot NH_2,HCl. \\ \text{M} & & \text{M} \end{array}$$

As, moreover, osones may be reduced to sugars with the aid of zinc dust and acetic acid, the osazones, also, may be indirectly reconverted into sugars. A given osazone, however, does not necessarily yield the sugar from which it was formed; glucosazone, for example, yields first *glucosone* and then fructose, the group, —CO·CHO, of the osone being converted into —CO·CH_2·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, therefore, affords a means of converting *glucose* into *fructose* (E. Fischer).

The reverse change may be effected by reducing fructose to sorbitol and mannitol (p. 314); the former may then be oxidised to glucose.

Glucose and fructose have 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 *methylenitan* (Butlerow) or *formose* (Loew) is produced. Methylenitan and formose consist of mixtures 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 these mixtures and in other ways, E. Fischer obtained a sugar, which he called *α-acrose*, and from which he succeeded in preparing ordinary glucose and fructose and many related compounds ; these syntheses marked an outstanding advance in organic chemistry, but, unlike most syntheses, afforded little evidence as to the structures of the products.

Polyhydric Monocarboxylic Acids

As already shown, there are two types of sugars represented respectively by glucose and fructose ; the former are classed as *aldoses*, the latter as *ketoses*. Although these two types are very similar in most respects, they differ notably in their behaviour on oxidation (p. 314) ; the aldoses, cautiously treated, are converted into monocarboxylic acids, $C_6H_{12}O_7$, by direct combination with one atom of oxygen, whereas the ketose molecules are broken down, giving two or more products.

The monocarboxylic acids, produced by the oxidation of the aldoses are readily soluble in water, and those derived from the common aldoses pass spontaneously into their *lactones* (p. 287), with the loss of one molecule of water ; gluconic acid, $C_6H_{12}O_7$, for example, gives *gluconolactone*, $C_6H_{10}O_6$, mannonic acid gives the optically isomeric *mannonolactone*, and so on. These lactones are crystalline, neutral compounds, which, in aqueous solution, pass into the corresponding acids, until equilibrium is attained,

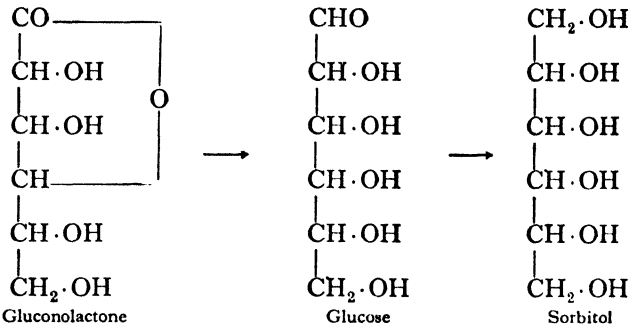
$$C_6H_{10}O_6 + H_2O \rightleftarrows C_6H_{12}O_7 ;$$

they are completely hydrolysed by alkalis.

Now these lactones can be reduced with sodium amalgam and water, in the presence of sulphuric acid,[1] and thus converted into the corresponding aldoses (E. Fischer). This reaction is of great importance, as it serves as a means of passing from the acid to the

[1] Unless the solution is kept acid, the lactone is hydrolysed and the sugar acid is *not* reduced.

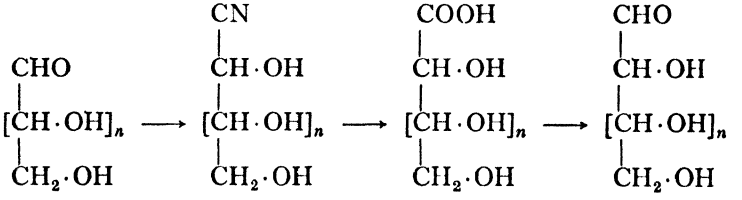
corresponding aldose, which may then be reduced to the alcohol. The following changes, for example, are thus rendered possible :



Gluconolactone — Glucose — Sorbitol

The Ascent and Descent of the Aldose Series

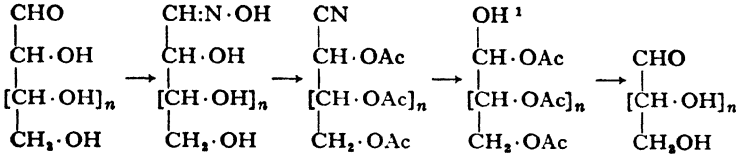
An aldose containing n carbon atoms may be transformed into an aldose containing $n+1$ carbon atoms by the following series of reactions : The aldose is combined with hydrogen cyanide, the cyanohydrin is hydrolysed to the carboxylic acid, and the *lactone* of this acid is then reduced as just described :



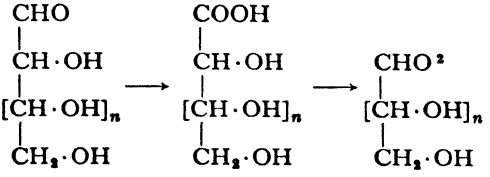
The conversion of *d*-mannose, $C_6H_{12}O_6$, into the aldoheptose, d-*mannoheptose*, $C_7H_{14}O_7$, was thus accomplished by E. Fischer, who, in a similar manner, transformed *d*-mannoheptose into d-*manno-octose*, $C_8H_{16}O_8$, and the latter into d-*mannononose*, $C_9H_{18}O_9$; the octose and the nonose, like many of the aldohexoses synthesised by E. Fischer, do not, so far as is known, occur in nature, but they are very similar to the natural monosaccharides in many of their properties.

An aldose containing n carbon atoms may be transformed into an aldose containing $n-1$ carbon atoms in the following manner : The oxime of the aldose is heated with acetic anhydride and sodium acetate, whereby the hydrogen atoms of all the alcoholic hydroxyl

groups are displaced by acetyl radicals and the group, $-CH{:}N\cdot OH$, is transformed into $-CN+H_2O$. The product is a polyacetyl derivative of a polyhydric nitrile; it gives, with an ammoniacal solution of silver (hydr)oxide, a precipitate of silver cyanide and a hydroxy-compound which is subsequently hydrolysed, with the formation of an aldose (Wohl's method). These changes are indicated below:



A similar transformation may sometimes be accomplished in a simpler manner by oxidising the aldose to the corresponding monocarboxylic acid, and then treating the latter with hydrogen peroxide in the presence of ferric acetate (Ruff's method),



Such interconversions are of great importance in showing the relationships of the sugars, and also prove that those so obtained from glucose and other straight chain structures are likewise derivatives of normal paraffins.

Disaccharides

Sucrose, or **cane-sugar,** $C_{12}H_{22}O_{11}$, is very widely distributed in nature; it occurs in large quantities in the ripe sugar-cane (15–20%) and in beetroot (some kinds of which contain as much as 20%), in smaller quantities in strawberries, pine-apples, and other fruits.

Practically the whole of the sucrose of commerce is manufactured

[1] $R\cdot CH(OAc)\cdot CN+AgOH = R\cdot CH(OAc)\cdot OH+AgCN$,
$R\cdot CH(OAc)\cdot OH+H_2O = R\cdot CH(OH)_2+C_2H_4O_2$,
$R\cdot CH(OH)_2 = R\cdot CHO+H_2O$.

[2] $R\cdot CH(OH)\cdot COOH+H_2O_2 = R\cdot CHO+CO_2+2H_2O$.

from beetroot and from the sugar-cane ; the processes of extraction are much the same in both cases, and expensive apparatus is required in order to obtain the largest possible yield of crystallised sucrose.

The sugar-canes are crushed in hydraulic presses ; but the beet-roots are cut into slices, and the sugar is extracted by a diffusion process. These different methods are necessary because if a crushing process were used for beetroot such a large proportion of colloidal matter would be extracted that the isolation of the sugar would be very difficult ; in the diffusion process the sucrose passes through the semi-permeable cell walls whereas most of the protein matter is retained. The expressed juice, or the sugar solution, is heated with about 1% of milk of lime in order to neutralise acids, and to coagulate the vegetable proteins which are always contained in the extract and which would undergo decomposition. The solution is treated with carbon dioxide in order to precipitate the excess of lime, and filtered; it is then evaporated under reduced pressure, in an apparatus heated with steam, until the syrup gives a large crystalline deposit on being cooled. The crystals are separated from the yellow or brown mother-liquor (*treacle*, *molasses*) in a centrifugal machine, and purified by recrystallisation from water, with the addition of charcoal.

The molasses still contain about 50% of sucrose, which does not crystallise from the syrup even on further evaporation, owing to the presence of impurities ; nearly the whole of this sucrose, however, can be profitably extracted by adding strontium hydroxide and then separating the precipitated strontium sucrosate (below) from the dark mother-liquor by filtration. This precipitate is suspended in water, decomposed with carbon dioxide, and the filtrate from the strontium carbonate is evaporated to a syrup ; the impurities having been removed, the sucrose separates in a crystalline form. The annual production of sucrose is about 25 million tons.

Sucrose crystallises from water in large four-sided prisms (sugar-candy), and is soluble in one-third of its weight of water at ordinary temperatures, but is almost insoluble in alcohol. It melts at about 160–161°, and does not immediately crystallise when it is cooled again, but solidifies to a pale-yellow, glassy mass, called *barley-sugar*, which, however, becomes opaque and crystalline in the course of time. At about 190-200° sucrose loses the elements of water, and is gradually converted into a brown mass, called *caramel*, which is largely used for colouring liqueurs, vinegar, soups, gravies, etc.

Warm, concentrated sulphuric acid decomposes sucrose ; when

a strong aqueous solution of sucrose is mixed with an equal volume of concentrated sulphuric acid, the mixture blackens and the carbonaceous product froths up, owing to the evolution of steam, carbon dioxide, and sulphur dioxide.

Sucrose is readily hydrolysed by dilute mineral acids, with the formation of glucose and fructose in equal quantities,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

Now, since fructose rotates the plane of polarisation to the left to a somewhat greater extent than an equal weight of glucose rotates it to the right, the mixture of the two sugars, which is thus formed, is slightly laevorotatory. When, therefore, a solution of sucrose, which is *dextrorotatory*,[1] is boiled with acids, the resulting solution is *laevorotatory*—that is to say, the direction of the rotation has been reversed or 'inverted.' Hence the hydrolysis of sucrose is usually called *inversion*, and the mixture of glucose and fructose is called *invert sugar*.

Invert sugar is a crystalline, brownish substance extensively used in the manufacture of preserves, confectionery, etc., as well as for the preparation of alcohol.

Sucrose does *not* reduce Fehling's solution or show other reactions of an aldehyde or ketone, but does so after it has been boiled with a mineral acid during a few minutes; this behaviour, the smell of burnt sugar which it gives when it is heated, and its rapid carbonisation with warm sulphuric acid serve for its detection. It may be estimated with the aid of a polarimeter and, after inversion, with Fehling's solution.

When it is boiled for a long time with hydrochloric acid (sp. gr. 1·1) it yields laevulic acid (p. 210). The action of yeast on a solution of sucrose is described later (p. 332).

When boiled with acetic anhydride and sodium acetate, sucrose is converted into *octa-acetylsucrose*, $C_{12}H_{14}O_3(O\cdot CO\cdot CH_3)_8$, m.p. 67°, and therefore its molecule contains eight hydroxyl groups; the behaviour of sucrose on hydrolysis shows that it has been formed, together with one molecule of water, by the combination of one molecule of glucose with one molecule of fructose.

Sucrose, like glucose and fructose, reacts readily with certain basic hydroxides, with the formation of sucrosates (*saccharosates*),

[1] $[\alpha]_D + 66{\cdot}5°$ in 10% aqueous solution.

one or more of the hydrogen atoms of the hydroxyl groups in the sucrose being displaced by a basic radical such as —Ca·OH. These sucrosates are produced by merely adding the metallic hydroxide to the sucrose solution. They are readily decomposed by much water and by carbon dioxide into sucrose and the hydroxide or carbonate of the metal.

Strontium sucrosate, $C_{12}H_{20}O_{11}(SrOH)_2$, is a granular substance of great commercial importance, owing to its use in separating sucrose from molasses, as described above.

Maltose, $C_{12}H_{22}O_{11}$, is produced together with dextrin (p. 327) 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 it is brought about by an enzyme, *diastase*, which is contained in the malt (p. 332).

Starch (50 g.) is heated with water (200 c.c.) on a water-bath until it forms a paste ; the product is cooled to 60°, malt extract (about 3 g.) is added, and the mixture is kept at this temperature during 1 hour. The solution is then heated to boiling, filtered, and evaporated to a syrup, from which, however, the crystallised sugar is not easily obtained.

Maltose crystallises with one molecule of water in needles, and is very soluble in water, the solution being strongly dextrorotatory [1] ; it reduces Fehling's solution, and ferments readily with yeast (p. 331). When boiled with dilute sulphuric acid, it is converted into glucose *only*,

$$C_{12}H_{22}O_{11}+H_2O = 2C_6H_{12}O_6,$$

a change which proves that maltose is a condensation product of the latter.

