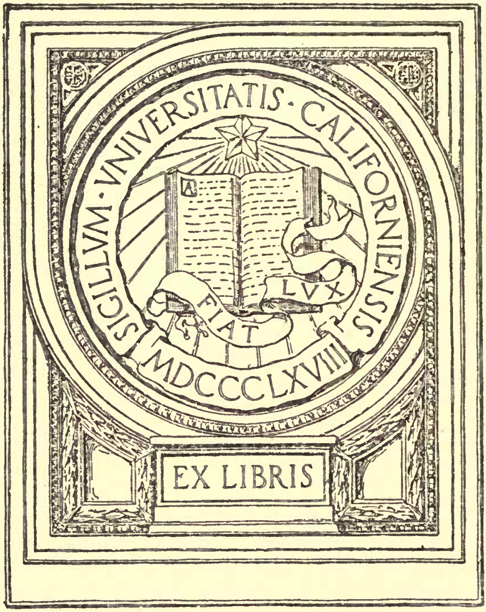


c/o Binjo Jhonubi

INTRODUCTION
TO
ORGANIC CHEMISTRY

STODDARD

INTRODUCTION
TO
ORGANIC CHEMISTRY

BY

JOHN TAPPAN STODDARD

PROFESSOR OF CHEMISTRY IN SMITH COLLEGE

SECOND EDITION

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET

To replace
399796

THE · MAPLE · PRESS · YORK · PA

PREFACE TO THE SECOND EDITION

The favorable reception accorded to this text has encouraged me to take advantage of this year's reprinting to make a number of corrections and changes that have been suggested during the four years since it first appeared.

Many minor alterations will be found, and a few portions have been entirely rewritten. Among the latter are the sections on the Natural Oils and Fats, on Uric Acid and the Purine Bases, and on the Proteins.

I trust that the revision will be found to have measurably improved the book and that its efficiency as an aid to the instruction of college students who are beginning the subject has been increased.

It gives me great pleasure to acknowledge my indebtedness to the friends whose criticisms and suggestions have aided me in my task, and I am under especial obligation to Professor Cook of Smith College and Dr. Harry L. Fisher of Columbia University who placed in my hands the corrections and notes they had made while using the book with their classes.

J. T. S.

NORTHAMPTON, MASS.

PREFACE TO THE FIRST EDITION

This book is intended to be used in connection with lectures, recitations, and laboratory work in the first course of Organic Chemistry in college. The author has endeavored to present the subject simply, directly, and connectedly, so that the student may gain a clear idea of the principles of organic chemistry and its relations to general chemistry. The fundamentally important questions of the constitution of organic compounds are discussed at some length in many typical cases. In these discussions, the facts in regard to the behavior of the substances are given first, and then the arguments by which the formulas are established. The student in this way is trained in the method of deriving constitutional formulas, and should soon be able to work out simple problems from a given statement of facts. Emphasis is laid on general reactions and characteristics, rather than on special facts relating to particular compounds; and the text is relieved from much detail by the use of tables giving names, formulas and properties of many groups of compounds. Many applications of organic chemistry to practical life are given so that the student may realize, in some measure, the part which the science of organic chemistry plays in ordinary life and in our industries.

The book is considerably smaller than many of the text-books on the subject, but it is believed that it is none the less complete in all the essential matter which is properly presented in a first course. The larger text-book is apt to bewilder the student by brief descriptions of too many compounds of minor importance, or to fill too many pages with discussions which can be conducted to better advantage by the lecturer.

The student often finds his course in organic chemistry at first difficult and confusing. It is so different from the inorganic chemistry that it takes him some time to get the new point of view. This is, perhaps, to some extent inevitable; but a good deal depends on the manner in which the subject is introduced. If details are subordinated and the fundamental principles are presented logically and with a few well-chosen illustrations of their applications, the first difficulties are soon overcome.

The order in which the various groups of compounds are to be treated is a more or less open question. The choice depends largely, in several instances, on the particular relations which it seems desirable to emphasize. What appears a logical sequence from one point of view, is, from another, illogical. No claim is made that the order given in this book is the best; and it should be said that it is not necessary that this order be strictly followed by those who use the book.

Numerous cross-references are given to help in binding the discussions into a coherent whole. Some references are made to books in which fuller treatment of certain subjects will be found, and a short list of books for collateral reading is given at the end of the volume.

I wish to express my sincere thanks to Professor H. W. Doughty of Amherst College and Professor E. P. Cook of Smith College, who have read the book in manuscript and have made many helpful suggestions. Professor Cook has also rendered great assistance in reading the proofs.

CONTENTS

TABLES

INTRODUCTION TO ORGANIC CHEMISTRY

CHAPTER I

PRELIMINARY DISCUSSION

Organic chemistry is the chemistry of the compounds of carbon. Although the fundamental laws and theories of chemistry are as applicable to these compounds as to all others, there are several reasons for their separate treatment.

In the first place, the number of compounds that contain carbon is extraordinarily large. The only other elements that enter into the composition of any very large number of substances are hydrogen and oxygen; and we shall see that hydrogen and oxygen are quite usually associated with carbon in the organic compounds. The association, however, is of such a nature that carbon is the dominant element, so to speak, remaining intact in very many of the chemical changes that occur, while hydrogen and oxygen are added, subtracted, or exchanged for other elements or groups of elements. The great number and variety of the compounds in which carbon is a constituent is of itself a sufficient ground for making their discussion a separate branch of study.

In the second place, there are certain general characteristics which distinguish the organic substances from the inorganic. Most of the compounds of carbon are decomposed at temperatures which are below a red heat, while many inorganic compounds withstand much higher temperatures; and organic compounds are more liable to change when exposed to the light and air than are the inorganic. The majority of organic substances are practically insoluble in water, which is the solvent of so many inorganic compounds, and are usually soluble in such liquids as ether, chloroform, alcohol, carbon disulphide, and benzene, in which few of the inorganic compounds dissolve.

Again, while the greater number of inorganic compounds with which we deal in aqueous solution react almost instantaneously with each other, if at all, the reactions between dissolved or liquid organic compounds, though occasionally rapid, are more frequently very slow, often requiring heat, and hours or even days for completion. This difference in behavior is explained by the fact that the inorganic compounds are electrolytes and the reactions are the reactions of ions, while comparatively few organic compounds are ionized, and their reactions are those of undissociated molecules.

These distinctions must not be understood to be absolute. Some carbon compounds, such as the carbides of the metals, the oxides of carbon, and others withstand very high temperatures, while a considerable number of inorganic compounds are decomposed at a moderate heat; and a number of organic substances dissolve in water and are electrolytes, while some inorganic compounds dissolve in the non-aqueous solvents which were named, and usually without ionization. The differences, however, are sufficiently general to justify the separate treatment.

Another peculiarity of organic substances is that among them we find many large groups of closely related substances—the relation being much closer than that which exists between the members of the inorganic classes of bases, acids and salts. The members of each of these organic groups not only give similar reactions with a given reagent, yielding similar products, but show a nearly uniform gradation in all their physical and chemical properties. This very much simplifies our study; for when we have learned the characteristics of one or two members of a group, detailed examination of the others becomes unnecessary.

A complete discussion of the compounds of carbon would include carbon monoxide, carbon dioxide, carbon disulphide, certain carbides, carbonic acid, and the carbonates—substances which are usually treated in inorganic chemistry on account of their close relations to inorganic compounds. All of these compounds, however, have also certain relations to other compounds of carbon, so that some reference to them which will bring out this relation should be made in organic chemistry.

Sources of Organic Compounds.—Carbon combines directly with hydrogen at high temperatures, and the hydrocarbons which are formed may be employed as the starting point for the preparation of a great variety of other organic compounds. Some simple organic substances may be made by the use of the oxides of carbon, its sulphide, chloride, and one or two carbides of the metals, and these may then be built up into more complex compounds by laboratory methods. But in actual practice the chief sources of organic compounds are in the products elaborated in plants and animals. These substances were the first to receive the name "organic," and for a long time it was believed impossible to produce any of them artificially from the elements or from so-called inorganic material. Among the important organic compounds which are found already formed in plants are starch, cellulose, the sugars; acids or salts of acids, such as oxalic, citric, tartaric acids; the alkaloids, such as quinine and strychnine, and many other substances of greater or less complexity. Petroleum contains many compounds of carbon and hydrogen. Many organic substances are also produced by the destructive distillation of coal, wood, and bones—those which are contained in the coal tar being of the greatest interest and practical value. Furthermore, fermentative processes produce ordinary alcohol from sugar, acetic acid from alcohol, and a number of other compounds.

It is interesting to note that we may trace the source of the natural organic substances to the carbon dioxide of the air, which, in turn, is supplied to the air by the combustion, decay, fermentation, etc., of plant and animal matter. All of the carbon in plants—and it is the chief element they contain—is derived from this gas which forms only about three ten-thousandths of the volume of the air. Under the influence of solar energy, carbon dioxide, water, and small quantities of other simple inorganic compounds taken up through the roots from the soil, are built up into the structure of the plant or vegetable, oxygen being returned to the air. The chemical processes in the growing plant are, in general, of a synthetic character, and "endothermic" or such as require the expenditure of energy (furnished by the sun) to produce them. But at the same time, processes of the opposite character, or analytic processes which are "exothermic," go on to some extent, as is shown by the fact that plants exhale carbon dioxide. Since the food of animals is either directly or indirectly of vegetable origin, the compounds which are formed in their bodies owe their principal constituent, carbon, to the same original source. But the chemical changes in the living animal are more largely of an analytic character than those in the growing plant. While new complex substances are built up from the food materials, the resolution of these into simpler compounds is all the time proceeding. These latter reactions, being exothermic, supply the energy which maintains the temperature and varied activities of the animal body.

In the greater number of these natural substances and in those directly obtained from them in the ways which have been mentioned, we find only three elements beside carbon, *viz.*, hydrogen, oxygen, and nitrogen. Many contain only carbon and hydrogen; a large number, carbon, hydrogen and oxygen; and a comparatively small number, carbon and nitrogen with either hydrogen, or both hydrogen and oxygen. A still smaller number of definite organic compounds containing sulphur or phosphorus are found in nature, and certain metals—chiefly potassium, sodium, and calcium—are present in the natural salts of organic acids.

While the number of elements that enter into the composition of the natural organic compounds is thus limited, many other elements may be introduced by laboratory methods. The chemist has by no means succeeded in making in his laboratory all the organic compounds which are found in nature, and where he has succeeded, it is very seldom that the steps of his processes are those followed by nature. Natural compounds are formed in living organisms at ordinary temperatures, while the laboratory products are usually obtained by the use of higher temperatures and under other conditions quite dissimilar to those which prevail in the plant or animal.

The immense number of compounds which carbon forms with four or five other elements must mean that the molecules of many of them are of great complexity; and in fact the evidence indicates that the carbon atoms possess the unusual property of combining with each other in what we picture to be chains or rings of atoms united by one or more of their valencies, while the remaining valencies serve to hold the other elements of the compound. Not only is this the case, but a given number of atoms of carbon and of one or two other elements often combine in varied relations, giving compounds of distinct properties. The molecules of such compounds of the same composition but different properties may be regarded as analogous to the patterns which may be made by putting together a definite number of colored or differently shaped blocks in various ways; and indeed the graphic formulas which the organic chemist uses to explain the variety he finds resemble such patterns with the atomic symbols used instead of blocks. It is thus seen that valency and the combinations which it permits must play an immensely greater part in the discussions of organic chemistry than it usually does in those of inorganic compounds.

Identification of a Substance as Organic.—This resolves itself into a test for *carbon*. Most organic substances burn, and if the substance chars or if the flame deposits lampblack on a cold surface which is brought into it, no further test is necessary. Many organic compounds show the presence of carbon by charring when heated in an ignition tube; but the most general test for carbon is the formation of carbon dioxide and its detection by lime water. The substance is heated with copper oxide in a test tube and any gases that are formed are led into lime water; or if the substance is a gas, or one which sublimes or distils before reacting with the copper oxide, its vapor is led through a tube containing hot copper oxide.