Maltose reacts normally with phenylhydrazine, yielding *maltosazone*, $C_{12}H_{20}O_9(N_2HC_6H_5)_2$, m.p. 206°, and gives with acetic anhydride *octa-acetylmaltose*, $C_{12}H_{14}O_3(C_2H_3O_2)_8$.

Lactose, or *milk-sugar*, $C_{12}H_{22}O_{11}$, so far, has been found in the animal kingdom only. It occurs in the milk of all mammals to the extent of about 4–8%, and is obtained as a by-product in the manufacture of cheese.

[1] For $C_{12}H_{22}O_{11},H_2O$, $[\alpha]_D$+129° in 10% aqueous solution.

When milk is treated with rennet, *casein* (p. 645) separates, and lactose remains in solution; on evaporation, the crude sugar is deposited in crystals, which are readily purified by recrystallisation from water.

Lactose crystallises with one molecule of water and dissolves in six parts of water at ordinary temperatures; it is very much less sweet than sucrose, and is dextrorotatory.[1] It reduces Fehling's solution, but much more slowly than does glucose; with phenylhydrazine it yields lactosazone, m.p. 200°, and with acetic anhydride, octa-acetyllactose. Lactose does not ferment readily with yeast, but it rapidly undergoes lactic fermentation (p. 172) under suitable conditions. It is decomposed, by boiling dilute sulphuric acid, into *glucose* and *galactose*,

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}}+H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Galactose}}{C_6H_{12}O_6}.$$

Starch and Cellulose

Polysaccharides

Starch, dextrin, and cellulose are all highly complex substances, the molecules of which seem to consist entirely of molecules of glucose which have combined with the loss of the elements of water; they are therefore classed as *polysaccharides*.

Starch, or *amylum*, $(C_6H_{10}O_5)_n$, is widely distributed throughout the vegetable world and is found in plants in the form of grains or nodules.

It occurs in large quantities in all kinds of grain, as, for example, in rice, barley, and wheat, and also in tubers, such as potatoes and arrowroot. In Europe, starch is manufactured principally from potatoes, but sometimes in other parts of the world from wheat, maize, and rice.

The potatoes are well washed, crushed, and macerated with water in fine sieves, whereon the starch passes through with the water leaving a pulp, consisting of gluten, cellulose, and other substances. The milky liquid deposits the starch as a paste, which is repeatedly washed by decantation, and then slowly dried.

The grain is first soaked in warm water, then ground in a mill, and the product is run into a large vat, where it is left to undergo

[1] For $C_{12}H_{22}O_{11},H_2O$, $[\alpha]_D+52{\cdot}5°$ in 10% aqueous solution.

lactic fermentation. During this process the sugar in the grain is converted into lactic, butyric, and acetic acids, and the gluten (p. 328) is brought into a less tenacious condition, which favours the subsequent washing of the starch in the manner described above.

When finely divided starch is examined under the microscope, it is seen to be made up of striated granules, having definite shapes and structures. Granules from different plants vary very much in appearance and in size, those of potato starch, as shown in Fig. 21

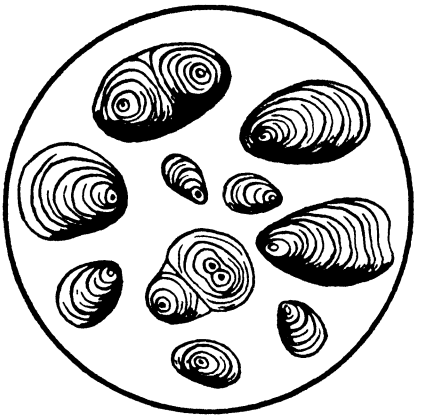


Fig. 21

(magnified 750 diameters), being comparatively large, those of barley starch considerably smaller.

Starch is insoluble in cold water, but when heated with water the granules swell and then burst. The contents of the cells (*amylose*, *granulose*) dissolve, but the cell-wall, or *starch-cellulose*, is insoluble, and can be separated by filtration ; on the addition of alcohol to the filtrate, the granulose is precipitated as an amorphous powder, which is known as *soluble starch*.

The gelatinous mass obtained when starch is heated with water 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 ; the colour disappears when the solution is heated, but reappears when the temperature falls again.

When boiled with dilute acids, starch is first converted into *dextrin*, $(C_6H_{10}O_5)_n$, and then into *glucose*,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6,$$

but the enzyme, *diastase*, decomposes it at 60–70° into *dextrin* and *maltose*, a process which is of much importance in the manufacture of alcohol and of spirituous liquors from grain (p. 332).

Since the molecule of starch is no doubt produced by the combination of n molecules of glucose, with the elimination of n or of $n-1$ molecules of water, its molecular formula must be either $n(C_6H_{12}O_6)-nH_2O$ or $n(C_6H_{12}O_6)-(n-1)H_2O$; it seems probable that many or all varieties of starch are mixtures of different compounds in which the numerical value of n ranges from about 100 upwards. The molecular formula of dextrin (and that of cellulose) may be written in the same way as that of starch, but n is doubtless a smaller number in the case of dextrin than in that of starch.

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 glucose (p. 113). It is produced by heating starch alone at about 200°, or, after moistening it with dilute acids, at 100–120° ; it is also formed by the action of malt diastase (*amylase*) on starch paste.

Dextrin is amorphous, soluble in water, and is largely used as a substitute for gum ; when boiled with dilute acids it is converted into *glucose*.

Dextrin is a mixture of various substances (amylodextrins, maltodextrins), the compositions of which are approximately expressed by the *empirical* formula, $C_6H_{10}O_5$.

Inulin, $(C_6H_{10}O_5)_n$, is a starch which occurs in many plants, especially in dahlia tubers, artichokes, and chicory ; it is readily soluble in hot water, is coloured yellow by iodine, and is hydrolysed by dilute sulphuric acid, giving fructose (p. 313).

Glycogen, or animal starch, $(C_6H_{10}O_5)_n$, 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 tasteless, odourless powder ; but it gives a wine-red colouration with iodine, and is almost entirely soluble in water to an opalescent

liquid ; it is probably very similar to starch in constitution and on hydrolysis with dilute mineral acids it is converted into glucose.

Gluten. Wheat flour contains about 70% of starch and 10% of a sticky, nitrogenous substance called *gluten*. An approximate separation of these two components may be brought about by kneading flour in a bag of thin calico under water, when the starch passes through with the water, forming a milky liquid, from which the starch is slowly deposited. The gluten remains in the bag as a tenacious, sticky, grey mass, which soon decomposes and smells disagreeably. Both starch and gluten are very valuable food-stuffs.

Cellulose, $(C_6H_{10}O_5)_n$, like starch, is very widely distributed throughout the vegetable kingdom. It is the principal component 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 less impure form may be obtained by extracting good filter-paper with hydrofluoric acid, in order to remove traces of silica, washing it well with water, and drying it at 100°.

Cellulose is insoluble in all the ordinary solvents, but it dissolves in an ammoniacal solution of cupric hydroxide (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 as an amorphous powder. Cellulose is also soluble in a concentrated solution of zinc chloride.

When heated with acetic anhydride at 180°, it yields *cellulose hexa-acetate*, $[C_{12}H_{14}O_4(O \cdot CO \cdot CH_3)_6]_n$, a flocculent solid.

The molecular formula of cellulose may be written $(C_6H_{10}O_5)_n$, where n probably exceeds 2000, and it is likely that several varieties of this substance occur in nature.

Concentrated sulphuric acid gradually dissolves cellulose, and when the solution is diluted with water and boiled, dextrin and ultimately glucose are produced. It is thus possible to obtain sugar, and consequently alcohol, from wood.

When unsized paper is immersed in concentrated sulphuric acid for a few seconds, and is 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 nitrates. When *purified* cotton-wool is treated with nitric acid, or, better, with a mixture of nitric and sulphuric acids, various nitrates of cellulose are produced, according to the quantity and concentration of the acids employed, and the length of time during which they are allowed to act.

If cotton-wool is soaked in a mixture of one volume of nitric acid (sp. gr. 1·5) and three volumes of concentrated sulphuric acid during about five minutes, and is then thoroughly washed and dried,[1] the product has, approximately, the composition of a hexanitrate, $C_{12}H_{14}O_4(O \cdot NO_2)_6$, and is called *gun-cotton.*

Gun-cotton is insoluble in a mixture of alcohol and ether; it burns rapidly and quietly, without smoke, when a flame is applied to it, but when fired with a detonator it explodes with great violence. It is used as an explosive, either alone or mixed with nitroglycerin, the mixture being known as *gelignite*, *ballistite* or blasting-gelatin.

Cordite is a mixture of gun-cotton and nitroglycerin, made into a gelatinous mass with the aid of acetone and vaseline, and then worked into threads; it is used as a smokeless powder.

When treated with a less concentrated mixture of nitric and sulphuric acids, cellulose is converted principally into *tetra-nitrate*, $C_{12}H_{16}O_6(O \cdot NO_2)_4$, and *penta-nitrate*, $C_{12}H_{15}O_5(O \cdot NO_2)_5$ (*pyroxylin*), both of which dissolve in a mixture of alcohol and ether; a solution of the mixed nitrates in alcohol and ether constitutes *collodion*, which is used for photographic and other purposes.

Celluloid or *xylonite* is a mixture of cellulose nitrates (principally the tetra-nitrate) and camphor, which has been heated at about 75° under great pressure; it is readily combustible, but is not explosive. Cellulose nitrates, dissolved in various solvents and mixed with pigments, are also very largely used as lacquers for motor-cars. The nitrates of cellulose are decomposed by alkalis, yielding nitrates of the alkalis and cellulose; they are, therefore, esters and not nitro-derivatives (p. 251).

Artificial silk, or *Rayon*, is the name given to various fibres which are now manufactured in very large quantities from cotton- or wood-cellulose; these materials have many of the physical properties of natural silk (the product of the silk-worm), but differ entirely from

[1] Gun-cotton is best dried with the aid of alcohol: it is dangerous to heat it, even at relatively low temperatures. The dry substance *may* be exploded by friction.

the latter in composition. Artificial silk is highly lustrous and can be dyed in a great many colours.

In the manufacture of artificial silk, crude cellulose is heated under pressure with dilute aqueous alkalis (or is treated in other ways) in order to free it from gum, oil, etc., and the purified cellulose or, more commonly, some easily prepared cellulose derivative, is dissolved in some suitable solvent. The liquid is then forced through sets of minute holes (spinnerets) into water or some liquid which precipitates the cellulose or cellulose derivative, or the solvent is rapidly evaporated as the solution is extruded, and the very fine fibres so obtained are then spun and made into fabrics.

The principal kinds of artificial silk are obtained as follows: (1) Cellulose is dissolved in an ammoniacal solution of cupric oxide and reprecipitated as cellulose by dilute acids (Cuprammonium process). (2) Cellulose is agitated with a solution of sodium hydroxide, and the swollen product (alkali cellulose) is pressed, shredded, and stored (ripened) during 2-3 days at 20°; it is then churned with carbon disulphide vapour and sodium hydroxide and converted into cellulose xanthate (p. 263), which is precipitated as cellulose by saline solutions of dilute acids (Viscose process). (3) Partially hydrolysed cellulose acetate, dissolved in acetone, is reprecipitated as such by rapidly evaporating the solvent of the extruded solution in air at 50–60° (Celanese or acetate silk). (4) Cellulose nitrate dissolved in alcoholic ether (collodion) is reprecipitated as such by the rapid removal of the solvent and the nitrate is converted into cellulose by treatment with ammonium hydrogen sulphide. This, the first method to be used (Chardonnet process), is now practically obsolete.

Esters of cellulose, such as the nitrate and acetate, and ethers, such as ethyl cellulose, are also useful plastics. *Cellophane* is usually cellulose, regenerated from the nitrate, or cellulose acetate.

Nylon is not a cellulose derivative; it is prepared by the condensation of adipic acid and hexamethylenediamine (Part III).

Fermentation and Enzyme Action

When the juice of grapes is kept during a few days at ordinary temperatures, it changes into wine; the sugars, glucose and fructose, contained in the juice are decomposed into alcohol and carbon

dioxide (p. 110). This change is brought about by a living vegetable organism (yeast), which is present on the grapes and their stalks and also in the air ; the process is called *fermentation*, and the living agent which causes the change is termed a *ferment*. All wines, beers, and spirits, as well as commercial alcohol, are prepared by a process of fermentation.

Yeast (*Saccharomyces*) consists of rounded, almost transparent, living cells about 0·01 mm. in diameter, which are usually grouped together in chain-like clusters ; when magnified (450 diameters), yeast cells have the appearance shown in Fig. 22. When placed in

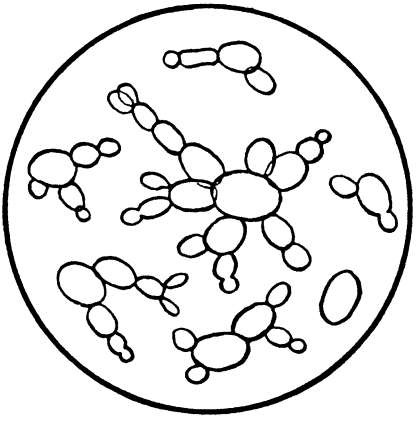


Fig. 22

solutions of certain sugars containing small quantities of mineral and nitrogenous substances, 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 varies widely from these limits the plant stops growing, and may ultimately be killed. The action of yeast is due to certain *enzymes* which are contained in the cells, and fermentation can be brought about by the juice of the cells, in the absence of the living organism. An enzyme is a complex nitrogenous organic substance, which acts catalytically in facilitating a chemical change ; as a rule, the action of a particular enzyme is limited to one, or to a few, substances only, and different enzymes usually produce different results. Enzymes lose their activity on being heated.