Test for Elements Combined with Carbon.—*Hydrogen* is usually indicated by the water produced in the test for carbon; but, as practically all organic substances contain hydrogen, a test for this element is seldom necessary

Nitrogen.—If, in the burning or charring of the substance, an odor like that of burning wool is noticed, this shows that nitrogen is a constituent of the substance. Many organic compounds, however, which contain nitrogen do not give this odor. In this case, the substance is ignited with sodium (or with a mixture of magnesium powder and sodium carbonate) in a test tube, and if nitrogen is present it forms a cyanide, which, when brought into solution, and digested with a few drops of a mixture of ferrous and ferric salts, gives a precipitate of Prussian blue when acidulated with hydrochloric acid. Certain substances which contain nitrogen fail, however, to give this test, since the nitrogen is disengaged as gas at a temperature below that at which the reaction with the metal occurs. In these cases it is necessary to prove that nitrogen is one of the gases evolved when the substance is heated, or when it is oxidized as in the quantitative determination of nitrogen. The other elements which may be present, such as *sulphur*, *phosphorus*, and the *halogens*, may be detected in the soluble product formed by the ignition of the substance with sodium, where they appear as sodium compounds and respond to the usual tests of inorganic chemistry. *Halogens* may be detected more simply by bringing a bit of the substance on a clean copper wire into the Bunsen flame; if a halogen is present it forms a volatile copper halide which colors the flame green. Or the substance may be ignited with calcium oxide, when the calcium halide is produced together with the carbonate, and after dissolving in dilute nitric acid the halogen is detected by adding silver nitrate. *Metals* which may be present are detected in the residue from ignition by the usual procedure of qualitative analysis.

Tests for Purity.—Before the quantitative composition of a compound can be determined, it is, of course, necessary to obtain it in a state of purity. The usual tests for the purity of solid and liquid organic compounds are the melting and the boiling points. If a solid melts abruptly at a certain temperature (or within a range of 0.5°) it is considered pure enough for most purposes. Impurities cause a more gradual melting, and at a temperature which is lower than that of the pure substance. Pure liquids have a constant boiling point, while in the case of mixtures the temperature generally rises as the distillation proceeds. There are, however, some mixtures of definite composition, such as alcohol and water, which have a constant boiling point under a given pressure. A change of pressure (distillation in a partial vacuum) reveals their character, for while the boiling point of a pure substance would still be constant, though different, under the new pressure, the boiling point of the mixture becomes inconstant until a new equilibrium is established with a different proportion of the components.[1]

Methods of Purification.—The general method for the purification of solid organic compounds is by fractional crystallization from an appropriate solvent. Organic liquids are purified by fractional distillation, the distillate being collected in separate portions or "fractions" for small ranges of temperature as shown by a thermometer suspended in the vapor. A partial

---

[1] Refer to the behavior of mixtures of hydrochloric and of nitric acids with water. For a discussion of the boiling points of mixtures see some Physical Chemistry.

separation of the constituent liquids is effected in this way, and the separation is made more complete by redistilling the fractions a sufficient number of times. When the substance is one which decomposes at or below its boiling point under ordinary atmospheric pressures, it may be distilled at a lower temperature without decomposition in a partial vacuum, (*e.g.*, in the preparation of glycerine). A method which is successful in a number of instances is by distillation in a current of steam, as in the preparation of aniline and nitrobenzene. Mixtures of solids or of liquids can frequently be separated into the individual constituents, or one constituent can be extracted in a state of purity, by taking advantage of the different solubilities in various solvents. A pure solid compound may sometimes be obtained from a mixture by sublimation (*cf.* benzoic acid).

No general methods are known for the purification of gases. Most frequently it is effected by absorbing one or more of the constituents of the mixture in certain liquids or solids. But usually it is necessary to prepare the gas as pure as possible from pure materials by a definite chemical action. Even then, in most cases, there are impurities of small amount which must be removed by absorption in some substance.

Quantitative Analysis.—Carbon and hydrogen are always determined in one operation, which consists in the complete oxidation of a weighed portion of the pure compound (usually by means of copper oxide) and absorbing the water in solid calcium chloride, and the carbon dioxide in a strong solution of potassium hydroxide. From the increase in weight of these substances, the amounts of hydrogen and carbon are calculated. The weight of the nitrogen may be determined (by the *Dumas* method) from the volume of gas collected over potassium hydroxide solution when the substance is oxidized by copper oxide in an apparatus from which the air has been displaced by carbon dioxide. This is often called the "absolute method." By the method of *Kjeldahl*, which is the one generally used in the analysis of foods and other complex mixtures, the nitrogen is converted into ammonium sulphate by heating the substance with concentrated sulphuric acid, and from this compound ammonia is set free by sodium hydroxide and absorbed in a measured quantity of standard acid. The amount of acid neutralized by the ammonia is determined by titration, and from these figures the amount of ammonia and hence of nitrogen is readily calculated. No satisfactory method for the direct determination of oxygen has been found, and the percentage of this element is usually estimated by subtracting the sum of the percentages found for the other elements from one hundred.

For the determination of sulphur or phosphorus, the substance is oxidized—usually by heating with fuming nitric acid in a sealed tube—so that these elements are converted into sulphuric or phosphoric acid, from which the amount of each is found by the ordinary methods of inorganic quantitative analysis. The halogens are determined as silver halides, being converted into this form by oxidizing the substance as above in the presence of silver nitrate.

If metals are present in organic compounds, as in the case of organic salts, it is usually sufficient to ignite a weighed amount of the substance, when the carbonate or oxide of the metal is left, and can be weighed as such, or the metal determined in the usual ways. Such metals as silver and platinum are, of course, left from the ignition in the metallic state.

The Empirical Formula.—Since the empirical formula of a compound is simply a record of the quantitative composition in terms of atomic weight units, it is found by translating the parts by weight, or the percentages obtained from the quantitative analysis, into these terms. The student is familiar with the method from his work in inorganic chemistry. The symbol of an element represents a definite number of atomic weight units, and the relative numbers of atoms of the several elements that make up the compound are found by dividing the percentages or proportional weights of the elements by their respective atomic weights. The quotients thus obtained are compared, and their ratios to each other expressed in the smallest whole numbers. For instance: A certain compound is found to have the following percentage composition: $C = 40.00$, $H = 6.67$, $O = 53.33$,

$$\left.\begin{aligned} 40.00 \div 12 &= 3.33 \\ 6.67 \div 1 &= 6.67 \\ 53.33 \div 16 &= 3.33 \end{aligned}\right\} \; 3.33 : 6.67 : 3.33 = 1:2:1$$

Therefore the composition in atomic weight units is most simply expressed in the formula CH_2O. Since the methods of quantitative analysis are always subject to small errors, the ratios of the quotients often cannot be expressed in exact whole numbers; in these cases, the values which are the nearest possible to whole numbers are taken as representing those numbers.

Molecular Formulas.—Since the empirical formula is merely an expression in chemical notation of the quantitative composition, any formula which is the multiple of the simplest one would express this fact with the same accuracy. Now it happens very often in organic chemistry that there are two or more distinct compounds of different properties which have the same percentage composition, and consequently the same empiricial formula. There are, for example, several different compounds which have the same composition and hence the same empirical formula as that taken for illustration above. This fact suggests that the molecules of these compounds are probably of different weights, and that while one of them may be properly represented by the formula CH_2O, the others have such formulas as: $C_2H_4O_2$, $C_3H_6O_3$, $C_4H_8O_4$, $C_6H_{12}O_6$, etc. We must, therefore, find the molecular weight of the compound in order to decide which of the possible multiple formulas belongs to it.

The student probably remembers the relation between the densities of gases or vapors and molecular weights: By the hypothesis of Avogadro, equal volumes of all gases, when measured under the same conditions of temperature and pressure, contain equal numbers of molecules. It follows that since density is the weight of a unit volume, the molecular weight of a gas or vapor can be found by comparing its density with the density of some gas whose molecular weight is known, such as hydrogen (2), oxygen (32), or air (whose average molecular weight is 28.96). This method can be employed only with substances which are gases, or are converted into vapor without decomposition. The densities of gases and of vapors can be determined by direct or indirect weighing, and measuring the volume. The vapor densities of volatile liquids or solids are usually found by the method of *Victor Meyer*, which consists in causing the vapor from a known weight of substance, formed suddenly at a temperature much above its boiling point, to displace its own volume of air. The apparatus is arranged so that this air is collected over water and measured at room temperature. By this method the molecular weight of one of the compounds whose empirical formula is CH_2O is found to be 30; hence the molecular formula is at once picked out from the possible multiples as CH_2O, since here the sum of the atomic weights is 30. It is obvious that the density determination, and hence the molecular weight calculated from it, need not be very exact, since the possible molecular weights which correspond to a given empirical formula are usually quite far apart; in the case taken for illustration, they would be 30, 60, 90, etc., and a determination which was within five units of the true value would be conclusive.

The molecular weights of substances which cannot be vaporized without decomposition are generally found from the effect which a given weight of the substance has in lowering the freezing point, or in raising the boiling point of some solvent.[1]

Another method for determining molecular weights in certain cases depends on an argument which may be made from the composition of the substance as compared with that of some substi-

---

[1] For these methods see Ostwald-Luther's Physico-Chemical Measurements.

tution product. This is best shown by an example. One of the compounds whose empirical formulas are all CH_2O is an acid. If we make the silver salt of this acid and determine the silver, we find that it amounts to 64.64 per cent. of the salt; the rest of the salt—the acid radical—making up the remaining 35.36 per cent. Since $64.64 : 35.36 = 107.88$ (atomic weight of silver): 59, for every atomic weight of silver there are 59 atomic weight units of the radical which contains all the carbon and oxygen of the acid, with any hydrogen which has not been displaced by the silver in the formation of the salt. Now we know that silver has a valence of one, and therefore each atomic weight of silver takes the place of one atomic weight of hydrogen. If we add the weight of one atom of hydrogen to the atomic weight units of the acid radical, we have the probable molecular weight of the acid, that is, 60. The simplest formula which agrees with this is $C_2H_4O_2$, that of the silver salt being $C_2H_3AgO_2$. But here, as in the case of the empirical formula, any multiple of this would satisfy the facts equally well, for the silver salt might be $C_4H_6Ag_2O_4$, or any multiple of $C_2H_3AgO_2$. If the salt which we analyzed really had one of these formulas, we should expect that an acid salt, containing only one atom of silver, could be obtained, and since we find in this case that such a salt cannot be made, the simple formula, $C_2H_3AgO_2$, is, in all probability, the correct one.

Structural Formulas.—In organic chemistry we not only find many instances of different compounds which have the same empirical formulas, and which must be distinguished by a knowledge of their molecular formulas, but there are also frequent cases in which two or more compounds have the same molecular formulas and are yet very different substances. There is only one way in which we can imagine the occasion of such differences, and that is by different relations of the elements to each other in the molecule. These we represent by formulas which are known as *constitutional*, *structural*, or *graphic formulas*, and with which the student is familiar to some extent in inorganic chemistry.

In such formulas, the atomic symbols are connected in different ways and in different groups. Compounds of the same molecular formula but of different properties are called isomeric compounds or *isomers*, and the phenomenon is known as *isomerism.* The subject will be discussed in connection with the various cases of isomerism which we shall meet in the course of our study.

Classification of Organic Compounds.—For reasons that need not be formally discussed at this point, the organic compounds are usually treated under two general classes: the *Aliphatic* and the *Aromatic compounds.* These names, like that of Organic Chemistry, have lost much of their original significance—many of the aliphatic compounds have no direct relationship to the fats and their derivatives, from which the name is taken, and many of the aromatic compounds are unlike the fragrant substances which suggested their name. There are, however, broad lines of distinction between the two groups of compounds, which justify the classification. In each of these two main classes, we shall find a number of well-defined smaller groups each containing compounds which are closely related to each other in both their physical and chemical properties, such as the several groups of the hydrocarbons, the alcohols, the acids, the carbohydrates, the phenols, etc.

Laboratory Operations.—Many of the reactions for the preparation of organic substances proceed very slowly as compared with those familiar in inorganic chemistry. The principal reaction is also more often complicated by secondary reactions, and therefore the yield of the desired product is frequently far below that indicated by the equation which represents the reaction.

Solvents are often necessary to bring about the intimate contact which is necessary for the reaction, and where, as is generally the case, one or more of the substances is insoluble in water, various organic solvents are employed, such as alcohol, acetone, acetic acid, chloroform, ether, benzene, phenol, etc., and in some instances, sulphuric, hydrochloric, or nitric acid. Frequently the solvent acts also as a necessary diluent.

The temperatures for organic reactions are usually not very high. In some cases, where heating is necessary, it is sufficient to distil the mixture, either immediately or after more or less prolonged preliminary boiling with a reflux condenser; or the substances may be dissolved in a high boiling solvent. Higher temperatures than those permitted by the boiling points are obtained by heating under pressure, ordinarily in sealed glass tubes.

In many instances, reactions succeed only when the temperature is kept low, on account of the instability of the desired product (as in the preparation of the diazo compounds, p. 313), or because other products are formed at higher temperatures. The heat developed in the reactions is often considerable, and its ill effects may be avoided by gradual addition of the reacting substances to each other and external cooling (*cf.* pp. 159, 294), or by dilution with indifferent solvents such as water, glacial acetic acid, alcohol, ether, or benzene.

CHAPTER II

THE PARAFFINS OR HYDROCARBONS OF THE METHANE SERIES

Among the hundreds of compounds which contain only carbon and hydrogen, there is a considerable group whose members resemble each other in a remarkable manner. Some of them are gases, some are liquids, and others solids; but they are all colorless, all insoluble in water, and are all characterized by great chemical indifference. Even such powerful agents as concentrated sulphuric acid, chromic acid, and fuming nitric acid, fail to attack them at ordinary temperatures. At higher temperatures these agents act very slowly with the production of carbon dioxide and water, and only very small amounts of intermediate compounds. Chlorine is the only agent which acts on these substances at all readily in the cold. It acts more rapidly in sunlight or when the temperature is raised, and the result of its action is a step-by-step replacement of hydrogen by chlorine. This may proceed until all of the hydrogen is replaced and compounds are formed which consist of carbon and chlorine alone. Bromine reacts in sunlight with the liquid and gaseous hydrocarbons with the production of similar substituted compounds.

These hydrocarbons have received the name of **paraffins** (*parum* and *affinis*) on account of their chemical indifference or "little affinity."

The results of analyses and molecular weight determinations show that their formulas can be arranged in a regular series. The hydrocarbon of the lowest molecular weight, 16, has the composition $C = 75$, $H = 25$, and these data lead to the molecular formula, CH_4. The next in molecular weight contains $C = 80, H = 20$ and as its molecular weight is 30 its formula is C_2H_6. The third with the molecular weight of 44 has $C = 81.82$, $H = 18.18$, and the formula C_3H_8. These molecular weights increase from the first to the second, and from the second to the third, by 14 atomic weight units, and the formulas by an increment of CH_2. The other paraffins have molecular weights and formulas which stand in a like relation to these and to each other, so that the molecular weight of any one of them can be expressed by $16 + 14n$, and their composition by $CH_4 + nCH_2$, where n is any number from 0 to 59. The last expression may be given the more compact form, C_nH_{2n+2}, in which n is any number from 1 to 60. C_nH_{2n+2} is, therefore, a general formula for the paraffins. Compounds having such relations as this, which can be expressed by a general formula, are said to form an *homologous series.* The percentage of hydrogen decreases rapidly at first, and then more and more slowly as we pass from CH_4 to the higher members of the series; but here, again, a general expression may be formulated for the percentage of hydrogen in any of the paraffins. This is: per cent. of hydrogen $= \frac{100(n+1)}{7n+1}$.[1]

With this orderly relationship in composition and molecular weight there is also found a generally uniform gradation in such physical properties as the boiling and the melting points. Many of the series from $n = 1$ to $n = 60$ are known and have been investigated, and the others could, undoubtedly, be made if there was any special object in so doing. Some of the formulas with the names and the melting and boiling points are given in the following table.

---

[1] In this discussion, for the sake of greater clearness, the atomic weight of hydrogen has been taken as 1 instead of 1.008. The more exact formula for the percentage of hydrogen is $\frac{100.8\ (n+1)}{7.008n + 1.008}$.

NORMAL PARAFFINS

Formula	Name	Melting Point	Boiling Point
CH_4	Methane	−184°	−160°
C_2H_6	Ethane	−172	− 93
C_3H_8	Propane	.....	− 37
C_4H_{10}	Butane	−135	0.6
C_5H_{12}	Pentane	.....	36.4
C_6H_{14}	Hexane	.....	70
C_7H_{16}	Heptane	.....	98.4
C_8H_{18}	Octane	.....	125.6
C_9H_{20}	Nonane	−51	149.5
$C_{10}H_{22}$	Decane	−31	173
$C_{11}H_{24}$	Undecane	−26	194
$C_{12}H_{26}$	Dodecane	−12	214.5
$C_{14}H_{30}$	Tetradecane	4	252.5
$C_{16}H_{34}$	Hexadecane	18	287.5
$C_{20}H_{42}$	Eicosane	37	205[1]
$C_{21}H_{44}$	Heneicosane	40	215[1]
$C_{23}H_{48}$	Tricosane	48	2341
$C_{31}H_{64}$	Hentriacontane	68	302[1]
$C_{35}H_{72}$	Pentatricontane	75	331[1]
$C_{60}H_{122}$	Hexacontane	101	....

But the number of hydrocarbons in the group is very much larger than indicated by this list. While there is only one compound of the formula CH_4, and only one for each of the formulas C_2H_6 and C_3H_8, there are two hydrocarbons of the formula C_4H_{10}, three whose composition and molecular weights correspond to C_5H_{12}, and a rapidly increasing number for each of the following members of the series.

As was stated in the first chapter, the explanation of such "isomeric" compounds is found in the theory that the same number of atoms is differently combined in molecules of the same composition and weight.

In the theory of valency, as the student knows, the atoms of a compound are supposed to be bound together by the force of

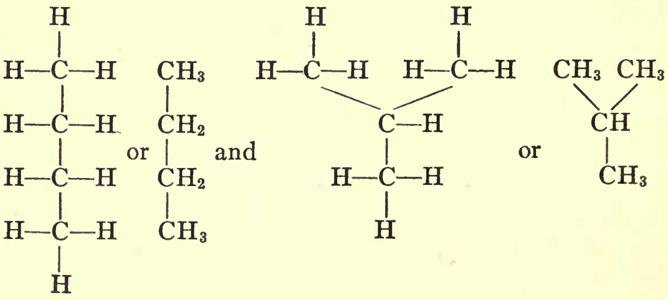
---

[1] At 15 mm. pressure.

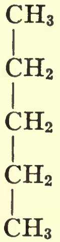
chemical affinity acting at certain points or through certain lines of union which are called "valencies." The number of valencies depends on the nature of the element, and is determined by the study of the simpler compounds which it forms with other elements—the valence of hydrogen being taken as the unit. Carbon is tetravalent in such simple compounds as CH_4, CCl_4, CO_2; and the formulation of the vast majority of its compounds is satisfactorily accomplished by the use of the tetrad carbon atom. (In CO, and a few other compounds carbon acts as a dyad and in one instance, at least, carbon appears to be a triad.) Of the other "organic elements," hydrogen is, of course, monovalent, oxygen divalent, and nitrogen either trivalent or pentavalent.

The theory of valency is the basis on which organic chemistry has been developed, and its value as a working hypothesis has been abundantly demonstrated by the results, which prove it to have been one of the most fruitful theories of natural science. By the linking of atomic symbols in accordance with the valence theory we can represent in graphic or structural formulas arrangements which clearly differentiate and, in a way, explain the various organic compounds.

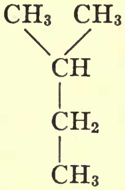
For instance, in the case of C_4H_{10} two different arrangements can be made:

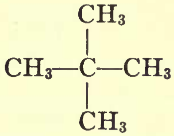


and for C_5H_{12}, the three arrangements:



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$





$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

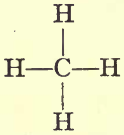
Moreover, these groupings are the only ones which can be made in which actual differences in the relations of the atoms are indicated. Now it happens that there are only two different compounds of the formula C_4H_{10}, and only three of the formula C_5H_{12} known, in spite of all attempts to make others; and this agreement between the number of theoretical formulas and the facts is found to extend to all such cases of chemical isomerism—that is, in no instance is a larger number of isomers known than is predicted by the possible structural formulas, and, though in many cases the whole number of isomers is not known, the validity of this explanation has been abundantly proved. It should be noticed, incidentally, that only one distinct grouping is possible for the formulas of the first three members of this series.

It is one thing, however, to find that for the observed differences of several compounds of the same molecular formula there is an equal number of possible structural formulas, and quite another to decide which particular grouping is the proper representation of each of these compounds. The problem can, however, be solved by studying the reactions by which the compounds are synthesized and those by which they are converted into other compounds. Illustrations of the methods and the reasoning employed for the selection of a definite arrangement for a particular compound will be given in a number of individual instances.

It is very important that the student should clearly understand that a formula of any sort is only a short-hand or pictorial record of observed facts. Hypothetical structural or graphic formulas are often useful as suggestions and incentives for investigation; but no formula of any kind should be accepted unless it is found to be in accordance with all the experimental facts. It may not accurately explain all these facts, and indeed few if any of our formulas do; but it must, at least, not be in contradiction with any of them.

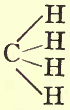
The empirical formula records only the elementary composition; the molecular formula adds to this the numbers of the several atoms in the molecule; and the graphic, constitutional, or structural formula is an attempt to represent the relations of these atoms to each other.

It should, perhaps, be pointed out, in order to prevent any possible misunderstanding later, that the relative positions which are given the symbols in the usual structural formulas are entirely without significance. It makes no difference in the meaning of the formula for methane, for instance, whether we write CH_4 or



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

or



In all three cases the one essential fact is that all four hydrogen atoms are directly united to one atom of carbon. In other words, in the usual formula no attempt is made to indicate the actual positions or space relations of the atoms of the molecule.

In more complex formulas the position of the symbols is frequently varied for the purpose of bringing out some special point or to emphasize certain facts in the behavior of the compound; and the student should accustom himself to recognize the identity of relationship or essential "structure" of these different arrangements.

We shall find, however, that there are a number of instances where isomeric compounds show differences, usually in their physical properties, for which the ordinary method of formulation can render no account; and that here a satisfactory explanation may be given for their differences by formulas which indicate the relative positions of the atoms and groups in space.

It is obvious that empirical and simple molecular formulas are of little use in organic chemistry, except as the first expression of composition and the basis for structural formulas. They are so similar in form that it is very difficult to remember them; and in many instances, as has been said, one formula often applies to a number of substances which are entirely distinct in physical and chemical properties, and therefore fails to represent an individual compound.

On the other hand, the structural formula is of the greatest importance, for by this mode of representation we can form a clear picture of the differences in molecular arrangement which explain the differences in the behavior of the compounds. In inorganic chemistry where the number of compounds consisting of the same two or three elements is never large, such formulas are interesting, but by no means so necessary for our study.

A good exercise for the student at this point is to write all of the possible formulas for a few of the paraffins higher than C_5H_{12}. He will find that while there are five arrangements for C_6H_{14}, there are nine for C_7H_{16} and eighteen for C_8H_{18}. Indeed, the number of combinations and hence of the possible isomers must, from the nature of the case, increase very rapidly. There are 75 for $C_{10}H_{22}$, 355 for $C_{12}H_{26}$, and 802 for $C_{13}H_{28}$.

The paraffins which are represented by formulas in which the carbon atoms are united in *unbranched chains*, that is, where no carbon atom is in combination with more than two other carbon atoms, are termed *normal paraffins*. It is these which are given in the table on page 17. The isomers or iso-hydrocarbons have branching chains of carbon atoms.

Nomenclature.—The first four of the normal paraffins have arbitrary names; the higher members of the series are named numerically by the use of the Greek numerals. The names of all paraffins, normal and isomeric, end in *ane*. Since ethane is composed of two CH_3 groups, $CH_3.CH_3$, propane of a CH_3 group and a C_2H_5 group ($CH_3.CH_2$), butane of a CH_3 group and a C_3H_7 group ($CH_3.CH_2.CH_2$), etc., and as these groups appear in many compounds, it is convenient to have simple names for them. They are, therefore, named from the corresponding hydrocarbon containing one more atom of hydrogen by substituting the termination *yl* for *ane;* thus CH_3 is *methyl*, C_2H_5 is *ethyl*, C_3H_7 is *propyl*, etc. Compounds which contain these groups are very commonly named from the groups, so that the names become descriptive of the composition. Thus ethane is dimethyl, propane is ethyl-methane, butane is propyl-methane or di-ethyl, etc. The general name of *alkyl* is given to these groups.