Enzymes, unlike inorganic catalysts, are gradually used up and disappear during the processes which they bring about. Some enzymes, originally believed to be distinct substances, have been proved to be mixtures of two components (named the enzyme and the co-enzyme respectively) which may differ very greatly in properties, and each of which plays a distinct part during the chemical change (Part III).

Yeast cells contain many enzymes, among others : (1) *Invertase*, which brings about the ' inversion ' (hydrolysis) of sucrose, and converts it into a mixture of glucose and fructose (p. 323).

(2) *Maltase*, which brings about the hydrolysis of maltose, and converts it into glucose (p. 324).

(3) *Zymase*, which brings about the alcoholic fermentation of glucose, fructose and mannose.

The fusel oil, produced in the preparation of alcohol, is formed by the action of yeast on certain amino-acids, which are themselves decomposition products of the proteins of vegetable matter (p. 624) ; it is separated from the alcohol by fractional distillation.

Beer is prepared from malt and hops. Malt is the grain of barley, which has been caused to sprout or germinate by being soaked in water and then kept in a moist atmosphere at a suitable temperature. During the process of germination an enzyme, *diastase* (*amylase*), 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. The malt is then stirred with water and kept at 60–65°, when *diastatic fermentation* sets in, and the diastase converts the *starch* in the malt into *dextrin* and *maltose* (p. 113). The solution (' *wort* ') is now boiled in order to stop the diastatic fermentation, and 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. The liquid is then cooled to from 5 to 20°, and *yeast* is added to it to set up alcoholic fermentation. The beer is afterwards run off and kept until ready for consumption.

Beer contains alcohol (3–6%), carbon dioxide, dextrin, sugars, hop-extracts and very small proportions of fusel oil, etc.

Light wines (claret, hock) are merely fermented grape-juice to which some additional sugar may have been added; if bottled before

fermentation has ceased they are ' sparkling ' (champagne, etc.). Strong wines (port, sherry) are those which have been ' fortified ' by the addition of alcohol (rectified spirit). The colour of red wines is derived from the skins of purple grapes.

Spirits are the distillates from fermented liquors : that of grape-juice affords brandy, that of sugar-cane juice gives rum, that of grain (usually barley), which has undergone diastatic and alcoholic fermentation, gives gin (when flavoured with juniper) or whisky. The smell and taste (bouquet, aroma) of wines and spirits is due to the presence of very small quantities of esters, aldehydes and other compounds.

The percentage of alcohol by weight in some of the better-known fermented liquors varies greatly, but is roughly as follows :

Brandy	35	Port	20	Claret	7
Whisky	35	Sherry	16	Burton Ale	5·5
Gin	35	Hock	8	Lager-beer	3

SUMMARY AND EXTENSION

Carbohydrates. The carbohydrates described above may be classed as follows :

Sugars { Monosaccharides { Aldoses : Glucose, Mannose, Galactose. / Ketoses : Fructose. / Disaccharides : Sucrose, Maltose, Lactose.

Starches / Celluloses { Polysaccharides : Starch, Dextrin, Inulin, Glycogen, Cellulose.

Only the more important members of each class are given as examples.

Monosaccharides. These compounds combine the properties of *alcohols* with those of *aldehydes* or *ketones*, and are classed as **aldoses** or **ketoses** respectively : the aldoses are further distinguished as *aldo-trioses*, *-tetroses*, *-pentoses*, etc., according to the number of carbon atoms in their molecules. All these compounds are derivatives of the normal paraffins, as shown below :

$$CH_3(OH)\cdot CHO,$$
$$CH_2(OH)\cdot CH(OH)\cdot CHO,$$
$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO,$$
$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO,$$
$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO.$$

The simplest hydroxyaldehyde is glycollic aldehyde (p. 243), and next in order of molecular weight comes glyceraldehyde (p. 248), but

these two relatively simple compounds are not usually considered as monosaccharides ; the third formula represents four optical isomerides and the number increases rapidly with each addition of the group $>CH \cdot OH$ to the molecule.

Preparation. **Aldoses** may be prepared by oxidising the corresponding alcohols ; hydrogen peroxide, in the presence of a trace of a ferrous salt (Fenton's reagent), is often used for this purpose (p. 248). Just as glycol gives glycollic aldehyde and glycerol gives glyceraldehyde (and also dihydroxyacetone, $HO \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH$), so also the higher polyhydric alcohols, such as erythritol, arabitol, mannitol, etc. (p. 257), give the corresponding tetroses, pentoses, hexoses, etc.

Aldoses may also be prepared from the corresponding acid by the reduction of its lactone in *acid* solution (p. 319).

Properties. The aldoses are closely related in chemical properties, and show the following very important reactions :

They are reduced by sodium amalgam and water to the corresponding polyhydric alcohols ; an aldohexose, for example, gives a hexahydric alcohol or *hexitol*, an aldopentose, a pentahydric alcohol or *pentitol*, and so on.

They are oxidised by nitric acid, by bromine and water, and by other reagents. The first product is a *mono*carboxylic acid, produced by the oxidation of the aldehyde group ; glucose, for example, gives *gluconic acid*, mannose gives the optically isomeric *mannonic acid*, xylose gives *xylonic acid*, and so on. These monocarboxylic acids, on further oxidation, are transformed into *di*carboxylic acids by the conversion of $—CH_2 \cdot OH$ into —COOH ; thus gluconic acid gives *saccharic acid*, $HOOC \cdot [CH \cdot OH]_4 \cdot COOH$, mannonic acid gives the optically isomeric *mannosaccharic acid*, and xylonic acid gives *trihydroxyglutaric acid*, $HOOC \cdot [CH \cdot OH]_3 \cdot COOH$.

The aldoses combine directly with hydrogen cyanide (1 mol.), forming *hydroxycyanides*, which may be hydrolysed to monocarboxylic acids. An aldo*hexose* is thus converted into an acid which is structurally identical with the oxidation product of an aldo*heptose*, and similarly in other cases the final result is the transformation of the —CHO group into $—CH(OH) \cdot COOH$. The aldoses readily reduce Fehling's solution, react with hydroxylamine, giving oximes, and with phenylhydrazine, giving either a phenylhydrazone or an osazone, according to the conditions of the experiment (p. 317). They may be converted into esters, such as nitrates, acetates, and benzoates, just as may the simple alcohols.

They react with alcohols in the presence of hydrogen chloride, forming glycosides, which are derived from the glycosidic or oxide structures of the aldoses.

Erythrose, $CH_2(OH) \cdot CH(OH) \cdot CH(OH) \cdot CHO$, is an example of

an *aldotetrose* ; it is obtained, mixed probably with the isomeric *keto-tetrose*, $CH_2(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH$, by the oxidation of erythritol.

Arabinose and **xylose** are optically isomeric *aldopentoses* of the constitution, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$. l-*Arabinose* is obtained by boiling cherry-gum, or gum-arabic, with dilute sulphuric acid ; it melts at 160°, and is dextrorotatory. l-*Xylose* is obtained by boiling wood-gum (xylan) with dilute sulphuric acid ; it melts at 143°, and is dextrorotatory Although these aldopentoses are both dextrorotatory, they are both distinguished from their enantiomorphously related isomerides (d-*arabinose* and d-*xylose*) by the letter *l*, which generally denotes a laevorotatory compound ; the reason for this is that they are related to *l*-glucose rather than to *d*-glucose as regards their configurations (Part III).

Both these aldopentoses are formed when bran, straw, and various other vegetable products are boiled with dilute sulphuric acid. Like the aldohexoses, they have a sweet taste, and reduce Fehling's solution, but they do not ferment with yeast ; when warmed with hydrochloric acid and a little phloroglucinol (p. 492), they give a cherry-red solution. They both yield furfural (p. 585) when they are distilled with hydrochloric or dilute sulphuric acid ; this reaction may be used for their detection and also for their estimation, since the furfural in the distillate may be isolated and weighed in the form of its very sparingly soluble phenylhydrazone.

Ketoses. Polyhydric ketones corresponding with fructose in structure are not so numerous as the aldoses, but various compounds of this type, such as *erythrulose*, $CH_2(OH)\cdot CH(OH)\cdot CO\cdot CH_2OH$, *arabinulose*, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH$, and *sorbose* (an optical isomeride of fructose), are known. The simplest ketose is dihydroxyacetone, which is not usually classed with the sugars.

Preparation. The ketoses just named, and also fructose, have been obtained with the aid of the *Sorbose bacterium*, which brings about the oxidation of the corresponding polyhydric alcohols (erythritol, arabitol, and sorbitol) to ketoses, and also that of the aldoses to the corresponding monocarboxylic acids.

Properties. The ketoses reduce Fehling's solution, and when treated with sodium amalgam and water they are transformed into a mixture of two polyhydric alcohols (p. 314) ; on oxidation they are converted into two (or more) relatively simple acids. They combine directly with hydrogen cyanide and react with phenylhydrazine yielding phenylhydrazones or osazones ; they also give oximes. They may be converted into glycosides (fructosides) just as may the aldoses.

Disaccharides, $C_{12}H_{22}O_{11}$. These sugars readily undergo hydrolysis by acids or enzymes into two molecules of the same or different

hexoses, and may be regarded as ether-like compounds produced by the elimination of water from the latter. Some, such as sucrose, have no reducing properties and do not form an osazone, while others, like lactose and maltose, reduce Fehling's solution and react with phenylhydrazine, etc. The reasons for this difference in behaviour are given in Part III.

Polysaccharides, $(C_6H_{10}O_5)_n$. The polysaccharides differ more widely from the other carbohydrates than the latter do among themselves, no doubt owing to their relatively high molecular weights. They are in general amorphous. They are hydrolysed by acids or enzymes, and are finally converted into monosaccharides.

CHAPTER 20

OLEFINIC AND ACETYLENIC DERIVATIVES

THE hydrocarbons already described may be divided into two groups, (1) the paraffins, which react by *substitution* only and are known as *saturated* hydrocarbons ; (2) the olefines, acetylenes, etc., which can form *additive* products and are called *unsaturated* hydrocarbons. The former contain carbon atoms united only by single bonds, whereas the latter have at least two carbon atoms which are united by a double or treble bond.

Now if attempts are made to extend such a distinction to other types of compound, it is found that almost every substance is capable under certain conditions of reacting additively ; aldehydes and ketones, for example, unite with hydrogen and with hydrogen cyanide to form alcohols and cyanohydrins respectively ; cyanides may be reduced, or hydrolysed to amides ; inner anhydrides, certain oxides, such as ethylene oxide, and lactones, give additive products by the fission of a carbon-oxygen bond ; amines of all classes combine directly with acids and with alkyl halides owing to a possible increase in the valency of the nitrogen atom, and so on. There are, in fact, comparatively few types of compounds which, like the paraffins, are really saturated and quite incapable of direct combination with some reagent or another.

As, therefore, for purposes of classification the use of the very comprehensive term unsaturated may give rise to ambiguity, all those compounds which owe their property of forming additive products to the presence of carbon atoms united by a double or treble bond, and in which the addenda combine with these carbon atoms, are distinguished as *ethylenic* (*olefinic*) or *acetylenic* as the case may be.

A few of the better-known compounds of this kind are described in this chapter : it will be seen that they show the chemical properties of ethylenic or acetylenic hydrocarbons as well as the reactions of their substituent atoms or groups, such as —Cl, —OH, —COOH, which have already been studied, but which may show differences from those of the same groups in saturated molecules.

Vinyl Compounds

The simplest olefinic compounds, substitution products of ethylene, are the vinyl derivatives; they contain the unsaturated *vinyl* radical, CH_2:CH—, combined with a halogen atom, CH_2:CHX, or a simple saturated univalent group, and are of little importance except for their use in the manufacture of plastics (Part III).

Vinyl chloride, chloroethylene, CH_2:CHCl, cannot of course be obtained by the action of chlorine on the olefine under ordinary conditions because addition of the halogen would occur; it is prepared on the large scale by the direct combination of acetylene and hydrogen chloride, or by treating ethylene dichloride with alkalis,

$$CH_2Cl \cdot CH_2Cl + NaOH = CH_2{:}CHCl + NaCl + H_2O.$$

It is a gas which polymerises readily giving *polyvinyl chloride*, a waxy product, used as an insulating covering for electric cables.

Vinyl bromide, CH_2:CHBr, is a liquid, boiling at 16°.

The halogen atoms in the vinyl halides and in other compounds containing the grouping $>$C:CX— (X, halogen) are very much more firmly held by the carbon atom to which they are combined than those in the alkyl halides: in consequence they do not undergo most of the reactions of the latter and are of little value in synthesis.

When the halogen derivatives are hydrolysed, they do not afford *vinyl alcohol* as might have been expected, because this structure, CH_2:CH·OH, undergoes isomeric change into acetaldehyde, $CH_3 \cdot CHO$; *polyvinyl alcohol*, however, and other derivatives of vinyl alcohol, are important plastics (Part III).

Vinyl acetate, CH_2:CH·O·CO·CH_3, is manufactured by treating acetylene with acetic acid in the presence of catalysts,

$$CH{:}CH + CH_3 \cdot COOH = CH_2{:}CH \cdot O \cdot CO \cdot CH_3;$$

it polymerises to polyvinyl acetate.

Allyl Compounds

The unsaturated complex, CH_2:CH·CH_2—, which is isomeric with the propenyl group, CH_3·CH:CH—, is called the *allyl* radical; certain allyl derivatives have been known for a long time, partly owing to their occurrence in nature, partly because they could be obtained from glycerol.

Allyl chloride, CH_2:CH·CH_2Cl, is now prepared commercially

from propylene as already described (p. 246); it is a lachrymatory liquid, boiling at 45°.

Allyl bromide, $CH_2{:}CH\cdot CH_2Br$, may be obtained in the laboratory by treating allyl alcohol with a mixture of hydrobromic and sulphuric acids; it is a liquid of sp. gr. 1·43 at 15° and boils at 71°.

Allyl iodide, $CH_2{:}CH\cdot CH_2I$, may likewise be obtained by treating allyl alcohol with iodine and phosphorus, but is also conveniently prepared from glycerol.

Iodine (30 g.) is mixed with glycerol (45 g.) in a large retort connected with a condenser, and the air is displaced by carbon dioxide, which is passed through the apparatus during the experiment. *Small* pieces of white phosphorus (18 g.) are added from time to time while the mixture is *very gently* warmed if necessary to start the reaction, and the allyl iodide is afterwards distilled.

It is probable that the glycerol is first converted into the triiodide, $CH_2I\cdot CHI\cdot CH_2I$, which then undergoes decomposition into iodine and allyl iodide; if phosphorus and iodine are employed in excess the allyl iodide is converted into *iso*propyl iodide,

$$CH_2{:}CH\cdot CH_2I+HI = CH_2{:}CH\cdot CH_3+I_2,$$
$$CH_2{:}CH\cdot CH_3+HI = CH_3\cdot CHI\cdot CH_3.$$

Allyl iodide is a mobile liquid of sp. gr. 1·89 at 15°, boiling at 102°, and has an odour of garlic; it resembles ethyl iodide in many respects, but has also the properties of an olefinic compound. When heated with potassium sulphide in alcoholic solution, it is converted into *diallyl sulphide*, just as ethyl iodide gives diethyl sulphide,

$$2CH_2{:}CH\cdot CH_2I+K_2S = (CH_2{:}CH\cdot CH_2)_2S+2KI.$$

The halogen atom of the group, $>C{:}CH\cdot CH_2X$, in contrast to that of a vinyl halide, is very reactive, even more so than that of an alkyl halide; the allyl halides, therefore, are very much used, particularly in the form of their Grignard reagents, in the synthesis of olefinic compounds in general.

Diallyl sulphide, $(CH_2{:}CH\cdot CH_2)_2S$, occurs in nature in many Cruciferae, and is obtained by distilling the macerated plants with water; it is a mobile, very unpleasant-smelling liquid, boiling at 139°. Another allyl derivative—namely, *allyl* iso*thiocyanate*—is found in nature in considerable quantities in black mustard seeds, and is known as *oil of mustard* (p. 365). *Diallyl disulphide*, $(C_3H_5)_2S_2$, occurs in garlic (*Allium sativum*).

Allyl alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, is formed and distils over when anhydrous glycerol is slowly heated to about 230° with twice its weight of hydrated oxalic acid ; the glycerol and the acid first react normally giving an ester, *dioxalin*, which at higher temperatures decomposes into carbon dioxide and allyl alcohol.

$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO \\ | \quad\quad | \\ CH\ {\cdot}O{\cdot}CO \\ | \\ CH_2{\cdot}OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2{\cdot}OH \end{array} + 2CO_2.$$

The liquid which passes over from about 220-230° is collected separately, and boiled with sodium hydroxide solution in order to hydrolyse allyl formate which may be present. The allyl alcohol is then separated from the aqueous solution by fractional distillation (with the aid of a long column), dried with anhydrous potassium carbonate, and finally distilled. In the first operation the thermometer dips into the *liquid*, but in the other distillations the temperature of the vapour is taken in the usual way.

Formic acid may be used instead of oxalic acid, as the monoformin (p. 161) which is first produced is decomposed into allyl alcohol, carbon dioxide and water.

Allyl alcohol is also obtained when acraldehyde (p. 341) is reduced with nascent hydrogen, a change which is exactly analogous to the formation of alcohol from acetaldehyde,

$$CH_2{:}CH{\cdot}CHO + 2H = CH_2{:}CH{\cdot}CH_2{\cdot}OH.^1$$

It is now manufactured from propylene (p. 246). It is a mobile, neutral liquid, boils at 96–97°, and has a very irritating smell ; it is miscible with water, alcohol, and ether.

Allyl alcohol has not only the properties of a primary alcohol, but also those of olefinic compounds in general. Its alcoholic character is shown by the following facts : It dissolves sodium with the evolution of hydrogen and forms esters with acids,

$$2CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2Na = 2CH_2{:}CH{\cdot}CH_2{\cdot}ONa + H_2,$$

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + CH_3{\cdot}COOH = CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O\ ;$$

[1] With molecular hydrogen and a catalyst acraldehyde gives propionaldehyde and some propyl alcohol (p. 346).

on oxidation with silver oxide it is converted, first into acraldehyde, 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 olefinic compound is shown by its behaviour towards chlorine and bromine, with which it combines directly, forming glyceryl $\alpha\beta$-dichloro- or $\alpha\beta$-dibromo-hydrin, isomeric with the corresponding $\alpha\gamma$-compounds obtained by treating glycerol with halogen acids (p. 249); on oxidation with permanganate it gives glycerol,

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

The structure of allyl alcohol, expressed above, is therefore fully established.

Acraldehyde (*acrolein*), $CH_2{:}CH\cdot CHO$, is formed during the partial combustion of fats, and when impure glycerol is distilled under ordinary pressure; also when allyl alcohol is cautiously oxidised under particular conditions (p. 346). It is prepared by distilling glycerol with potassium hydrogen sulphate,

$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot OH \end{array} \longrightarrow \begin{array}{l} CH\cdot OH \\ \| \\ CH \\ | \\ CH_2\cdot OH \end{array} \longrightarrow \begin{array}{l} CHO\,[1] \\ | \\ CH_2 \\ | \\ CH_2\cdot OH \end{array} \longrightarrow \begin{array}{l} CHO \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

Acraldehyde is a liquid, boils at 52°, and has an exceedingly irritating and disagreeable odour, like that of scorched fat; it produces sores when brought in contact with the skin, and its vapour causes a copious flow of tears. Like other aldehydes, it reduces ammoniacal solutions of silver hydroxide with the formation of a mirror, gives Schiff's reaction and combines with sodium hydrogen sulphite; it rapidly undergoes polymerisation into an amorphous, brittle substance named *disacryl*.

On reduction acraldehyde may be converted into allyl alcohol; on exposure to the air, or on treatment with silver oxide, it readily

[1] Compare isomeric change of vinyl alcohol (p. 338).

undergoes oxidation, yielding acrylic acid. That it is olefinic is shown by the fact that it combines directly with bromine, forming *acraldehyde* (*acrolein*) *dibromide*, $CH_2Br \cdot CHBr \cdot CHO$, an additive product.

The relationship of acraldehyde, allyl alcohol and acrylic acid is just the same as that of acetaldehyde, ethyl alcohol and acetic acid.

Crotonaldehyde (*crotonal*), $CH_3 \cdot CH{:}CH \cdot CHO$, is one of the next homologues of acraldehyde ; it is obtained by heating acetaldehyde with dilute hydrochloric acid, or with a solution of zinc chloride, aldol being formed as an intermediate product (p. 141),

$$2CH_3 \cdot CHO = CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO,$$
$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO = CH_3 \cdot CH{:}CH \cdot CHO + H_2O.$$

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* (below).

Mono-olefinic Acids

Acrylic acid, $CH_2{:}CH \cdot COOH$, is the simplest olefinic acid and the first member of a homologous series $C_nH_{2n-2}O_2$; it is an oxidation product of allyl alcohol and of acraldehyde and may also be obtained from hydracrylic acid (p. 269), which on distillation loses the elements of water,

$$CH_2(OH) \cdot CH_2 \cdot COOH = CH_2{:}CH \cdot COOH + H_2O ;$$

this change may be compared with the formation of ethylene from alcohol. Acrylic acid may be prepared by heating β-bromopropionic acid with alcoholic potash, just as ethylene is obtained from ethyl bromide,

$$CH_2Br \cdot CH_2 \cdot COOH = CH_2{:}CH \cdot COOH + HBr.$$

Acrylic acid boils at 141° ; it smells like acetic acid, is miscible with water, and when kept for a long time, gives a solid polymeride. It is a monocarboxylic acid, and forms metallic salts and esters just as do the fatty acids ; it differs from the latter, however, in being an olefinic compound, as is shown by the formation of additive products. It combines directly with nascent hydrogen (from sodium amalgam and dilute acid), giving propionic acid ; with bromine,

giving $\alpha\beta$-dibromopropionic acid; and with halogen acids, yielding β-halogen derivatives [1] of propionic acid,

$$CH_2{:}CH\cdot COOH + HBr = CH_2Br\cdot CH_2\cdot COOH.$$

Ethyl acrylate, $CH_2{:}CH\cdot COOC_2H_5$, is manufactured from ethylene cyanohydrin (p. 244), which is hydrolysed, esterified and dehydrated in one operation by heating it with alcohol and sulphuric acid,

$$CH_2(OH)\cdot CH_2\cdot CN + C_2H_5\cdot OH = CH_2{:}CH\cdot COOC_2H_5 + NH_3.$$

It boils at 100° and polymerises readily.

Methyl α-methylacrylate, $CH_2{:}C(CH_3)\cdot COOCH_3$, is manufactured by dehydrating acetone cyanohydrin, and boiling the product, $CH_2{:}C(CH_3)\cdot CN$, with methyl alcohol and sulphuric acid; it polymerises readily, giving important plastics (*Diakon*, *Perspex*) used for the production of glass substitutes, lenses, mirrors, etc.

Crotonic acid, $CH_3\cdot CH{:}CH\cdot COOH$, one of the next normal homologues of acrylic acid, may be obtained by methods similar to those given for acrylic acid—namely, by oxidising crotonalcohol or crotonaldehyde, by heating β-hydroxybutyric acid, and by treating α-bromobutyric acid with alcoholic potash. It melts at 72°, and resembles acrylic acid in general behaviour.

Iso*crotonic acid* (m.p. 15°) has the same structure as crotonic acid, but differs from the latter in physical properties; the relationship between the two acids is explained later.

Oleic acid, $C_{18}H_{34}O_2$, is a higher member of the same homologous series as acrylic and crotonic acids and is an important constituent of many glycerides (p. 252). It melts at about 14° and is odourless, but it oxidises on exposure to the air and becomes rancid.

On oxidation with permanganate it first gives *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$, which is then converted into a mixture of normal *nonylic acid* (*pelargonic acid*), $CH_3\cdot[CH_2]_7\cdot COOH$, and *azelaic acid*, $COOH\cdot[CH_2]_7\cdot COOH$; such changes are the usual result of the oxidation of olefinic compounds (p. 95). On reduction with hydrogen (p. 256), oleic is transformed into stearic acid.

These facts prove that oleic acid has the constitution,

$$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot COOH.$$

This view is fully confirmed by treating oleic acid with ozone, and

[1] In such reactions the halogen atom usually combines with that unsaturated carbon atom which is the more remote from the carboxyl group.

decomposing the ozonide with water; the products are nonylic acid and azelaic acid (p. 96).

Elaidic acid (m.p. 51°) has the same structure as oleic acid, from which, however, it differs in physical and chemical properties (p. 350).

Ricinoleic acid,

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH_2 \cdot CH{:}CH \cdot [CH_2]_7 \cdot COOH,$$

is a hydroxymono-olefinic acid which, as a glyceride, forms the main component of castor oil; when it is heated with sulphuric acid it loses the elements of water and gives a mixture of linoleic acid (p. 345) and a structural isomeride of the latter; it is therefore used in the manufacture of drying oils.

Olefinic acids of the acrylic series may be prepared from olefinic alcohols, aldehydes and halides by methods analogous to those used in the case of the saturated acids,

$$CH_2{:}CH \cdot CH_2 \cdot OH \longrightarrow CH_2{:}CH \cdot CHO \longrightarrow CH_2{:}CH \cdot COOH,$$
$$CH_2{:}CH \cdot CH_2I \longrightarrow CH_2{:}CH \cdot CH_2 \cdot CN \longrightarrow CH_2{:}CH \cdot CH_2 \cdot COOH.$$

They are more usually prepared by heating the monohalogen derivatives of the fatty acids with alcoholic potash, quinoline or dimethylaniline; this last method is used more particularly for the preparation of $\alpha\beta$-unsaturated acids because only the α-halogen substituted fatty acids are easily produced directly from the saturated compounds (p. 180).