The iso-paraffins are, perhaps, most satisfactorily named on a similar principle, as substituted methanes, taking the carbon atom which is united to the largest number of other carbon atoms as the carbon of the original methane. Thus the two isomeric pentanes whose formulas are given on page 19 would be called dimethyl-ethyl-methane and tetramethyl-methane; isobutane would be trimethyl-methane. The formulas of these compounds may be written in a more compact manner on one line with points to separate the groups and indicate the valences instead of lines: dimethyl-ethyl-methane $(CH_3)_2:CH.CH_2.CH_3$ or $(CH_3)_2:CH.C_2H_5$, tetramethyl-methane $(CH_3)_2:C:(CH_3)_2$, trimethyl-methane $(CH_3)_3:CH$.

Occurrence of the Paraffins.—Petroleum consists almost wholly of mixtures of hydrocarbons, often with small amounts of compounds containing sulphur, nitrogen, and occasionally phosphorus. In the Pennsylvania oils the hydrocarbons are almost exclusively members of the paraffin series, while other oils, such as the Russian, are chiefly mixtures of other hydrocarbons. From the Pennsylvania petroleum the individual paraffins from CH_4 to $C_{30}H_{62}$ have been isolated. The process of separating the single hydrocarbons from such mixtures is, however, a difficult and tedious matter, so that petroleum cannot be regarded as a practical source for their preparation.

Crude petroleum finds considerable employment as fuel, but much of it is separated by distillation into "fractions," which are characterized by a certain range of the boiling point and have a specific gravity lying between certain limits. Each of these fractions contains more than one hydrocarbon, and in the order of their boiling points and increasing specific gravities are known by the commercial names given in the table:

		Boiling Between	Specific Gravity	Contains Chiefly
	Petroleum ether	40°–60°	0.665–0.670	C_5H_{12}–C_6H_{14}
Gasoline	Benzine or naphtha	70°–90°	0.680–0.720	C_6H_{14}–C_7H_{16}
	Ligroin	90°–120°	....	C_7H_{16}–C_8H_{18}
	Kerosene	150°–300°	0.780–0.820	C_8H_{18}–$C_{18}H_{38}$
	Lubricating oils	above 300°		
	Paraffin	melts 38°–56°	0.87–0.93	$C_{27}H_{56}$–$C_{30}H_{62}$

These products are purified by washing successively with sulphuric acid and caustic soda, to remove basic and acid impurities. Sulphur is removed by treatment with copper oxide. From the last fraction, solid "paraffin" is separated by cooling.

The yield of the more valuable light oils is increased by carrying out the distillation of the heavier oils in such a way that part of the condensing vapors run back into the boiling oil. The temperature is so high that the condensed hydrocarbons are decomposed, or "cracked," as it is technically termed, into others of smaller molecular weight. Distillation under pressure is also effective.

Vaseline or *petrolatum* is obtained from the residuum of the heavier oils, when these are distilled in a partial vacuum.

Since all inflammable gases and vapors form explosive mixtures when mixed in certain proportions with air, the lighter and more volatile oils must always be used with great care to avoid the ignition of such mixtures by a flame or electric spark. The occasional explosion of kerosene lamps is due to the presence of some of these lighter oils, which should have been removed in its preparation.

The quality of *kerosene* is tested by finding at what temperature it gives vapors which "flash" on its surface when it is slowly heated and a small flame brushed over it from degree to degree. This "flashing point" should be above the temperature which the oil in a lamp can reach. A "fire test" is also made, and consists in determining the temperature at which the oil takes fire and burns. Both the flashing point and the fire test depend somewhat on the apparatus employed. Each of the United States has its own specification and method of testing prescribed by the law.

The uses of the various petroleum products as solvents, for cleansing, etc., as fuels and illuminants, as in gasoline engines and kerosene lamps and stoves, as lubricating oils, and, in the case of paraffine, for candles, etc., are well known.

While petroleum is the chief natural product in which the paraffins occur, some of the gaseous members of the series, notably methane, are constituents of natural gas, and of the "fire-damp" of coal mines; and some of the solid members occur in earth wax or ozokerite. Considerable amounts of gasoline are obtained from natural gas. Various paraffins are products of the natural decomposition of organic matter, or are produced in the processes of destructive distillation of coal, wood, etc.; but these are mostly the first members of the series or those of large molecular weight which form the solid paraffins.

Although the mixtures of the various hydrocarbons of the methane series, which are obtained from petroleum and other sources, are of very great importance, no practical application whatever has been made of any member of the series by itself. The individual paraffins are, however, of great interest to the chemist, not only in themselves and in the relationship they have to one another, but also because many other organic compounds may advantageously be viewed as derived from them by the substitution of various elements or groups for part or all of the hydrogen they contain, and can be made in the laboratory in this way. Since the same remarks apply to the other series of hydrocarbons, organic chemistry is sometimes defined as the "*chemistry of the hydrocarbons and their derivatives.*"

Methane, CH_4, with other gaseous paraffins, escapes from petroleum as it issues from the ground; and it is the chief component of natural gas and of the "fire-damp" which finds its way into coal mines from fissures in the coal, and often occasions disastrous explosions. It is a frequent product of the decomposition of organic matter under certain conditions, as when vegetable matter—dead leaves, etc.—decays under water, and hence is contained in the gas which is disengaged on stirring the bottom of stagnant pools. On this account it has sometimes been called "marsh gas." It is always formed in the destructive distillation of coal, wood, etc.; and is present in coal gas to the amount of 30–40 per cent.

Methane can be made in the laboratory by several methods, some of which may be used for its actual preparation, while others are chiefly of theoretical interest. We shall here, and in the future, designate the former "methods of preparation," the latter "methods of formation."

Formation.—(*a*) Methane is produced in small amounts, but mixed with hydrogen and other hydrocarbons, when an electric arc between carbon electrodes is formed in an atmosphere of hydrogen. It is also formed: (*b*) when the vapor of carbon disulphide mixed with hydrogen sulphide or with steam is passed through a tube containing heated copper. The reactions are:

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4$$

$$CS_2 + 2H_2O + 6Cu = 2Cu_2S + 2CuO + CH_4$$

(*c*) When mixtures of carbon monoxide or carbon dioxide and hydrogen are passed over finely divided nickel (obtained by reduction of the oxide with hydrogen) which is heated to about 250°, the nickel acting as a contact agent. If the gases are mixed in the proportion indicated by the equations, the reaction is complete and the methane is pure:

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

(*d*) When aluminium carbide is brought into water:

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$

(*e*) When halogen substitution products of methane are reduced by "nascent" hydrogen.

The first four of these methods show that methane, and therefore the great variety of compounds which can be made from it, can be synthesized from the elements; for carbon disulphide, water, both of the oxides of carbon, and aluminium carbide can be produced by the direct union of their constituent elements.

Preparation.—Some of the methods of formation can, of course, be used for the preparation of methane, but the methods chosen for the preparation of substances are naturally selected on account of the simplicity of the apparatus and conduct of the process, and the yield of the resulting product. (1) The most usual method of preparing methane is by heating a mixture of sodium acetate and soda-lime (a mixture of sodium and calcium hydroxides). Sodium acetate has the formula $C_2H_3NaO_2$, and the reaction is:

$$C_2H_3O_2Na + NaOH = Na_2CO_3 + CH_4$$

The methane made in this way is not quite pure and cannot be freed from small amounts (up to 8 per cent.) of hydrogen which, with other substances, is formed by the action of heat on sodium acetate alone. (2) Pure methane is most readily prepared from methyl iodide, CH_3I (made from methyl alcohol), by placing in an alcoholic solution of this substance some zinc which has first been coated with copper by treatment with a dilute solution of copper sulphate. A compound of the metal with the methyl iodide is first formed, CH_3ZnI, and then this reacts with the alcohol or the water which is mixed with it as follows:

$$CH_3ZnI + HOH = CH_4 + ZnI(OH)$$

Properties.—Methane is the lightest compound gas that is known, being a little lighter than ammonia and having the specific gravity of 0.557 (air = 1). Its flame is almost colorless, and like every combustible gas and vapor, it forms explosive mixtures with oxygen or with air.

In common with the other paraffins, methane is hardly acted on at ordinary temperatures by any agent except chlorine or bromine. The action is slow in diffused daylight, but more rapid in sunlight. The chlorine replaces the hydrogen of methane, with the production of hydrogen chloride and the successive formation of CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. When mixed with twice its volume of chlorine, methane explodes in direct sunlight with the separation of finely divided carbon:

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

By reactions with methyl chloride, CH_3Cl, the synthesis of organic substances can be carried on from the elements.

As it has proved impossible to obtain more than one compound of the formula CH_3Cl, and only one of the formula CH_2Cl_2, the four hydrogen atoms of methane must all be similarly related to the carbon atom.

Ethane, C_2H_6, occurs in petroleum and natural gas. It may be formed (1) by the reaction of sodium or zinc on methyl iodide:

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

This reaction leads to the conclusion that ethane is di-methyl with the constitutional formula, $CH_3.CH_3$. Ethane may be prepared, like methane, (2) by the reduction of its halogen substitution products by the action of coppered zinc on an alcoholic solution of ethyl iodide, C_2H_5I, and (3) by heating the sodium salt of propionic acid, $C_3H_5O_2Na$, with soda-lime, the reaction being like that for the preparation of methane from sodium acetate. Ethane is similar to methane in its properties, but is more easily liquefied and burns with a slightly luminous flame.

General Methods for the Formation of Paraffins.—1. The first method just given for the production of ethane (1) may be used for the formation of the other hydrocarbons of this series. When two different alkyl halides are employed, however, a mixture of products results. For instance, from the action of sodium on a mixture of methyl and ethyl iodides in ethereal solution, propane, $CH_3.CH_2.CH_3$, is formed by the union of the methyl and ethyl radicals:

$$CH_3I + CH_3.CH_2I + 2Na = CH_3.CH_2.CH_3 + 2NaI$$

but at the same time ethane is formed from the union of methyl to methyl, and butane from the union of two ethyl radicals. Since the mixed products are not easily separated, this method is chiefly useful in syntheses from single alkyl halides, which yield hydrocarbons containing double the number of carbon atoms of the halide.

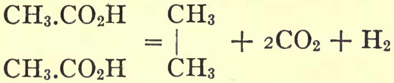
The paraffins may also be formed:

2. From halides containing the same number of carbon atoms (*a*) By reduction with "nascent" hydrogen (sodium amalgam, zinc and hydrochloric acid, or concentrated hydriodic acid). (*b*) By the formation of zinc alkyls and their reaction with water (p. 36). (*c*) By means of the Grignard reaction (p. 37). The iodides and bromides are most suitable for these reactions.

3. By distilling the sodium salts of acetic acid or its homologues with soda-lime. The product is a hydrocarbon whose molecule contains one less carbon atom than the salt:

$$CH_3.CH_2.CO.ONa + NaOH = CH_3.CH_3 + Na_2CO_3$$

4. Another reaction by which two like alkyl groups may be combined to a paraffin hydrocarbon occurs in the electrolysis of the organic acids or salts which contain these groups. By the electrolysis of acetic acid, for instance, the CH_3 groups which it contains unite in pairs forming ethane, which is evolved at the positive pole together with carbon dioxide, while hydrogen escapes at the negative pole:



$$\begin{array}{l} CH_3.CO_2H \\ \\ CH_3.CO_2H \end{array} = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + H_2$$

This reaction is, however, often accompanied by other reactions, giving different products from those indicated by the equation above.

5. By the addition of hydrogen to unsaturated hydrocarbons:

$$CH_2{:}CH_2 + H_2 = CH_3.CH_3$$

This reaction takes place readily in the case of the lower members of the series in the presence of platinum black, and may be effected for the higher members by heating the unsaturated hydrocarbon with hydriodic acid in a sealed tube.

The possibility of isomeric paraffins begins with the fourth, butane, C_4H_{10}, as has already been shown (p. 18); but the constitutional formula for propane, $CH_3.CH_2.CH_3$ with a CH_2 and two CH_3 groups, shows that two different mono-substitution products are possible, $CH_3.CH_2.CH_2Cl$ and $CH_3.CHCl.CH_3$; and these compounds are readily prepared. They correspond to the two butanes which may be regarded as propane in which one hydrogen atom is replaced by a CH_3 group.

Very few of the iso-hydrocarbons can be successfully prepared by the sodium synthesis, because of the mixture of products which is formed. They are best made by reduction of the corresponding halides, which in turn are prepared from the corresponding alcohols by methods which will be discussed further on.