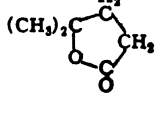
They may also be prepared from ketonic acids, many of which can be easily obtained with the aid of ethyl acetoacetate: the ketonic acid is first reduced to the corresponding hydroxy-compound and the latter is then heated alone or with some dehydrating agent, or converted into the halogen acid and then treated as above.

The olefinic acids show considerable differences in behaviour, determined by the relative positions of the olefinic binding and the carboxyl group. Thus many $\alpha\beta$-unsaturated acids when heated with aqueous alkali yield saturated hydroxy-acids,

$$CH_2{:}CH \cdot COOH + H_2O = CH_3 \cdot CH(OH) \cdot COOH,$$

whereas $\beta\gamma$-unsaturated acids, heated with dilute sulphuric acid, often yield lactones (p. 287), such as *iso*caprolactone,

$$(CH_3)_2C{:}CH \cdot CH_2 \cdot COOH =$$



Poly-olefinic Acids

Sorbic acid, $CH_3 \cdot CH{:}CH \cdot CH{:}CH \cdot COOH$, is an example of a *di-olefinic acid*; it was first obtained from the sap of the mountain ash and is easily synthesised by condensing crotonaldehyde with malonic acid in the presence of pyridine,

$$CH_3 \cdot CH{:}CH \cdot CHO + CH_2(COOH)_2 = CH_3 \cdot CH{:}CH \cdot CH{:}C(COOH)_2,$$
$$CH_3 \cdot CH{:}CH \cdot CH{:}C(COOH)_2 = CH_3 \cdot CH{:}CH \cdot CH{:}CH \cdot COOH + CO_2.$$

It melts at 134·5° and can be reduced catalytically to *n*-hexylic acid.

Linoleic or *linolic acid*,

$$CH_3 \cdot [CH_2]_4 \cdot CH{:}CH \cdot CH_2 \cdot CH{:}CH \cdot [CH_2]_7 \cdot COOH,$$

has already been mentioned as a constituent of the glycerides of certain fats and oils; it is particularly abundant in those vegetable oils, such as linseed oil, which have the property of drying on exposure to the air, as it rapidly absorbs oxygen. It is a liquid di-olefinic acid and can be converted into stearic acid by catalytic reduction.

Linolenic acid, $CH_3 \cdot [CH_2 \cdot CH{:}CH]_3 \cdot [CH_2]_7 \cdot COOH$, is a tri-ethylenic monocarboxylic acid, which also occurs as glyceride in linseed oil in considerable proportions.

In addition to their use in the preparation of paints and varnishes, drying oils are employed in the manufacture of oil cloth and linoleum.

Acetylenic Acids

Propiolic acid, $CH{:}C \cdot COOH$, is the simplest acetylenic acid. It can be prepared by heating $\alpha\beta$-dibromopropionic acid with alcoholic potash, just as acetylene is obtained from ethylene dibromide; also by treating the Grignard compound of acetylene (p. 105) with carbon dioxide. It melts at 18° and has the properties indicated by its structural formula. Like acetylene, potassium propiolate gives an explosive copper derivative with ammoniacal cuprous chloride.

Stearolic acid, $CH_3 \cdot [CH_2]_7 \cdot C{:}C \cdot [CH_2]_7 \cdot COOH$, is obtained when oleic acid is treated with bromine, and the dibromide thus obtained is heated with alcoholic potash; it melts at 48°.

Its structural formula is established by its method of formation and by the fact that its ozonide is decomposed by water giving the same products as does the ozonide of oleic acid.

Acetylenedicarboxylic acid, $HOOC \cdot C{:}C \cdot COOH$, is obtained from

dibromosuccinic acid and alcoholic potash and melts at 178°. It is reduced by sodium amalgam and acetic acid to succinic acid and in other ways behaves as indicated by its structure. Its potassium salt decomposes into potassium propiolate and carbon dioxide, when its aqueous solution is heated.

Diacetylenedicarboxylic acid, $HOOC \cdot C \vdots C \cdot C \vdots C \cdot COOH$, is obtained by the action of potassium ferricyanide on the copper derivative of propiolic acid. It explodes violently when it is heated.

From the foregoing account it will be seen that the substituent atoms or groups of an unsaturated hydrocarbon behave, on the whole, in the same way as those of a saturated compound. Thus allyl alcohol may be oxidised first to acraldehyde and then to acrylic acid ; the aldehyde may be reduced to the alcohol, the latter may be converted into allyl bromide and so on. It must, however, be borne in mind that an olefinic molecule in general is much more reactive than the corresponding saturated structure, because the ethylenic bond itself readily undergoes modification. Consequently in attempting to bring about any desired change in the structure of an olefinic compound the reagent for this purpose must be carefully chosen.

For the oxidation of acraldehyde to acrylic acid, or for its reduction to the alcohol, reagents should be tried which do not in general disrupt or reduce, as the case may be, the ethylenic bond : in the former case silver oxide, for example, would be suitable and in the latter, nascent, not molecular, hydrogen (p. 256), or the Ponndorf reagent (p. 156).

Considerations of this kind have, of course, a general application ; only after the whole structure of a molecule has been studied can its behaviour be forecast with any confidence. Even then it may not be possible to select at once the best reagent for a given purpose, particularly in processes of oxidation and reduction, where there is such a wide choice, and the matter can only be decided by experiment or by reference to the literature.

Although the various types of olefinic compounds already mentioned are all members of some homologous series, it is not necessary to describe these series in a general manner as has been done hitherto ; this is mainly because only a few members of each are of much importance, but also because the series becomes so complex by the rapidly increasing number of isomerides differing in chemical behaviour.

Thus whereas there are only four butyl chlorides, there are eight structurally different chlorobutenes as shown below :

$CHCl{:}CH\cdot CH_2\cdot CH_3$	$CH_2{:}CCl\cdot CH_2\cdot CH_3$	$CH_2{:}CH\cdot CHCl\cdot CH_3$
1-Chloro-1-butene	2-Chloro-1-butene	3-Chloro-1-butene
$CH_2{:}CH\cdot CH_2\cdot CH_2Cl$	$CH_3Cl\cdot CH{:}CH\cdot CH_3$	$CH_3\cdot CCl{:}CH\cdot CH_3$
4-Chloro-1-butene	1-Chloro-2-butene	2-Chloro-2-butene

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CHCl \qquad\qquad \begin{matrix}CH_2Cl\\CH_3\end{matrix}\!\!>\!C{:}CH_2$$

1-Chloro-2-methyl-1-propene — 3-Chloro-2-methyl-1-propene

In some cases all the isomerides which might be predicted from the formula do not actually exist, owing to the occurrence of isomeric change ; thus some of the alcohols theoretically derived from the chlorobutenes could not for this reason be obtained by the hydrolysis of the latter, or in other ways (p. 338).

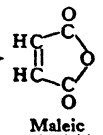
Nomenclature. Many unsaturated compounds have trivial names from which those of their substitution or addition products are also derived. Their systematic names are based on those of the saturated hydrocarbons (p. 60), the positions of the substituents and double bonds being shown as usual by numbers or letters, as illustrated above by the chlorobutenes and by the systematic name octadeca-9:12-dienoic acid or heptadeca-8:11-diene-1-carboxylic acid for linoleic acid.

Stereoisomerism of Olefinic Compounds

Maleic and fumaric acids are two interesting and, theoretically, very important, closely related compounds which are dicarboxylic derivatives of ethylene. *Maleic acid*, $C_4H_4O_4$ (m.p. 130°), was first obtained from malic acid (p. 281) from which it derives its name, and its anhydride is now prepared commercially by oxidising benzene with air, in the presence of vanadium pentoxide at 400°. When malic acid is heated at about 130° it slowly loses a molecule of water giving *fumaric acid*, $C_4H_4O_4$, and the latter at a much higher temperature loses a further molecule of water giving an *anhydride*, $C_4H_2O_3$, which distils,

$$HOOC\cdot CH\cdot CH(OH)\cdot COOH \longrightarrow HOOC\cdot CH{:}CH\cdot COOH \longrightarrow$$

Malic acid — Fumaric acid



Maleic anhydride

The formation of the intermediate product (fumaric acid) in this transformation was not at first recognised, and as the acid, obtained by the hydrolysis of the anhydride, was maleic acid, the anhydride was naturally called *maleic anhydride.*

Fumaric acid, $C_4H_4O_4$, was discovered later in Iceland moss, in which it occurs in the free state ; it melts at 287° and, when heated, gives *maleic* and not fumaric anhydride.

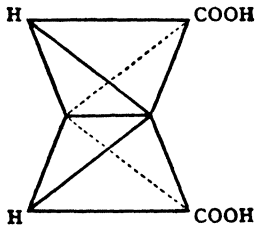
Maleic and fumaric acids differ more or less in all their physical properties such as m.p., sp. gr., solubilities, etc., as do also all corresponding metallic salts and esters of the two acids, in the formation of which only the hydrogen atoms of the carboxyl groups are concerned.

Both acids, however, show the usual reactions of olefinic compounds, and combine directly with certain atoms or groups giving saturated additive products ; when this occurs the two acids may still behave like ordinary isomerides, and with a particular reagent give *two different* products; or *one* product only may be formed from both. Thus both maleic and fumaric acids combine with bromine forming *different* dibromosuccinic acids, $C_4H_4Br_2O_4$, and on oxidation with permanganate they afford *different* dihydroxysuccinic acids, $C_4H_4O_4(OH)_2$, by combination with two —OH groups (p. 96). On the other hand they are both reduced by sodium amalgam and an acid, giving succinic acid, $C_4H_6O_4$, and they both combine with hydrogen bromide giving the same monobromosuccinic acid, $C_4H_5BrO_4$.

Now the structures of maleic and fumaric acids can only be expressed by one and the same formula, HOOC·CH:CH·COOH, which shows that they are both ethylenedicarboxylic acids ; that the two carboxyl groups are united to different carbon atoms is proved by the formation of both acids from malic acid, and their conversion into succinic acid or its derivatives, all of which are compounds of well-established structures. Further, neither acid can contain the group $>C(COOH)_2$, which would decompose into $>CH\cdot COOH$ and CO_2 if the acid were heated. It is clear, therefore, that the isomerism of maleic and fumaric acids, which for a long time could not be explained, is of a type not yet considered.

This and similar cases of isomerism among olefinic compounds were explained by Wislicenus as follows, on the basis of Le Bel and van't Hoff's theory: Olefinic compounds contain (at least) two carbon atoms united together by two valencies of each. Represent-

ing the molecule of such a compound of the type $CR_2{:}CR_2$ with the aid of the tetrahedral models, it will be seen that when two corners of the one tetrahedron are joined to two corners of the other (to represent the double binding) the four groups, R, now lie in *one plane*. Further, the carbon atoms which are united by the double binding are no longer free to rotate, relatively to one another, about an axis joining their centres, whereas singly bound atoms must be supposed free to do so (p. 305). If, then, all the four groups, or any three of them, are identical, or if any two united with one and the same carbon atom are identical, only one arrangement is possible; if, however, the compound is of the type $CRX{:}CR_1X_1$—that is to say, if each of the carbon atoms is combined with two different atoms or groups—then *two* isomerides, represented respectively by the following figures, are possible, and it makes no difference whether R and R_1, or X and X_1, are identical or different:



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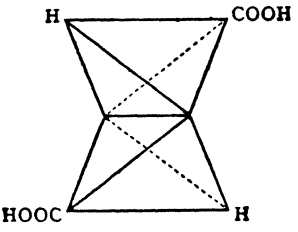
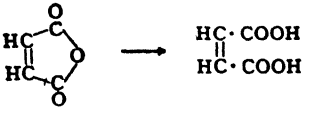


II

The existence of maleic and fumaric acids, therefore, is thus accounted for in quite a simple way, but it remains to be decided which arrangement represents maleic and which fumaric acid.

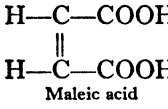
Now maleic anhydride is a ring compound analogous to succinic anhydride, and when it is treated with water, maleic acid is gradually produced,

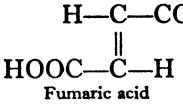


it is reasonable to assume that in this relatively low temperature reaction no change in configuration (arrangement in space) occurs, but that when fumaric acid is transformed into maleic anhydride such a change does occur as a result of the comparatively high

temperature employed. It is clear, therefore, that (I) above represents maleic acid and (II) fumaric acid.

For ordinary purposes, the projections of such models are employed and the *configurations* of the two acids are expressed in the following manner :

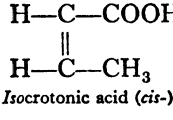

Maleic acid

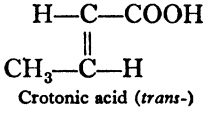

Fumaric acid

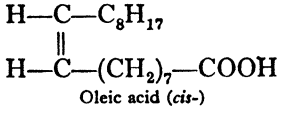
On reduction, maleic and fumaric acids give one and the same product — namely, succinic acid, $HOOC \cdot CH_2 \cdot CH_2 \cdot COOH$ — because as soon as the carbon atoms become singly bound they have the property of free rotation, and by the mutual actions of the different atoms and groups a position of equilibrium is attained (p. 305).

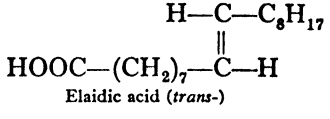
Isomerism such as that of these two acids is generally called *geometrical isomerism*, and the compounds are referred to as the *cis*- and *trans*-isomerides respectively ; the *cis*-isomeride is that in which atoms or groups R and R_1 or X and X_1 (above) are in juxtaposition.

This type of isomerism is also exhibited by crotonic and *iso*-crotonic acids, and by oleic and elaidic acids, whose configurations may be expressed as follows :


*Iso*crotonic acid (*cis*-)


Crotonic acid (*trans*-)


Oleic acid (*cis*-)


Elaidic acid (*trans*-)

Geometrical isomerides, unless they also contain an asymmetric group, possess at least one plane of symmetry (the plane of the paper in the usual projections) and each is identical with its mirror-image ; they are, therefore, *optically inactive*.

Many other examples of stereoisomerism of this type are given later (p. 528).

An extension of the significance of the ordinary constitutional

formulae in summarising the behaviour of a molecule is provided by the study of geometrical isomerism ; an examination of any olefinic structure will show the possibility or otherwise of two (or more) stereoisomeric forms. Thus it can easily be seen that of the chlorobutenes given above, three, namely 1-chloro-1-butene, 1-chloro-2-butene and 2-chloro-2-butene, might exist in *cis-* and *trans-* forms, whereas only one, 3-chloro-1-butene, will exist in *d-* and *l-*optically active, but not in *cis-* and *trans-*, forms.

It is perhaps not superfluous at this point to stress the difference between the terms *structure* or *constitution* (which are synonymous) and *configuration*. Structural formulae show to which atom or atoms every atom in the molecule is *directly* united, but take no account of the relative positions in space. Configurational formulae show the former and indicate at the same time how the atoms are arranged in space.

As examples of substances differing in *structure* the following may be cited : (1) *n*-Propyl and *iso*propyl alcohols, (2) Propionaldehyde and acetone, (3) Ethylamine and dimethylamine, (4) Succinic and *iso*succinic acids, (5) Methyl acetate and ethyl formate ; whereas (1) *d-* and *l-*Lactic acids, (2) *d-*, *l-* and *Meso*tartaric acids, (3) Glucose and galactose, (4) Maleic and fumaric acids, etc., differ respectively in *configuration*, but have identical *structures*.

CHAPTER 21

CYANOGEN AND RELATED COMPOUNDS

THE cyanogen compounds contain the univalent radical cyanogen, —CN (Gay-Lussac); in many respects they are closely related to the corresponding halogen derivatives, although they contain the univalent *group of atoms*, CN, in the place of a *single atom* of halogen, as shown by the following examples:

Cl_2, HCl, KCl, AgCl, $HgCl_2$, $HO \cdot Cl$, $C_2H_5 \cdot Cl$,
$(CN)_2$, 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 'radical'; the univalent group, CN, plays much the same part as the atom of chlorine, just as the radical ammonium may play the part of a single atom of an alkali metal.

The cyanogen radical plays important roles in organic chemistry; it may be substituted for a halogen atom, or formed from an amide group, and is readily transformed into $—CH_2 \cdot NH_2$, —CHO or —COOH.

Cyanogen (*dicyanogen*), $NC \cdot CN$, is produced when ammonium oxalate is strongly heated with phosphorus pentoxide,

$$NH_4OOC \cdot COONH_4 = NC \cdot CN + 4H_2O,$$

a reaction which shows that cyanogen is the nitrile (p. 359) of oxalic acid, oxalonitrile.

A mixture of anhydrous ammonium oxalate and phosphorus pentoxide is heated in a glass tube sealed at one end, and the products are collected in a solution of potassium hydroxide (p. 353); the latter is then tested for cyanide (p. 15).

Cyanogen is prepared [1] by heating silver cyanide or mercuric cyanide (p. 358) 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, $(CN)_n$, called *paracyanogen*, is produced; this

[1] Owing to the highly poisonous character of cyanogen and many of its derivatives, great care should be observed in their preparation.

compound is a polymeride of cyanogen, and when heated at a high temperature it is completely resolved into cyanogen gas, just as trioxymethylene is converted into formaldehyde under like conditions (p. 136).

Cyanogen is also prepared by heating potassium cyanide with cupric sulphate in aqueous solution ; the cupric cyanide, which is first precipitated, undergoes decomposition into cyanogen and cuprous cyanide (compare behaviour of potassium iodide with cupric sulphate),

$$4KCN+2CuSO_4 = C_2N_2+2CuCN+2K_2SO_4.$$

Cyanogen is an easily liquefiable gas (b.p. $-21°$) ; it has a peculiar smell, is extremely *poisonous*, and burns with a characteristic bluish, red-edged flame, yielding carbon dioxide and nitrogen.

It is soluble in water (about 3–5 vol. in 1), more readily in alcohol (about 23 vol. in 1), but its solutions soon decompose, and a brown amorphous precipitate (' azulmic acid ') is deposited ; the solution then contains ammonium oxalate and other substances.

When cyanogen is treated with hydrochloric acid, it is first converted into oxamide, and then into oxalic acid (and ammonium chloride),

$$NC\cdot CN+2H_2O = NH_2\cdot CO\cdot CO\cdot NH_2,$$
$$NH_2\cdot CO\cdot CO\cdot NH_2+2H_2O = HOOC\cdot COOH+2NH_3 ;$$

these changes are the reverse of those which occur when ammonium oxalate is heated with phosphorus pentoxide.

All substances which contain the cyanogen group behave in a similar manner, and are converted on hydrolysis into carboxylic acids or their salts, *amides* being formed as intermediate products ; *this is a very important general reaction.*

Cyanogen is readily absorbed by a solution of potassium or ammonium hydroxide, cyanide and cyanate being produced,

$$C_2N_2+2KOH = KCN+KOCN+H_2O,^1$$

just as potassium chloride and hypochlorite are formed from chlorine and potassium hydroxide.

Cyanogen chloride, CNCl, is formed by the action of chlorine on a solution of hydrogen cyanide,

$$HCN+Cl_2 = CNCl+HCl.$$

[1] It was in this way that Wöhler obtained ammonium cyanate and urea (p. 263).

It is a very poisonous liquid, boils at 12·5°, and readily undergoes spontaneous polymerisation into *cyanuric chloride*, $C_3N_3Cl_3$, which melts at 154°, and is decomposed by water at about 125°, yielding cyanuric acid,

$$C_3N_3Cl_3+3H_2O = C_3N_3O_3H_3+3HCl.$$

Cyanogen iodide, CNI, sublimes in colourless needles when a mixture of iodine and mercuric cyanide is heated; it is very poisonous.

Hydrogen cyanide (hydrocyanic or prussic acid), H·CN or H·NC, was discovered by Scheele; it occurs in plants, sometimes in considerable quantities, in combination with glucose and benzaldehyde in the form of a well-defined, crystalline glycoside,[1] known as *amygdalin*. Bitter almonds and cherry-kernels contain this glycoside; when they are macerated and kept in contact with water, the amygdalin is decomposed by an enzyme, *emulsin*,[2] into hydrogen cyanide, benzaldehyde, and glucose,

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}}+2H_2O = \underset{\text{Benzaldehyde}}{C_7H_6O}+HCN+\underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

Hydrogen cyanide is formed when a mixture of acetylene and nitrogen is heated very strongly (at about 2000°). It is also produced when ammonium formate is heated with phosphorus pentoxide; this change is analogous to the formation of cyanogen from ammonium oxalate, and may be demonstrated in a similar manner (p. 352),

$$H\cdot COONH_4 = HCN+2H_2O.$$

Hydrocyanic acid is prepared by the distillation of potassium cyanide or potassium ferrocyanide, with dilute sulphuric acid,

$$KCN+H_2SO_4 = KHSO_4+HCN,$$

$$\underset{\text{Potassium ferrocyanide}}{2K_4Fe(CN)_6}+3H_2SO_4 = 6HCN+\underset{\text{Ferrous potassium ferrocyanide}}{FeK_2Fe(CN)_6}+3K_2SO_4;$$

in the latter reaction, only one-half of the potassium ferrocyanide yields hydrogen cyanide.

[1] The term *glycoside* is also applied to certain derivatives of sugars which, on treatment with acids or alkalis, yield a sugar, or a mixture of two or more sugars, and one or more other substances (phenols, alcohols, aldehydes, acids, etc.) as decomposition products.

[2] The emulsin and the amygdalin are contained in separate cells and are only brought together when the tissues suffer disruption.

The anhydrous acid may be prepared (by expert chemists only) by dropping cold 50% sulphuric acid on to lumps of potassium cyanide ; it is often used in the preparation of hydroxy-cyanides (p. 151).

Anhydrous hydrogen cyanide is a liquid ; it boils at 26° and crystallises in a freezing mixture, melting again at −15° ; it has an odour similar to that of oil of bitter almonds, and burns with a pale-blue flame, with the formation of carbon dioxide, water, and nitrogen. It is a terrible poison, very small quantities of the acid (liquid or vapour), or of its soluble salts, being sufficient to cause death.[1]

Hydrogen cyanide dissolves readily in water, but the solution undergoes decomposition, with the 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 when a trace of some mineral acid is present, more quickly if the solution is heated with mineral acids or alkalis.

On reduction with zinc and hydrochloric acid, hydrogen cyanide is converted into methylamine,

$$HCN+4H = CH_3\cdot NH_2.$$

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 the liberation of the acid, for which reason potassium cyanide, for example, in contact with moist air, always smells of hydrogen cyanide.

The *detection* of hydrocyanic acid or of a cyanide is usually based on the following test (p. 15) : The aqueous solution is made strongly alkaline with potassium hydroxide, a few drops of ferrous sulphate solution are added, and the liquid is warmed ; potassium ferrocyanide is thus formed, and on the addition of ferric chloride to the acidified solution, a blue colouration or a precipitate of Prussian blue is produced.

The *constitution* of hydrogen cyanide may be expressed by the

[1] As an antidote, a suspension of ferrous hydroxide in sodium carbonate solution, obtained by adding the latter in excess to a solution of ferrous sulphate, should be administered immediately.

formula, H·C⋮N, for the following reasons: The acid is produced from ammonium formate, by a change similar to that by which methyl cyanide is formed from ammonium acetate (p. 359),

$$H\cdot COONH_4 = H\cdot CN + 2H_2O,$$
$$CH_3\cdot COONH_4 = CH_3\cdot CN + 2H_2O;$$

when heated with alkalis 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 would seem probable that the hydrogen atom in hydrogen cyanide is in a similar state of combination.

Other facts, however, point to the formula H·NC, corresponding with those of the *iso*cyanides (p. 361) and it would seem, therefore, that hydrogen cyanide shows tautomerism (p. 203),

$$H\cdot CN \rightleftharpoons CN\cdot H,$$

and exists principally in the form of H·CN.

Hydrogen cyanide is sometimes called formonitrile (p. 359).

Potassium cyanide, KCN, may be obtained synthetically by gently heating potassium in cyanogen. It used to be prepared on the large scale by strongly heating potassium ferrocyanide alone, or with potassium carbonate, out of contact with the air,

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2,$$
$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe,$$

and a mixture of sodium and potassium cyanides was manufactured by fusing potassium ferrocyanide with sodium,

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The pure potassium salt may be prepared by passing hydrogen cyanide into alcoholic potash, and separating the precipitated crystals. It crystallises in plates, and is very readily soluble in water, but nearly insoluble in anhydrous alcohol; it is extremely posionous[1] and should not come into contact with the skin.

Fused potassium cyanide is a reducing agent; it liberates the

[1] Compare footnote, p. 355.

metals from many metallic oxides, being itself converted into potassium cyanate,

$$KCN+PbO = KCNO+Pb,$$

hence its use in some metallurgical operations ; in solution, it is much employed in inorganic analysis, but for many purposes it has now been supplanted by sodium cyanide.

Potassium cyanide is a *most important* reagent in organic chemistry since it reacts with halogen compounds in general (excepting those in which the halogen atom is directly combined with carbon of an aromatic nucleus, p. 425) and gives cyanides (p. 359), which are intermediate products in the ascent of a homologous series (p. 224), and are convertible into acids, aldehydes, and amines.

Sodium cyanide, NaCN, is now used, especially for large-scale operations, instead of the more expensive potassium salt, and is manufactured by running melted sodamide on to red-hot charcoal,

$$NaNH_2+C = NaCN+H_2 ;$$

the fused product is filtered, and cast into iron moulds, and is thus obtained in crystalline masses containing 97·5–98% of sodium cyanide.