We may add to the properties of the paraffins, that as the molecular weights increase they burn with a more luminous, and presently with a smoky flame, and that the higher members cannot be distilled at ordinary pressure, but undergo decomposition into other lighter hydrocarbons, often with separation of carbon.

The iso-hydrocarbons have boiling points which are lower than those of the corresponding normal paraffins, and different from each other. In general, a higher boiling point and a longer unbranched chain of carbon atoms are found to go together. Thus the boiling point of normal pentane with a chain of five carbon atoms is 36.4°, that of dimethyl-ethyl-methane (isopentane) with a chain of four atoms is 30°, and that of tetra-methylmethane, 9°.

Identification of the Paraffins.—An organic substance which is lighter than water and insoluble in it but soluble in ether and benzene, which is not attacked in the cold by fuming nitric acid or concentrated sulphuric acid, and reacts very slowly with bromine, is probably a paraffin. Many commercial mixtures, such as the products of petroleum, when subjected to these tests do show some reaction, but this is because of the presence of small amounts of hydrocarbons of other series, and after the partial reaction is over, the pure paraffins remain. They may therefore be purified in this way. The individual paraffins are identified by their melting or boiling points, and by the results of quantitative analysis. The iso-compounds are distinguished not only by melting and boiling-point determinations but also by the substitution products which can be obtained from them.

CHAPTER III

THE HALOGEN SUBSTITUTION PRODUCTS OF THE PARAFFINS

The chlorine and bromine substitution products of the paraffins are, as already indicated (p. 15), the only halogen derivatives which can be made directly from the hydrocarbons; but since this action gives a mixture of products, it is not a very practical method for their preparation. The action of chlorine and bromine is increased by heat or sunlight, and also by the presence of certain substances, such as ferric chloride, aluminium or antimony chloride, or iodine, which act as "halogen carriers." Alkyl chlorides, bromides, and iodides are usually prepared from the corresponding alkyl hydroxides known as alcohols, which have the general formula, $C_nH_{2n+1}OH$. The replacement of the hydroxyl group by the halogen is effected, in the case of the lower members of the series, by the action of the gaseous hydrogen halides on the alcohol in the presence of anhydrous zinc chloride which acts as a water-absorbing agent. For instance:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl \leftrightarrows \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

Zinc chloride cannot be employed when the higher alcohols of the series are used, since it acts directly on the alcohol and gives rise to other products.

The bromides and iodides (but not the chlorides) can be prepared by distilling the alcohols with an excess of an aqueous solution of hydrobromic or hydriodic acid. In some instances a halide salt is mixed with the alcohol and the halogen acid set free by treatment with sulphuric acid. Ethyl bromide, C_2H_5Br, for example, is readily made by distilling a mixture of alcohol, potassium bromide, and sulphuric acid. In every case a large excess of the hydrogen halide is necessary, since the reaction, as indicated in the above equation, is a reversible one.

The method of most general applicability is the treatment of the alcohol with a phosphorus halide:

$$\underset{\substack{\text{Propyl}\\ \text{alcohol}}}{3C_3H_7OH} + PCl_3 = \underset{\substack{\text{Propyl}\\ \text{chloride}}}{3C_3H_7Cl} + P(OH)_3$$

This method is the one almost always used in the preparation of alkyl bromides and iodides. It is not necessary, however, to employ the phosphorus halides themselves, but simply to add bromine or iodine, a little at a time, to the alcohol in which red phosphorus has been placed. After standing for some time the alkyl halide is obtained by distillation.

General Properties.—Methyl chloride, methyl bromide, and ethyl chloride, are gases at ordinary temperatures. The other alkyl halides up to those of high molecular weight are liquids which are almost insoluble in water, but very soluble in alcohol or in ether. The lower alkyl halides burn, and methyl and ethyl chlorides give a green-edged flame. All of them are colorless, though the iodides become brown after a time, on account of iodine which is separated by slight spontaneous decomposition and dissolves in the unchanged iodide. As shown in the following table the boiling points are higher as the molecular weights increase; and, for corresponding halides, are highest for the iodides and lowest for the chlorides. The specific gravities of the compounds of a given halogen decrease as the molecular weight is larger, and the specific gravities of the different halides of the same alkyl show the same gradation as the boiling points, increasing from the chlorides (which are all lighter than water) to the iodides.

SOME NORMAL ALKYL HALIDES (Primary)

	CHLORIDE		BROMIDE		IODIDE	
	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity
Methyl	—23.7°	0.952 (0°)	4.5°	1.732 (0°)	45°	2.293 (18°)
Ethyl	14	0.918 (8)	38.4	1.468 (13)	72.3	1.994 (14)
Propyl	46.5	0.912 (0)	71	1.383 (0)	102.5	1.786 (0)
Butyl	78	0.907 (0)	101	1.305 (0)	130	1.643 (0)
Amyl	107	0.901 (0)	129	1.246 (0)	156	1.543 (0)
Hexyl	133	0.892 (16)	156	1.193 (0)	182	1.461 (0)
Heptyl	159	0.881 (16)	179	1.113 (16)	201	1.386 (16)
Octyl	180	0.880 (16)	199	1.116 (16)	221	1.345 (16)

The relation between structure and physical properties is illustrated by the following table of the boiling points and specific gravities of the isomeric butyl halides:

	CHLORIDE		BROMIDE		IODIDE	
	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity
Normal butyl...... $CH_3.CH_2.CH_2.CH_2X$	78°	0.907 (0°)	101°	1.305 (0°)	130°	1.643 (0°)
Iso-butyl........... $(CH_3)_2CH.CH_2X$	68.5	0.895 (0)	92	1.204 (16)	119	1.640 (0)
Secondary butyl..... $CH_3.CH_2.CHX.CH_3$	67.5	0.871 (20)	91.3	1.250 (25)	119	1.626 (0)
Tertiary butyl...... $(CH_3)_2CX.CH_3$	55	0.866 (0)	72	1.215 (20)	100	1.571 (0)

The chemical reactivity of the normal halides is greatest in the iodides and least in the corresponding chlorides; it also increases from the higher members to the lowest. Methyl iodide is, therefore, the alkyl halide of greatest activity. Alkyl iodides are converted into bromides or chlorides by bromine or chlorine. Bromine is not displaced by chlorine, but a bromide may be changed into a chloride by antimony pentachloride. The halides react more or less readily with many substances, and are consequently of great importance in organic synthesis.

The following are typical reactions:

1. *With Hydroxyl Compounds.*—With water or alkalies the

halogen is exchanged for the hydroxyl group and alcohols are formed:

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + HOH \rightleftarrows \underset{\substack{\text{Methyl}\\\text{alcohol}}}{CH_3OH} + HI$$

$$\underset{\substack{\text{Ethyl}\\\text{bromide}}}{C_2H_5Br} + KOH = \underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} + KBr$$

The reaction with water is reversible, and to render it complete, heat and a considerable excess of water are necessary, while that with the base goes more readily. Moist silver oxide, which reacts like a hydroxide, effects the exchange still more easily, and usually without heating:

$$\underset{\substack{\text{Ethyl}\\\text{chloride}}}{C_2H_5Cl} + AgOH = \underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} + AgCl$$

This replacement of the halogens by hydroxyl takes place most easily with the alkyl iodides and least rapidly with the chlorides. If, however, potassium hydroxide acts in an alcoholic instead of an aqueous solution, the character of the reaction is altered: the replacement by hydroxyl does not occur, but instead, the halogen and an atom of hydrogen are withdrawn from the halide with the production of an "unsaturated" hydrocarbon (p. 42):

$$\underset{\text{Ethyl bromide}}{CH_3.CH_2Br} + KOH = \underset{\text{Ethylene}}{CH_2{:}CH_2} + KBr + H_2O$$

2. *With Certain Salts.*—The inorganic salts most employed in the reactions are those of silver. With these a fairly ready reaction usually takes place, with the formation of the insoluble silver halide and compounds in which the alkyl group is united to the acid radical of the silver salt, thus:

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + AgNO_3 = \underset{\substack{\text{Methyl}\\\text{nitrate}}}{CH_3NO_3} + AgI$$

$$2\underset{\substack{\text{Ethyl}\\\text{bromide}}}{C_2H_5Br} + Ag_2SO_4 = \underset{\substack{\text{Ethyl}\\\text{sulphate}}}{(C_2H_5)_2SO_4} + 2AgBr$$

Organic salts of sodium and potassium act in a similar way,

$$CH_3Cl + KCN = CH_3CN + KCl$$

Methyl chloride · Methyl cyanide

$$C_2H_5I + C_2H_3O_2Na = C_2H_3O_2C_2H_5 + NaI$$

Ethyl iodide · Sodium acetate · Ethyl acetate

The alkyl compounds formed in these reactions are named as alkyl salts of the several acids, and are given the group name of "esters" or "ethereal" salts. The alkyl halides themselves obviously belong to this same group.

3. *With ammonia*, the halogen is replaced by NH_2, the "amino" group,

$$C_2H_5Br + NH_3 = C_2H_5NH_2.HBr$$

Ethyl bromide · Ethyl amine hydrobromide

4. The alkyl halides, as well as all halogen substitution products of the paraffins, are converted into the respective hydrocarbons by "*nascent*" *hydrogen:*

$$C_2H_5I + HH = C_2H_6 + HI$$

Attention should be called to the fact that the metathetical reactions with alkyl halides, which have been described, progress slowly as compared with the almost instantaneous reactions of this kind which occur between inorganic salts and bases. The explanation given for this is that the organic halides are ionized very slightly, if at all.

5. *With Metals.*—The reaction of alkyl halides with sodium has already been given (p. 28) as a means of synthesizing the paraffins. A compound containing zinc was also used for the same purpose. Zinc, magnesium, and some other metals react with the alkyl halides as follows:

$$C_2H_5I + Zn = C_2H_5ZnI$$

When this zinc ethyl iodide is boiled for some time it is converted into zinc ethyl $(C_2H_5)_2Zn$:

$$2C_2H_5ZnI = (C_2H_5)_2Zn + ZnI_2$$

Zinc ethyl iodide is a solid, but the zinc alkyls are liquids of repugnant odor, which take fire spontaneously in the air, so that their preparation and their use as reagents must all be conducted in an atmosphere of an indifferent gas, usually carbon dioxide. They are immediately decomposed by water with the production of hydrocarbons:

$$(C_2H_5)_2Zn + 2H_2O = 2C_2H_6 + Zn(OH)_2$$

The Grignard Synthesis.—The use of zinc alkyls and their halide salts has been generally displaced by the employment of corresponding magnesium compounds; since it has been found that these are more easily prepared, and have the further advantage of not igniting spontaneously in the air.

Clean dry magnesium turnings are covered with anhydrous ether and the organic halogen compound is gradually added. Absence of moisture is essential to success. After the reaction, evaporation of the ether leaves the magnesium compound in combination with one molecule of ether, *e.g.*, $C_2H_5MgI, (C_2H_5)_2O$. Other solvents besides ether, such as benzene, can be used, if a little ether or anisol is added as a catalyzer, and in this case the magnesium compound is obtained free from ether. In many instances the preliminary preparation of the magnesium compound is not necessary, the two organic substances which are to be synthesized being brought together in the presence of magnesium and ether.

Almost all the halogen derivatives of organic compounds, except acyl halides (p. 114), form addition compounds with magnesium, and these substances, which are called *Grignard reagents*, are of the greatest service to the organic chemist on account of the wide variety of syntheses which can be effected by their means. Some of the reactions with Grignard reagents are given here for convenience in future reference.

1. With water and other hydroxyl compounds, they yield hydrocarbons:

$$CH_3MgBr + H_2O = CH_4 + MgBrOH$$
$$C_6H_5MgBr + H_2O = C_6H_6 + MgBrOH$$

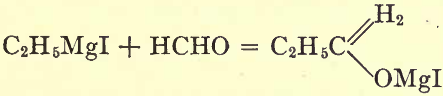
2. They absorb carbon dioxide, forming products which yield organic acids when treated with inorganic acids:

$$C_2H_5MgI + CO_2 = C_2H_5CO.OMgI$$
$$C_2H_5CO.OMgI + HCl = C_2H_5CO.OH + MgICl$$

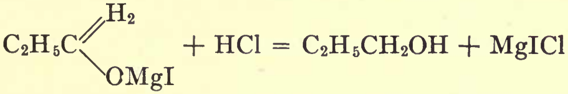
3. They absorb dry oxygen and the products yield primary alcohols or phenols when treated with an acid:

$$2RMgBr + O_2 = 2RO.MgBr$$
$$RO.MgBr + HCl = R.OH + MgBrCl$$

4. They form additive compounds with most substances which contain a carbonyl group (CO), and these yield alcohols when acted on by water or an inorganic acid. In this way primary alcohols may be prepared by means of formaldehyde:

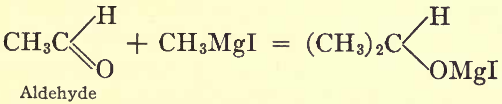


$$C_2H_5MgI + HCHO = C_2H_5C\begin{array}{l} H_2 \\ OMgI \end{array}$$

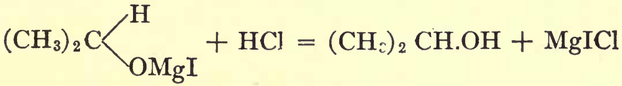


$$C_2H_5C\begin{array}{l} H_2 \\ OMgI \end{array} + HCl = C_2H_5CH_2OH + MgICl$$

With other aldehydes secondary alcohols are formed:



$$CH_3C\begin{array}{l} H \\ O \end{array} + CH_3MgI = (CH_3)_2C\begin{array}{l} H \\ OMgI \end{array}$$



$$(CH_3)_2C\begin{array}{l} H \\ OMgI \end{array} + HCl = (CH_3)_2\,CH.OH + MgICl$$

Ketones, *e.g.*, $CH_3.CO.CH_3$, and esters, in a similar manner give tertiary alcohols.

5. Aldehydes can be prepared from formic esters, and ketones from cyanogen, cyanides, and amides.

6. With many halides of metals and non-metals they enter into reaction with the production of the alkyl, or alkyl-halogen derivatives of these elements:

$$SnBr_4 + 4C_2H_5MgBr = (C_2H_5)_4Sn + 4MgBr_2$$
$$SiCl_4 + C_2H_5MgBr = C_2H_5SiCl_3 + MgBrCl$$

Methyl chloride is a commercial product made from trimethylamine hydrochloride (p. 132), which is obtained as a by-product in the beet-sugar industry. It is compressed to a liquid and used for the production of cold (like ammonia), and is extensively employed in the manufacture of various coal tar dyes. **Ethyl chloride** is also made on the large scale and used in the preparation of ethyl mercaptan, C_2H_5SH (p. 238) which is employed in making "sulphonal" (p. 240).

While there is only one methyl and one ethyl chloride, bromide, or iodide known or possible, isomeric alkyl halides begin with the two propyl halides, $CH_3CH_2CH_2Cl$, $CH_3.CHCl.CH_3$, and increase rapidly in number as we go higher in the series. There are four butyl bromides, $CH_3.CH_2.CH_2.CH_2Br$, $(CH_3)_2CH.$-CH_2Br, $CH_3.CH_2.CHBr.CH_3$, and $(CH_3)_3CBr$; and eight pentyl bromides.

Among the halogen substitution products of the paraffins, which contain more than one halogen atom, may be mentioned: **Methylene iodide,** CH_2I_2, which is one of the heaviest known liquid compounds (specific gravity 3.292 at 18°). By mixing with benzene, liquids of any specific gravity between 0.8736 (benzene) and 3.292 can be prepared, and may be used for the indirect specific gravity determination of solids, and for the separations of solids of different specific gravities. It is made by the reduction of iodoform, or tri-iodomethane, by hydriodic acid in the presence of phosphorus:

$$CHI_3 + HI = CH_2I_2 + I_2$$

This is a typical instance of the use of hydriodic acid as a reducing agent. The student will recall from his study of inorganic chemistry that hydrogen iodide is an endothermic and hence an unstable compound, separating easily into hydrogen and iodine. The phosphorus facilitates the reaction by uniting with the iodine as it is set free; the phosphorus iodide then reacts with the water which is present, giving phosphorous acid and hydriodic acid again.

Tri-iodomethane, CHI_3, commonly known as *iodoform,* is a yellow crystalline substance, which is prepared by warming an aqueous solution of alcohol and sodium carbonate with iodine. Its formation is often used as a test for alcohol, but several other organic substances give iodoform under similar conditions. It is used as an antiseptic in surgery, often in preparations where it is mixed with other substances to disguise its peculiar odor.

Tri-chlormethane, $CHCl_3$, or *chloroform,* is the well-known anæsthetic which was discovered in 1831 and first used for this purpose in 1848. It is prepared by the action of bleaching powder on alcohol or acetone or from chloral hydrate by reactions which will be discussed under those topics. Chloroform is a colorless liquid of ethereal odor and a sweetish taste. It is slightly soluble in water to which it imparts its odor and taste. It is readily volatile, but not inflammable. Chloroform is an excellent solvent for many organic compounds; it dissolves rubber and fats, and is a useful cleansing agent. In the air and light chloroform undergoes a slow decomposition with the formation of chlorine, hydrogen chloride, and carbonyl chloride, $COCl_2$. Consequently great care must be taken in regard to its purity when it is used for anesthesia. When heated with an alcoholic solution of potassium hydroxide, chloroform is decomposed with the formation of potassium formate:

$$\underset{\text{Chloroform}}{CHCl_3} + 4KOH = \underset{\text{Potassium formate}}{HCO.OK} + 3KCl + 2H_2O$$

If ammonia is added to the mixture of alcoholic potash and chloroform, potassium cyanide is produced:

$$CHCl_3 + NH_3 + 4KOH = KCN + 3KCl + 4H_2O$$

A similar reaction occurs when a primary amine (p. 127) is used in place of ammonia, and the unmistakable odor of the product serves as a test for chloroform and for the primary amines (*cf.* p. 132).

Tetra-chlormethane, CCl_4, or *carbon tetrachloride,* is the final product when chlorine acts on methane. It is prepared commercially by passing the vapor of carbon disulphide mixed with chlorine through red-hot porcelain tubes, or by leading chlorine into the liquid disulphide in which a little iodine has been dissolved, and which acts as a catalyzer:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

Carbon tetrachloride is a heavy liquid which is not inflammable and is an excellent solvent for fats. It is sold for extinguishing fire as "pyrene," and is much used for cleansing purposes, often mixed with benzine or gasoline, under the name of "carbona."

It is hydrolyzed by a hot solution of potassium hydroxide with the production of potassium carbonate:

$$CCl_4 + 6KOH = K_2CO_3 + 4KCl + 3H_2O$$

On heating with "molecular" silver, tetrachlor-methane is converted into *hexachlorethane,* $CCl_3.CCl_3$, a crystalline substance of camphor-like odor, which is hydrolyzed by potash at 200° into potassium oxalate.

SOME POLYHALOGEN DERIVATIVES

	Chloride		Bromide		Iodide	
	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity	Boiling Point	Specific Gravity
Methylene, CH_2X_2	41.6°	1.38	98.5°	2.50	180°	3.33
Methenyl, CHX_3	61	1.50	151	2.90	melts 119°	4.01
Carbon tetrahalide, CX_4	76.8	1.63	189		unstable	
Ethylene, CH_2XCH_2X	83.7	1.27	129	2.18		2.07
Ethylidene, $CH_3.CHX_2$	57.5	1.19	112.5	2.10	178	2.84

While the chlorine substitution products of the paraffins, which contain two or more chlorine atoms, can be formed by direct step-by-step replacement of hydrogen with chlorine, this method is not a practical one for the preparation of the individual members, because of the mixtures it gives. Hence other methods are employed for making the chlorides and other polyhalogen derivatives.

Besides such special methods as have just been given for the methane derivatives, there are certain methods of general application for the derivatives of the higher paraffins. Dihalogen compounds, in which the two halogen atoms are united to one carbon atom, are obtained by the action of phosphorus pentahalides on aldehydes and ketones:

$$\underset{\text{Aldehyde}}{CH_3.CHO} + PCl_5 = \underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} + POCl_3$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + PCl_5 = \underset{\text{Dichlorpropane (2.2)}}{CH_3.CCl_2.CH_3} + POCl_3$$

The isomeric dihalogen derivatives with the halogen atoms united to different carbon atoms can be made from the corresponding dihydroxyl alcohols—glycols—as the monohalogen compounds are from the simple alcohols—the reaction involving two steps:

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} \rightarrow \underset{\text{Glycolbromhydrin}}{CH_2Br.CH_2OH} \rightarrow \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

These halides are also the product of the direct addition of halogen to unsaturated hydrocarbons of the olefine series (p. 44):

$$\underset{\text{Ethylene}}{CH_2:CH_2} + Br_2 = \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

Compounds of this type are useful in synthetic work, since they may form a step in the conversion of a monosubstituted compound to various disubstituted compounds. We shall meet with illustrations of such transformations.

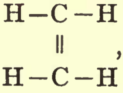
It should be remarked that isomerism in the alkyl polyhalides begins with the derivatives of ethane. Thus there are two dihalides of ethane represented by the formulas, $CH_2Cl.CH_2Cl$, ethylene chloride, and $CH_3.CHCl_2$, ethylidene chloride. Similarly there are two tri-halides, two tetra-halides, but only one penta- and one hexa-halide. As we go higher in the series the number of halogen substituted isomers increases rapidly.

Hydrolysis of Halogen Derivatives.—All the halogen derivatives of the paraffins are subject to hydrolysis. The normal course of the hydrolysis is the replacement of each halogen atom by an hydroxyl group (*cf.* p. 34). When the compound contains only one halogen atom attached to any one carbon atom, the product is the corresponding hydroxyl compound—a simple or a polyhydroxyl alcohol (p. 59). But when the halogen derivative contains groups of the types: $-CHX_2$, $-CX_2-$, or $-CX_3$, which would give two or three hydroxyl groups united to the same carbon atom, such products being unstable pass at once into stable forms by splitting off water. Thus from $R.CHX_2$ we get an aldehyde, $R.CHO$ (p. 77); from $R.CX_2.R$, a ketone, $R.CO.R$ (p. 89); and from $R.CX_3$, an acid, $R.CO.OH$ (pp. 98, 99, 103).

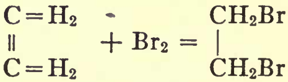
CHAPTER IV

UNSATURATED HYDROCARBONS

There are two other series of hydrocarbons, which are so related to the paraffins and to each other that a brief consideration of them may properly be given at this point. In each of these series the members show a constant difference of 14 between their molecular weights and consequently, like the paraffins, a formula difference of CH_2. The percentage of hydrogen is, however, less than in the corresponding paraffins which have the same number of carbon atoms, and less in one series than in the other; the difference expressed in their formulas being that of two atoms of hydrogen in each case. The general formulas for these series are, therefore, C_nH_{2n} and C_nH_{2n-2}. In neither of these series is a compound known which contains only one carbon atom. Such compounds would have the formulas, CH_2 and CH, with carbon acting as a divalent element in one, and as a monovalent element in the other. Both series begin with compounds containing two atoms of carbon: C_2H_4, ethylene, and C_2H_2, acetylene; and the series are called from these first members the *ethylene series* and the *acetylene series*, respectively. It is characteristic of the hydrocarbons of both series that they absorb chlorine and bromine, uniting additively with these halogens to form compounds of the types, $C_nH_{2n}Cl_2$ and $C_nH_{2n-2}Cl_4$, substances which can be formed from the corresponding paraffins by substitution, and which can be converted into these paraffins by nascent hydrogen.