It is also made commercially by passing ammonia through a heated mixture of sodium and charcoal,

$$2Na+2NH_3 = 2NaNH_2+H_2,$$
$$NaNH_2+C = NaCN+H_2,$$

or by heating calcium cyanamide (p. 363) with carbon and common salt,

$$NC\cdot NCa+C+2NaCl = CaCl_2+2NaCN.$$

In another process, an intimate mixture of sodium carbonate and carbon is strongly heated in an atmosphere of nitrogen,

$$Na_2CO_3+4C+N_2 = 2NaCN+3CO.$$

Sodium cyanide resembles the potassium salt in properties and is largely used in extracting gold from ores by the MacArthur-Forrest process, in working up residual ores of copper, lead, and zinc, in the case-hardening of steel, in the electroplating industry, and for destroying vermin, etc.

Silver cyanide, AgCN, is obtained as a curdy precipitate when an aqueous solution of potassium cyanide is added to a solution of silver nitrate ; it is insoluble in dilute acids, but is converted into soluble compounds by ammonium hydroxide and by potassium

cyanide ; silver cyanide is thus very similar in its properties to silver chloride, from which, however, it differs in that, when heated, it is decomposed completely (into silver and cyanogen).

Mercuric cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid. The solution, on evaporation, deposits the salt in anhydrous crystals, which are moderately soluble in water ; when strongly heated, the salt is decomposed into mercury and cyanogen.

Mercuric cyanide does not show the ordinary reactions of a mercuric salt or those of a cyanide ; in aqueous solution it is not ionised to an appreciable extent.

The cyanides of many of the metals, like many of the metallic chlorides, form complex salts with one another. Silver cyanide, for instance, gives with potassium cyanide a soluble complex salt, $KAg(CN)_2$, which is used in electroplating ; the compound, $KAu(CN)_4$, may be obtained in a similar manner by treating auric cyanide, $Au(CN)_3$, with potassium cyanide. These complex salts crystallise unchanged from water, but are decomposed by mineral acids in the cold, with the evolution of hydrogen cyanide. Like the soluble simple cyanides, they are extremely poisonous.

In addition to the above, numerous other complex metallic cyanides are known, the more important of which are potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. These salts are not very poisonous, and are more stable than the compounds just described. On treatment with mineral acids, in the cold, they do not yield hydrogen cyanide, but hydrogen is substituted for the alkali metal only, and an acid, such as hydroferrocyanic acid, is liberated,

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

Potassium ferrocyanide, $K_4Fe(CN)_6$ (yellow prussiate of potash), is formed when ferrous hydroxide is treated with an aqueous solution of potassium cyanide,

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

It used to be manufactured by fusing together in an iron vessel nitrogenous animal refuse (horn-shavings, hair, blood, etc.), crude potashes (containing potassium carbonate), and iron borings. The cold product was extracted with hot water, and the filtered solution evaporated.

Potassium ferrocyanide and various thiocyanates are now manufactured from '*spent oxide*,' the material obtained in purifying coal-gas from hydrogen sulphide, by passing the coal-gas through layers of ferric hydroxide. Spent oxide contains Prussian blue (ferric ferrocyanide), ammonium thiocyanate, and other ammonium salts, together with 30–40% of sulphur. It is first extracted with water, then mixed with lime, in order to convert the ferric ferrocyanide into ferric hydroxide and soluble *calcium ferrocyanide*,

$$Fe_4[Fe(CN)_6]_3+6Ca(OH)_2 = 4Fe(OH)_3+3Ca_2Fe(CN)_6,$$

and the latter is then extracted with water ; the residue is used as a source of sulphur in the manufacture of sulphuric acid. The solution of the calcium salt is next treated with the theoretical quantity of potassium chloride, to form the very sparingly soluble *potassium calcium ferrocyanide*, $K_2CaFe(CN)_6$, which is separated, and heated with a solution of potassium carbonate in order to convert it into potassium ferrocyanide ; the solution is filtered from calcium carbonate and evaporated.

Potassium ferrocyanide crystallises in lemon-yellow, hydrated ($3H_2O$) prisms ; it is soluble in about 4 parts of water. When warmed with concentrated (90%) sulphuric acid it gives carbon monoxide,

$$K_4Fe(CN)_6+6H_2O^1+6H_2SO_4 = 6CO+2K_2SO_4+FeSO_4+3(NH_4)_2SO_4,$$

but when boiled with dilute sulphuric acid it gives hydrogen cyanide (p. 354).

Solutions of ferric salts in excess give with potassium ferrocyanide a precipitate of Prussian blue, or ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$.

Sodium nitroprusside, $Na_2Fe(CN)_5(NO),2H_2O$, is obtained by treating potassium ferrocyanide with nitric acid, separating the precipitated potassium nitrate, and then neutralising the solution with caustic soda ; it forms red prisms readily soluble in water, and its alkaline solution gives a violet colouration even with traces of hydrogen sulphide (p. 16).

Potassium ferricyanide, $K_3Fe(CN)_6$ (red prussiate of potash), is prepared by passing chlorine into a 10% solution of potassium ferrocyanide, until the liquid ceases to give a blue precipitate with ferric salts ; on evaporation, potassium ferricyanide separates in dark red crystals.

[1] The water necessary for this decomposition is partly derived from the crystals of the salt, partly from the 90% acid.

The transformation of potassium ferrocyanide into ferricyanide is a process of oxidation, and other oxidising agents, such as nitric acid and lead dioxide, produce the same result.

Potassium ferricyanide gives, with ferrous salts, a precipitate of Turnbull's blue, which is doubtless the same as Prussian blue ; it is employed as a mild oxidising agent, because in alkaline solution, in presence of an oxidisable substance, it is converted into potassium ferrocyanide,

$$2K_3Fe(CN)_6+2KOH = 2K_4Fe(CN)_6+H_2O+O.$$

When paper is treated with a solution of potassium ferricyanide and ferric ammonium citrate it becomes blue on exposure to light, owing to the reduction of the ferric salt and the subsequent production of Prussian blue ; such sensitised paper is used in the reproduction of engineering drawings (blue prints), etc.

The **alkyl cyanides** or **nitriles,** $R\cdot CN$, may be prepared by heating the alkyl halides, or the salts of the alkyl sulphuric acids, with *potassium* or *sodium* cyanide in aqueous alcoholic solution,

$$KCN+C_2H_5I = C_2H_5\cdot CN+KI,$$
$$KCN+K(C_2H_5)SO_4 = C_2H_5\cdot CN+K_2SO_4 ;$$

they are also obtained by distilling the ammonium salts, or the amides, of the fatty acids with some dehydrating agent, such as phosphorus pentoxide,

$$CH_3\cdot COONH_4 = CH_3\cdot CN+2H_2O,$$
$$C_2H_5\cdot CO\cdot NH_2 = C_2H_5\cdot CN+H_2O,$$

and when *ald*oximes are treated with acetyl chloride or acetic anhydride,

$$CH_3\cdot CH{:}NOH = CH_3\cdot CN+H_2O.$$

The lower members of the series, such as *methyl cyanide* (b.p. 82°) and *ethyl cyanide* (b.p. 98°), are mobile liquids, possessing a strong but not disagreeable smell, and are readily soluble in water ; the higher members, as, for example, octyl cyanide (b.p. 216°), $C_8H_{17}\cdot CN$, are almost insoluble in water.

When boiled with acids or alkalis they are decomposed, with the formation of acids, the —CN 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 carboxylic acids, such compounds may also be named after the acids which they yield on hydrolysis; methyl cyanide, $CH_3 \cdot CN$, for example, is called *acetonitrile*; ethyl cyanide, $C_2H_5 \cdot CN$, *propiononitrile*, and so on.

On reduction with zinc and sulphuric acid, or, better, with sodium and alcohol, the alkyl cyanides are converted into primary amines,

$$CH_3 \cdot CN + 4H = CH_3 \cdot CH_2 \cdot NH_2.$$

The two reactions just given show that the alkyl group is directly united with carbon.

When alkyl cyanides are reduced with anhydrous stannous chloride in ether, saturated with hydrogen chloride, aldimines are formed (p. 497).

The **alkyl *iso*cyanides, *iso*nitriles** or **carbylamines,** $R \cdot NC$, are isomeric with the corresponding cyanides. They may be prepared by heating the alkyl halides with *silver* cyanide,

$$C_2H_5I + AgCN = C_2H_5 \cdot NC + AgI,$$

and by treating primary amines with chloroform and alcoholic potash (p. 216),

$$CH_3 \cdot NH_2 + 3KOH + CHCl_3 = CH_3 \cdot NC + 3KCl + 3H_2O.$$

The *iso*nitriles or carbylamines are mobile liquids, sparingly soluble in water; they have an almost unbearable odour and are poisonous.

They boil at lower temperatures than the isomeric cyanides; *methyl* iso*nitrile*, $CH_3 \cdot NC$, for example, boils at 59°; *ethyl* iso*nitrile*, $C_2H_5 \cdot NC$, at 79°. They differ from the nitriles, inasmuch as they are *not* decomposed by boiling alkalis, but they are readily hydrolysed by dilute mineral acids, yielding formic acid and an amine,

$$C_2H_5 \cdot NC + 2H_2O = C_2H_5 \cdot NH_2 + H \cdot COOH;$$

on reduction with hydrogen in the presence of nickel they are converted into secondary amines,

$$C_2H_5 \cdot NC + 2H_2 = C_2H_5 \cdot NH \cdot CH_3.$$

These reactions are totally different from those of the nitriles, and show that the alkyl group in the *iso*nitrile is united with nitrogen and not with carbon—that is to say, the nitriles are derivatives of

H·CN, whereas the *iso*nitriles may be regarded as derived from the isomeride of the constitution, H·NC.

When nitrogen was considered to function sometimes as a quinquevalent element the formula of an *iso*nitrile was written, R·N⋮C; in accordance with the electronic theory of valency it is now written R·N⇄C.

Cyanic acid, HO·CN, or HN:C:O, is produced when cyanuric acid (p. 354) is heated, and the vapours are condensed in a receiver, cooled in a freezing mixture,

$$C_3N_3O_3H_3 = 3HO\cdot CN.$$

It is a strongly acid, unstable liquid, and when kept at about 0° it rapidly undergoes polymerisation into an opaque, porcelain-like mass which consists of cyanuric acid, and a large proportion of another polymeride, called *cyamelide*. It decomposes very rapidly in aqueous solution, giving carbon dioxide and ammonia,

$$HO\cdot CN + H_2O = CO_2 + NH_3,$$

and therefore cannot be prepared by the decomposition of its salts with mineral acids.

Potassium cyanate, KO·CN, is slowly produced when potassium cyanide undergoes atmospheric oxidation, and also when cyanogen chloride is dissolved in a solution of potassium hydroxide; 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. It is crystalline, readily soluble in water and aqueous alcohol, but nearly insoluble in anhydrous alcohol; it rapidly decomposes in aqueous solution with the formation of ammonium and potassium carbonates,

$$2KO\cdot CN + 4H_2O = (NH_4)_2CO_3 + K_2CO_3.$$

When a solution of this cyanate is mixed with ammonium sulphate and evaporated, *urea* is formed, ammonium cyanate being the intermediate product (p. 263).

Esters of cyanic acid are *not* known, but alkyl derivatives of *iso*cyanic acid were discovered by Wurtz.

The *alkyl* iso*cyanates* or *carbimides*, R·N:CO, are obtained when potassium cyanate is heated with a potassium alkyl sulphate and when an alkyl iodide is heated with silver cyanate; they are unpleasant smelling, volatile liquids.

Ethyl iso*cyanate* (b.p. 60°) is decomposed when it is heated with aqueous alkalis giving ethylamine,

$$C_2H_5 \cdot N{:}CO + 2KOH = C_2H_5 \cdot NH_2 + K_2CO_3;$$

it combines with alcohols forming urethanes (p. 223),

$$C_2H_5 \cdot N{:}CO + R \cdot OH = C_2H_5 \cdot NH \cdot CO \cdot OR,$$

and with primary or secondary amines to form substituted ureas,

$$C_2H_5 \cdot N{:}CO + R \cdot NH_2 = C_2H_5 \cdot NH \cdot CO \cdot NHR.$$

Other esters, prepared in a similar manner, behave like ethyl *iso*cyanate, and the fact that they give an amine on hydrolysis shows that they are derived from *iso*cyanic acid, HN:CO.

Phenyl carbimide, $C_6H_5 \cdot N{:}CO$ (p. 446), is employed for the detection and identification of —OH, —NH_2, or >NH groups, as it reacts readily at ordinary temperatures with compounds which contain such groups, and gives a phenylurethane or a substituted urea which is usually crystalline.

Cyanamide, $NC \cdot NH_2$, is formed by the action of ammonia on cyanogen chloride, and its important derivative, **calcium cyanamide,** $NC \cdot NCa$, is manufactured by strongly heating calcium carbide with nitrogen (in the presence of calcium chloride),

$$CaC_2 + N_2 = NC \cdot NCa + C;$$

the crude product (*Nitrolim* or *Kalkstickstoff*), which is used as a fertiliser, undergoes decomposition in the soil, giving first *cyanamide* (m.p. 41°) and then urea (p. 264),

$$NC \cdot NCa + CO_2 + H_2O = NC \cdot NH_2 + CaCO_3,$$
$$NC \cdot NH_2 + H_2O = CO(NH_2)_2.$$

Calcium cyanamide is also used for the manufacture of urea and cyanides (p. 357).

Sodium cyanamide, CN_2Na_2, used for the preparation of secondary amines (p. 227), is obtained by heating sodamide with carbon at about 400°,

$$2NaNH_2 + C = CN_2Na_2 + 2H_2.$$

Fulminic acid, CNOH, is isomeric with cyanic acid. It is a strong acid and is formed by the decomposition of its salts, the fulminates, with mineral acids. **Mercuric fulminate,** $(CNO)_2Hg, \frac{1}{2}H_2O$, is prepared by the interaction of alcohol, nitric acid, and mercury;

the changes which occur are complex. Mercuric fulminate is a crystalline solid which explodes violently when it is struck and is used as a detonator.

Thiocyanic acid, or sulphocyanic acid, HS·CN or SC:NH, is obtained as a salt when an alkali cyanide is heated with sulphur,

$$KCN+S = KS\cdot CN,$$

the change being analogous to the formation of cyanates by the oxidation of cyanides.

Thiocyanic acid is liberated when potassium thiocyanate is treated with dilute sulphuric acid, but it is very unstable. It has a very penetrating odour and, with moderately concentrated sulphuric acid, gives carbon oxysulphide and ammonia,

$$HS\cdot CN+H_2O = COS+NH_3.$$

Potassium thiocyanate, KS·CN, is prepared by fusing potassium cyanide (or ferrocyanide) with sulphur, extracting the mass with alcohol, and concentrating the alcoholic solution; it forms very deliquescent needles. The *ammonium salt*, $NH_4S\cdot CN$, is prepared by heating alcoholic ammonia with carbon disulphide at 100° under pressure,

$$4NH_3+CS_2 = NH_4S\cdot CN+(NH_4)_2S,$$

and also by the fractional crystallisation of the salts contained in the aqueous extract of ' spent oxide ' (p. 359).

When heated at 170° it gradually undergoes isomeric change into *thiourea* or *thiocarbamide*, $NH_2\cdot CS\cdot NH_2$, a crystalline substance, which melts at 172°.

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 $[Fe(SCN)_6]'''$ ions. Thiocyanates are also employed in dyeing and calico-printing as mordants, and are known commercially as ' rhodanates.'

Alkyl thiocyanates, RS·CN, are produced by distilling the alkyl iodides with potassium thiocyanate, or by treating the mercaptides (especially lead mercaptides) with cyanogen chloride,

$$(C_2H_5S)_2Pb+2ClCN = 2C_2H_5S\cdot CN+PbCl_2.$$

They are volatile liquids possessing a slight smell of garlic; when oxidised with nitric acid they are converted into alkylsulphonic

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, and that the esters are derived from an acid of the constitution $HS \cdot C{:}N$.

The **alkyl *iso*thiocyanates,** or **mustard-oils,** RN:C:S, are produced when the alkyl thiocyanates are heated at 180°, or repeatedly distilled, intramolecular (isomeric) change (p. 263) taking place,

$$C_2H_5 \cdot S \cdot C{:}N \longrightarrow C_2H_5 \cdot N{:}C{:}S$$

The alkyl group in these compounds is combined with nitrogen, as shown by the fact that when heated with hydrochloric acid they are decomposed into primary amines, carbon dioxide, and hydrogen sulphide,

$$C_2H_5N{:}CS + 2H_2O = C_2H_5 \cdot NH_2 + CO_2 + H_2S.$$

The *iso*thiocyanates, therefore, are analogous to the alkyl *iso*cyanates, and are derived from an *iso*thiocyanic acid of the constitution, HN:C:S.

Allyl *iso*thiocyanate, 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 glycoside, potassium myronate (*sinigrin*), $C_{10}H_{18}NS_2O_{10}K$, which is soluble in water; its solution gradually undergoes fermentation (owing to the presence of an enzyme, *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 *iso*thiocyanate may be obtained synthetically by heating allyl iodide with potassium thiocyanate, because the allyl thiocyanate, which is first formed, undergoes isomeric change into the *iso*thiocyanate; it is a pungent-smelling liquid, boiling at 151°, and when placed on the skin it produces blisters.

The three acids, hydrocyanic, cyanic and thiocyanic, show tautomerism (p. 203),

$$H \cdot CN \rightleftharpoons CN \cdot H,$$
$$HO \cdot CN \rightleftharpoons OC{:}NH,$$
$$HS \cdot CN \rightleftharpoons SC{:}NH,$$

but in no case have both forms of the acids been separated or isolated. When the hydrogen atom is displaced (indirectly) by an alkyl group tautomerism becomes impossible and the alkyl deriva-

tives have a fixed structure. In the case of hydrocyanic and thiocyanic acid two series of derivatives, corresponding respectively with the given formulae, have been described, namely the cyanides, R·CN, and *iso*cyanides, R·NC, and the thiocyanates, RS·CN, and *iso*thiocyanates, RN:CS ; alkyl cyanates, RO·CN, however, are unknown.

When a tautomeric compound such as one of the above acids is also an electrolyte the anion at first sight might appear to have two possible structures,

$$^{-}C \equiv N \quad \text{or} \quad C \rightleftarrows N^{-}, \qquad ^{-}O-C \equiv N \quad \text{or} \quad O=C=N^{-} \text{ etc.}$$

In such cases, however, the ions would probably be resonance forms (p. 390) and the difference would disappear : it is impossible, therefore, to assign to potassium cyanide, a strong electrolyte, either the formula KCN or KNC ; it is $K^{+}[CN]^{-}$. Silver cyanide, however, is co-valent and it has been shown that in its crystals a chain structure,

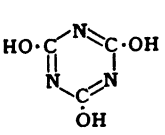
$$—Ag—C \equiv N \longrightarrow Ag—C \equiv N \longrightarrow Ag—,$$

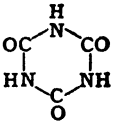
is present. Such a difference in constitution may account for the different reactions of potassium and silver cyanides with alkyl halides.

Cyanuric acid, $(HOCN)_3$, is produced by the hydrolysis of cyanuric chloride, $(CNCl)_3$ (p. 354), and separates from water in large prisms $(+2H_2O)$: on distillation it is converted into cyanic acid. Its *esters* are obtained by treating cyanuric chloride with sodium alkyl oxides,

$$(CNCl)_3+3NaOEt = (CN\cdot OEt)_3+3NaCl,$$

but when these *alkyl cyanurates* are heated strongly they undergo isomeric change into *alkyl* iso*cyanurates*, esters of *iso*cyanuric acid, $(CO\cdot NR)_3$; the latter, on hydrolysis with alkalis, give a carbonate and a primary amine, whereas the former give a metallic cyanurate and an alcohol. Cyanuric and *iso*cyanuric acids are tautomeric and may be respectively represented by the formulae,





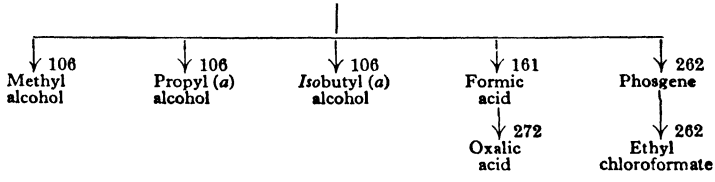
but only one form of the acid has been isolated.

SYNTHETIC COMMERCIAL PRODUCTS

In the past, the three important compounds, methyl alcohol, acetic acid, and acetone were obtained from the products of the destructive distillation of wood, and used directly for various domestic and commercial purposes, as well as for the preparation of many of their derivatives; these raw materials are now manufactured in other ways and many others are obtained from the highly complex mixture resulting from the cracking of petroleum.

The sources, and some of the transformations, of the more important commercial products which are thus formed are given in the following table; it will there be seen that ethyl alcohol, although still prepared on the large scale by fermentation processes, is now obtainable by other methods, which are becoming increasingly important.

PRODUCTS MANUFACTURED FROM CARBON MONOXIDE

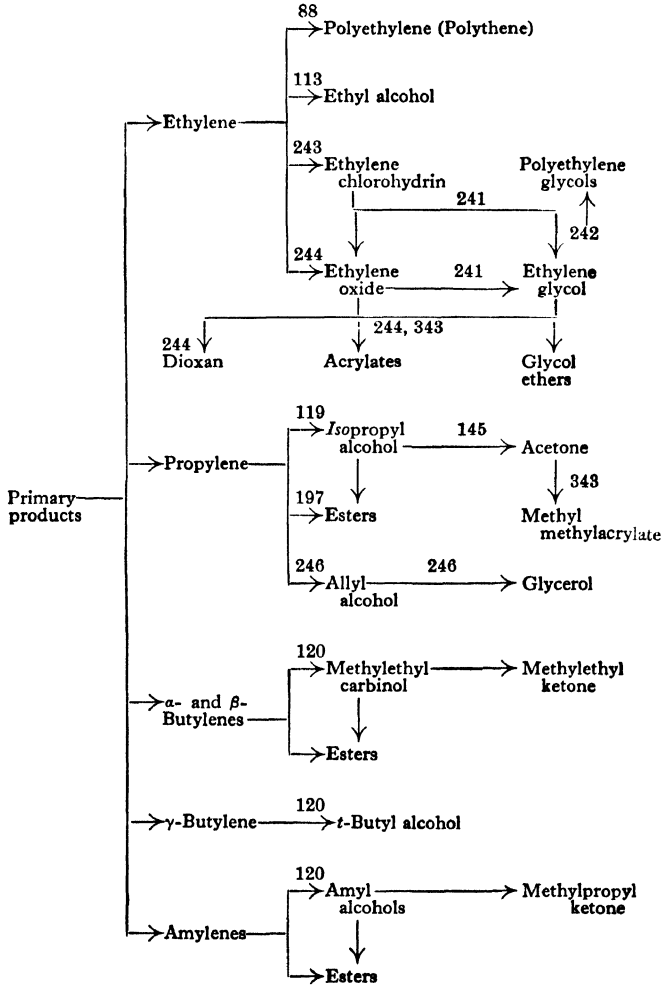


(*a*) Also obtained from fusel oil.

The figures indicate the pages on which the relevant reactions are mentioned.

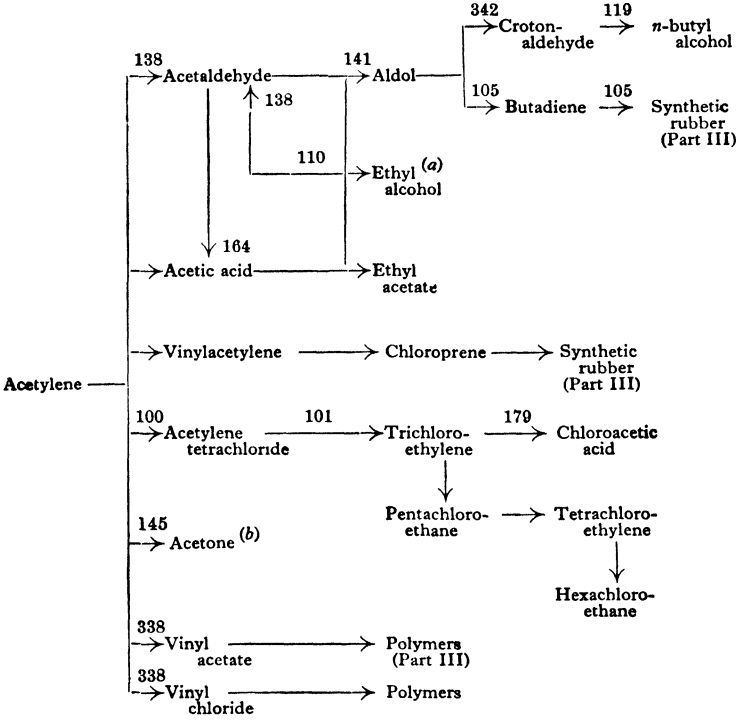
The carbon monoxide is prepared either from steam and coke or from natural methane; in the latter case, by partial oxidation or by reaction with steam under suitable conditions.

PRODUCTS MANUFACTURED FROM CRACKED PETROLEUM (p. 67)



The figures indicate the pages on which the relevant reactions are mentioned.

PRODUCTS MANUFACTURED FROM ACETYLENE AND ETHYL ALCOHOL



(*a*) Alcohol is obtained by fermentation (p. 113), but might be produced from acetaldehyde; in Great Britain it is the source of most of the compounds in the upper portion of the table.

(*b*) Also a product of cracked petroleum.

The figures indicate the pages on which the relevant reactions are mentioned.

PREPARATIONS

The following are some of the typical compounds for which methods of preparation are described in detail. Many others may be prepared with the aid of the experimental data which are given throughout the book.

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Heavy type indicates the more important of two or more references to a compound or subject dealt with in any part of the book.

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