On account of this behavior, the hydrocarbons of these series are termed "*unsaturated*" *hydrocarbons*. In making a graphic formula for ethylene, with the assumption that carbon is here, as usually, tetravalent, we must write  $\begin{array}{c}H-C-H\\ \Vert\\ H-C-H\end{array}$, with a double bond between the carbon atoms. Any other formula would require an unusual valency for carbon. With a very few exceptions, such as CO, carbon appears everywhere to be tetravalent, and there seems to be no good reason for believing that its valency in these compounds is an exception to the general rule. On the contrary, the facts that a hydrocarbon of the formula CH_2 cannot be obtained, and that only one compound of the type $CH_2.CHCl$ can be made, are in favor of the tetravalency of carbon in ethylene and the symmetrical formula, $CH_2{:}CH_2$. Again, if carbon was here trivalent, we might expect to find hydrocarbons containing a single trivalent atom, such as $C{\equiv}H_3.C{=}H_2$, which must then of necessity have an odd number of hydrogen atoms. But no such compounds are known, and on the contrary, *all formulas of known hydrocarbons contain an even number of hydrogen atoms.*

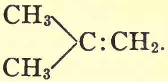
The symmetrical formula  $\begin{array}{c}CH_2\\ \Vert\\ CH_2\end{array}$ with the double bond is, therefore, usually accepted for ethylene and similar formulas for its homologues; but it must be remarked that the double bond, instead of denoting a firmer union, indicates a weak point in the molecule. It readily gives place to a single linkage, as in the reaction with bromine:

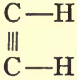


$$\begin{array}{l}C=H_2\\ \Vert\\ C=H_2\end{array} + Br_2 = \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}$$

and in oxidation processes is the point where the compound breaks down most easily with the production of substances which have a smaller number of carbon atoms in the molecule.

The members of the ethylene series have only one double bond, as for instance, propylene $CH_3.CH:CH_2$, and the isomeric butylenes,

$CH_3.CH_2.CH:CH_2$, $CH_3.CH:CH.CH_3$, and  $\begin{matrix}CH_3\\ CH_3\end{matrix}\!>C:CH_2$.

In acetylene, C_2H_2, a triple bond between the two carbon atoms is indicated for reasons of the same kind as those given for the double bond in the ethylene series, and this triple bond is weaker than the double bond. *Acetylene* is  $\begin{matrix}C-H\\ \vert\vert\vert\\ C-H\end{matrix}$; *allylene*, or *methylacetylene*, the next number of the series, is $CH_3.C\vdots CH$.

The acetylene series contains two groups—the acetylene group proper, in which there is one triple bond; and the *di-olefines*, which are isomeric with the acetylenes, but have two double bonds instead of one triple bond. Thus, *allene*, $CH_2:C:CH_2$, a di-olefine, is isomeric with allylene given above.

The name *olefine* (oil-forming) was given to ethylene because this gas forms an oil by its additive reaction with chlorine. From this the general name of olefines was given to the members of the ethylene series; and the isomers of the acetylenes, which have two double bonds, are known, by analogy, as di-olefines. A more systematic mode of naming these unsaturated compounds is to use the ending **ene** to indicate the ethylene state with one double bond, **diëne** for the di-olefines with two double bonds, and **ine** for compounds, like acetylene, which have one triple bond. These endings are added to the stem of the name for the paraffin with the same number of carbon atoms. Thus, corresponding to *ethane*, C_2H_6, we should have *ethene*, C_2H_4, and *ethine*, C_2H_2; and in the next group, *propane*, C_3H_8; *propene*, $CH_3.CH:CH_2$; *propadiëne*, $CH_2:C:CH_2$; and *propine*, $CH_3.C\vdots CH$.

UNSATURATED HYDROCARBONS

Ethylene Series C_nH_{2n}	Boiling Point	Acetylene Series C_nH_{2n-2}	Boiling Point
Ethylene, $CH_2:CH_2$........	−103°	Acetylene, $CH\vdots CH$......	−83.8°
Propylene, $CH_3.CH:CH_2$....	−48	Allylene, $CH_3.C\vdots CH$....	.....
Butylene, $C_2H_5.CH:CH_2$....	−5	Dimethyl-	
Butylene, $CH_3.CH:CH.CH_3$	1	Acetylene, $CH_3.C\vdots C.CH_3$.	27–28
Butylene, $(CH_3)_2C:CH_2$....	−6	Ethyl-	
Amylene, $C_2H_5CH:CH.CH_3$	36	Acetylene, $C_2H_5.C\vdots CH$..	18
Amylene, $(CH_3)_2CH.CH:CH_2$	20–21	Methyl-Ethyl-	
Amylene, $(CH_3)(C_2H_5)C:CH_2$	31–32	Acetylene $C_2H_5.C\vdots C.CH_3$	55–56
Amylene, $(CH_3)_2C:CH.CH_3$	36–38	Propyl–	
Hexylene, $C_4H_9.CH:CH_2$	68–70	Acetylene (n), $C_3H_7.C\vdots CH$	48–49
Heptylene, $C_5H_{11}.CH:CH_2$	96–99	Iso-Propyl–	
Octylene, $C_6H_{13}.CH:CH_2$	122–123	Acetylene, $(CH_3)_2CH.C\vdots H$	28–29

$C_n H_{2n-4}$ *Series*

$(CH_3)_2CH.CH_2.CH:CH.C(CH_3):C:CH_2$ Boils 172°–176

$C_n H_{2n-6}$ *Series*

Diacetylene	$CH:C.C:CH$	....
Dipropargyl	$CH:C.CH_2.CH_2.C\vdots CH$	85°

Formation.—Various unsaturated hydrocarbons, chiefly ethylene and acetylene are formed in small amounts in the destructive distillation of organic substances and are consequently found in coal gas. They are formed, theoretically, by the removal of pairs of hydrogen atoms from the paraffins:

$$C_2H_6 - 2H \rightarrow C_2H_4 - 2H \rightarrow C_2H_2 - 2H \rightarrow 2C$$

These changes probably occur in gas retorts, and account for the large percentage of hydrogen (up to 50 per cent.) and the small amounts of saturated hydrocarbons found in coal gas, as well as for the deposits of carbon in the compact form of "gas carbon," in the outlet of the retorts.

The preparation of the ethylene hydrocarbons may be effected:

1. By removal of the halogen from alkyl dihalides by means of a metal acting on an alcoholic solution:

$$CH_2Br.CH_2Br + Zn = CH_2{:}CH_2 + ZnBr_2$$

2. By heating an alkyl monohalide with potassium hydroxide in an alcoholic solution:

$$CH_3.CH_2Br + KOH = CH_2{:}CH_2 + KBr + H_2O$$

(The use of an alcoholic solution of the hydroxide is important, since in aqueous solution the presence of the water causes the replacement of the halogen by hydroxyl: $CH_3.CH_2Br + KOH = CH_3.CH_2OH + KBr$.)

3. From alkyl hydroxides (alcohols) by withdrawing the elements of water:

$$CH_3.CH_2OH - H_2O = CH_2{:}CH_2$$

This may be effected by anhydrous zinc chloride, phosphorus pentoxide, syrupy phosphoric acid, or by concentrated sulphuric acid. In the reaction with sulphuric acid intermediate products are formed.

Ethylene or **ethene,** C_2H_4. Ethylene is usually prepared by heating alcohol with about six times its weight of concentrated sulphuric acid to about 170°. (Syrupy phosphoric acid may be advantageously substituted for sulphuric acid.) It is a colorless gas of peculiar, somewhat sweetish odor, which burns with a luminous flame. It is one of the most important of the illuminating constituents of coal gas. It decomposes at about 400° with the production of hydrocarbons of the paraffin, acetylene, and benzene series. By the electric spark discharge it is decomposed first into acetylene and hydrogen, and then into carbon and hydrogen. *Reactions.* 1. Ethylene combines directly with the halogens, most energetically with chlorine and least readily with iodine.

$$\underset{\text{Ethylene}}{CH_2{:}CH_2} + Br_2 = \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br}$$

In chlorine it burns with a smoky flame. 2. A mixture of ethylene and hydrogen is synthesized to ethane at about 300° by finely divided nickel as contact agent. 3. Not only does ethylene unite with the halogens, but it also combines additively with hydrogen bromide and iodide forming ethyl halides:

$$CH_2{:}CH_2 + HBr = \underset{\text{Ethyl bromide}}{CH_3.CH_2Br}$$

The reaction is more energetic with hydrogen iodide than with hydrogen bromide, and hydrogen chloride does not react at all. 4. With hypochlorous acid, $HClO$ (in aqueous solution), ethylene combines directly, forming monochlor-alcohol or ethylene *chlorhydrin*:

$$CH_2{:}CH_2 + HOCl = \underset{\substack{\text{Ethylene}\\\text{chlorhydrin}}}{CH_2Cl.CH_2OH}$$

We shall find later that the chlorhydrins form important steps in certain syntheses. 5. A similar reaction occurs between ethylene and sulphuric acid, ethylene being slowly absorbed by the concentrated acid with the formation of ethyl sulphuric acid (*cf.* p. 120):

$$C_2H_4 + H_2SO_4 = \underset{\substack{\text{Ethyl sulphuric}\\\text{acid}}}{(C_2H_5)HSO_4}$$

6. Organic acids also react slowly with the formation of analogous compounds. 7. Oxidizing agents act on ethylene very readily.

This description of the properties and reactions of ethylene applies in a general way to the other members of the series. The first of these "alkenes" are gases, then come a number of hydrocarbons which are liquids, insoluble in water but soluble in alcohol and in ether. The higher members of the series are crystalline solids.

Acetylene, C_2H_2, is formed in small amounts when an electric arc is produced between carbon poles in an atmosphere of hydrogen. This gives another method for the synthesis of organic compounds from the elements (*cf.* p. 26), since acetylene is readily converted into other hydrocarbons from which the greatest variety of derivatives can be made. Acetylene is also formed as one of the products of the incomplete combustion of other hydrocarbons, which occurs when the supply of oxygen is limited. The gases that come from a Bunsen burner, when the flame has "struck back" and is burning at the bottom of the tube, contain acetylene, though in small amounts (less than 1 per cent. of the gases). Methods of formation similar to those given for ethylene may be employed for acetylene and its homologues:

$$CH_2Br.CH_2Br + 2KOH = CH{:}CH + 2KBr + 2H_2O$$

$$CHBr_2.CHBr_2 + 2Zn = CH{:}CH + 2ZnBr_2$$

But since the manufacture of calcium carbide has become commercial, the common mode of preparation is through the reaction of this substance with water:

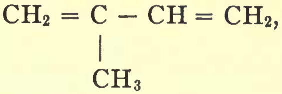
$$C_2Ca + 2H_2O = C_2H_2 + Ca(OH)_2$$

This may be regarded as another elementary synthesis; for while calcium carbide is actually made from lime, CaO, and coke (C) in the electric furnace, the calcium oxide can be made from the metal calcium and oxygen.

Properties.—Acetylene is a gas of garlic-like odor. When made from commercial carbide it is contaminated with small amounts of ill-smelling gases, such as phosphine, and hence the odor of the ordinary gas is not that of pure acetylene. It burns with an exceedingly bright flame, which gives much smoke unless the gas is burnt in special burners whose tips deliver about one-half of a cubic foot per hour. It can be liquefied quite readily (by a pressure of 83 atmospheres at 18°), but cannot be safely used in the liquid state or even under a pressure of more than two atmospheres, since under these circumstances it is liable to explode violently with the production of hydrogen and finely divided carbon. This instability indicates that acetylene possesses an unusual amount of stored or potential energy. It is in fact an endothermic compound which absorbs 58.7 calories in its formation (*cf.* p. 53). It is slightly soluble in a number of liquids, and dissolves quite freely in acetone (24 vols. of acetylene in 1 vol. acetone under atmospheric pressure) forming a solution in which, even under considerable pressure, it is not explosive. Such solutions are used as a convenient source of the gas for lighting purposes. Otherwise it is generated as it is used, as in bicycle and automobile lamps, or is stored in small gas holders under slight pressure for household lighting. Mixtures of acetylene and air are explosive through a remarkably wide range of proportions: beginning with only 3.5 per cent. of acetylene by volume and ending with 82 per cent. For comparison it may be stated that the range for hydrogen is from 5 to 72 per cent.; for carbon monoxide, 13 to 75 per cent.; for water gas, 9 to 55 per cent.; coal gas, 6 to 29 per cent.; and for methane, 5 to 13 per cent.

When acetylene is passed through a tube heated to dull redness, it "polymerizes" by the union of its molecules, and forms, among other compounds, benzene, C_6H_6, which is the most important hydrocarbon of the aromatic series.

Acetylene and its homologues unite additively with the halogens, with hydrogen (in the presence of platinum black), and with the halogen acids. They are readily oxidized by oxidizing agents in solution (*e.g.*, $KMnO_4$), showing reactions which are analogous to those of ethylene and its homologues. All compounds of the acetylene series that have a triple bond between two carbon atoms at the end of the chain give a distinctive reaction with ammoniacal solutions of silver or cuprous chloride. This consists, in the case of acetylene, in the precipitation of carbides of these metals, C_2Ag_2 and C_2Cu_2, compounds in which the metal has taken the place of the hydrogen of the acetylene, and which are consequently called "acetylides." When dry, these compounds explode when struck or when heated to 100°. With hydrochloric acid, copper acetylide gives acetylene.

Of the di-olefines, *isoprene*, C_5H_8 or  $$\underset{\displaystyle CH_3}{CH_2 = \overset{}{C}} - CH = CH_2,$$ is of special interest, because of the recent discovery that it can be converted into India rubber. Isoprene is a liquid, boiling at 37°. It is one of the products of the destructive distillation of rubber, and is formed when turpentine is passed through a red hot tube. Its conversion into India rubber is the effect of a polymerization, or union of several molecules to a more complex one of the same composition.

Hydrocarbons of the Formulas, C_nH_{2n-4}, C_nH_{2n-6}. The compound of the lowest molecular weight corresponding to the general formula C_nH_{2n-4} which is theoretically possible would be C_4H_4, and this might have the structure $CH_2{:}C{:}C{:}CH_2$ or $CH{\vdots}C.CH{:}CH_2$. The higher members of the series would have similar constitutions with either three double linkages or one double and one triple linkage, on the assumption that the carbon atoms of each compound form open chains. One such hydrocarbon with three double bonds has been obtained by the withdrawal of the elements of water from the natural di-olefine alcohol *geraniol* (p. 87) and has the formula $(CH_3)_2CH.CH_2.CH{:}CH.$-$C(CH_3){:}C{:}CH_2 = C_{10}H_{16}$. This hydrocarbon unites additively with six atoms of hydrogen or of bromine with the formation of saturated compounds, $C_{10}H_{22}$ and $C_{10}H_{16}Br_6$. Other open-chain hydrocarbons of this series are practically unknown.

A large number of hydrocarbons known as terpenes which occur in the vegetable kingdom have the same composition, but are proved to be *cyclic* compounds in which the carbon atoms form closed chains or rings (p. 257).

In the series of open-chain hydrocarbons of the formula C_nH_{2n-6} the simplest is *diacetylene*, $CH{\vdots}C.C{\vdots}CH$, which can be made from propiolic acid (p. 111), $CH{\vdots}C.CO.OH$, through diacetylene-dicarboxylic acid, $CO.OH.C{\vdots}C.C{\vdots}C.CO.OH$. *Dipropargyl*, $CH{\vdots}C.CH_2.CH_2.C{\vdots}CH$, $= C_6H_6$, can be made from the tetrabromide of diallyl, $CH_2Br.CHBr.CH_2.CH_2.CHBr.CH_2Br$, by splitting off hydrogen bromide by means of alcoholic potassium hydroxide. This mode of formation and its acetylene-like properties establish its constitution as given in the formula. This hydrocarbon is of especial interest because it is isomeric with benzene, the most important of the cyclic hydrocarbons. It is a liquid boiling at about 85°, having a specific gravity of 0.81. It slowly changes to a shellac-like mass, which decrepitates when heated.

No open-chain hydrocarbons with more than three double or two triple linkages are definitely known.

Heats of Combustion and of Formation

Knowledge of the amount of heat which is produced by a given weight of a substance used for fuel, such as the different kinds of coal, petroleum, water gas, and coal gas, is, of course, of practical importance.

Since the gaseous and liquid fuels are composed largely of hydrocarbons, the heating value of individual hydrocarbons as well as that of the hydrogen and carbon monoxide, which are usually present in fuel gases, is also important. To the chemist, the heating value of these compounds is of special interest, because by its aid he can find the "heat of formation" of the compounds, which gives information in regard to their stability and, to some extent, to their reactivity with other compounds.

It is assumed that the student is familiar with the units of heat measurement, the small or gram-calorie and the large or 1000 gram-calorie. The latter is used in the following discussion.

By the *heat of formation* is understood the number of heat units which are given out or absorbed in the formation of a gram-molecular weight of the compound from its elements. This is readily determined when the compound can be made by the direct union of its elements, as in the case of water, carbon dioxide, etc., but in other cases it must be arrived at by an indirect method. The method depends on the fact that the same amount of energy is required to separate the elements of a compound as is set free in their union. The product of a reaction which is attended with the production of heat—an exothermic reaction—has less potential energy and hence greater stability in proportion to the amount of heat evolved, and, similarly, the instability of a compound is greater the greater the heat which is absorbed in its formation, and the greater the potential energy which it therefore possesses.

Now, the heat of formation of a compound must be equal to the heat which its elementary constituents would produce on oxidation, less the heat of combustion of the compound. For the amount of energy which is necessary to break the union of the elements will fail to appear as heat when the compound is burned. If, therefore, we know the heats of combustion of the constituent elements and of the compound, the heat of formation is their difference. In the table are given the heats of combustion and of formation of a number of hydrocarbons which we have been studying, as well as those of their constituents, carbon and hydrogen. For use in determining the heats of formation both are given for the gram-molecular weight of the compounds, but in the first column, the heats of combustion for one gram are also given as is usual in the practical evaluation of fuel substances.

	Heat of Combustion			Heat of Formation
	One Gram	One Gram-molecule		One Gram-molecule
Hydrogen	34.2	69.0		
Carbon	7.83	94.0		
Paraffins			Difference	
CH_4	13.3	213.5		18.5
			158.8	
C_2H_6	12.4	372.3		22.7
			156.1	
C_3H_8	12.0	528.4		29.6
			158.8	

Paraffins	Heat of Combustion One Gram	Heat of Combustion One Gram-molecule	Difference	Heat of Formation One Gram-molecule
C_4H_{10}	11.8	687.2		33.8
			159.9	
C_5H_{12}	11.7	847.1		36.9
Unsaturated Hydrocarbons				
C_2H_4		341.1		−15.1
			158.2	
C_3H_6		499.3		−10.3
			151.3	
C_4H_8		650.6		1.4
C_2H_2		315.7		−58.7
			157.9	
C_3H_4		473.6		−53.6

It will be noticed that while the heat of combustion for the same weight of different hydrocarbons decreases as the molecular weights increase, the figures for the gram-molecular quantities show a fairly constant increase of about 158 calories for each addition of CH_2.

We may, therefore, reckon the gram-molecular heat of combustion for any hydrocarbon if we know what it is for one member of an homologous series. For instance, knowing the heat of combustion of methane (213.5) we may find that of $C_{11}H_{24}$ as follows: $C_{11}H_{24} = CH_4 + 10CH_2$; hence, $213.5 + (10 \times 158) = 1793.5$ which is the gram-molecular heat of combustion of $C_{11}H_{24}$. As this is the heat from 156.192 grams (gram-molecular weight) of undecane, the heat obtainable from one gram would be $1793.5 \div 156.192 = 11.48$ cal.

To find the heat of formation of a hydrocarbon, the procedure is as follows: Ethane has as its heat of combustion 372.3 cal. The gram-molecule of ethane contains 24 grams of carbon and 3 g-mols. of hydrogen, and the heat which would be developed by burning these amounts of carbon and hydrogen is $7.83 \times 24 = 188$ cal. and $69 \times 3 = 207$, or in all, 395; the heat of formation of ethane is, therefore, $395 - 372.3 = 22.7$ cal. For acetylene $(7.83 \times 24) + (69 \times 1) - 315.7 = - 58.7$ calories. (For further discussion of thermochemistry the student is referred to a Physical Chemistry.

Halogen Derivatives of Unsaturated Hydrocarbons

There are two types of these derivatives which are quite different in their behavior: those in which the halogen is united to an unsaturated carbon atom, one that is linked to another carbon atom by a double or triple bond, as $CH_2{:}CHBr$, or $CI\vdots C.CH_3$; and those where the halogen is joined to a saturated carbon atom, or one linked to another carbon atom by a single bond, as $CH_2{:}CH.CH_2Br$ or $CH\vdots C.CH_2Cl$.

In compounds of this second type, the halogen is readily replaced by hydroxyl, cyanogen, and other groups as in the case of the alykl halides; while with halogen derivatives of the first type these reactions do not take place. 1. Compounds of the first type where the halogen is united to a carbon atom with a double bond may be made by the action of alcoholic potassium hydroxide on dihalogen derivatives of the saturated hydrocarbons:

$$\underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br} + KOH = \underset{\text{Vinyl bromide}}{CH_2{:}CHBr} + KBr + HOH$$

$$\underset{\text{Propylidene chloride}}{CH_3.CH_2.CHCl_2} + KOH = \underset{\text{Chlorpropylene}}{CH_3.CH{:}CHCl} + KCl + H_2O$$

Their formation also takes place by direct addition of the hydrogen halide to hydrocarbons of the acetylene series:

$$CH\vdots CH + HBr = CH_2{:}CHBr$$

But with another molecule of the hydrogen halide this gives an alkyl dihalide:

$$CH_2{:}CHBr + HBr = CH_3.CHBr_2$$

Vinyl chloride, $CH_2:CHCl$, is a gas; the **bromide,** $CH_2:CHBr$, is a liquid of ethereal odor, boiling at 16°; **vinyl iodide,** $CH_2:CHI$, is also a liquid, which boils at 56°. The chloride and bromide change to white solids when exposed to sunlight, being "polymerized" (several molecules combined to one). Reagents such as potassium hydroxide, sodium ethylate, or sodium acetate do not give substitution products, but cause the compounds to break down into acetylene and the halogen acid. The hydrocarbon radical, $CH_2:CH -$, in these compounds is called *vinyl* and appears in other derivatives.

Bromacetylene, $CBr\vdots CH$, is made from bromethylene by means of alcoholic potash:

$$CHBr:CHBr - HBr = CBr\vdots CH$$

Bromacetylene is a gas which condenses to a liquid in a freezing mixture, and polymerizes to a solid in the light. **Iodoacetylene.** $CI\vdots CH$, is a crystalline solid, of disagreeable odor, and apparently very poisonous.

2. Compounds of the second type in which the halogen is united to a saturated carbon atom have the characteristics both of unsaturated hydrocarbons and of alkyl halides. The best known halogen compounds of this class are obtained from allyl alcohol, $CH_2:CH.CH_2OH$, and from propargyl alcohol, $CH\vdots C.$-CH_2OH (*cf.* p. 69), by the action of phosphorus halides. **Allyl chloride,** $CH_2:CH.CH_2Cl$, and the corresponding allyl bromide and iodide are liquids boiling at 46°, 70°, and 103°, respectively. They have an odor resembling that of mustard. The **propargyl halides** are also liquids and give metallic derivatives such as are characteristic of the acetylene grouping.

The reactions on page 54 show how various saturated and unsaturated halogen derivatives may be made from each other. The splitting off of halogen and hydrogen by alcoholic alkali, and the addition of halogens or hydrogen halides to the resulting unsaturated compounds give means for making halogen derivatives of almost any type. From ethyl bromide, for instance, all possible halogen derivatives of ethane, ethylene, and acetylene, as well as ethylene and acetylene themselves, may be obtained:

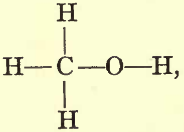
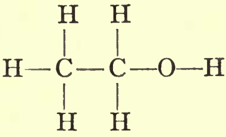
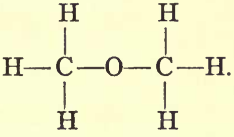
$$\begin{aligned}
&CH_3.CH_2Br \xrightarrow{-\ HBr} CH_2{:}CH_2 \xrightarrow{+\ Br_2} CH_2Br.CH_2Br \xrightarrow{-\ HBr} \\
&CHBr{:}CH_2 \xrightarrow{+\ Br_2} CHBr_2.CH_2Br \xrightarrow{-\ HBr} CBr_2{:}CH_2 \xrightarrow{+\ Br_2} \\
&CBr_3.CH_2Br \xrightarrow{-\ HBr} CBr_2{:}CHBr \xrightarrow{+\ Br_2} CBr_3.CHBr_2 \xrightarrow{-\ HBr} \\
&CBr_2.CBr_2 \xrightarrow{+\ Br_2} CBr_3.CBr_3.
\end{aligned}$$

CHAPTER V

THE ALCOHOLS—HYDROXYL DERIVATIVES OF THE ALIPHATIC HYDROCARBONS

Among the many organic compounds which contain hydrogen and oxygen, there are several important groups of substances, the members of each of which show general characteristics, and a similarity in behavior such as marks the different series of hydrocarbons which we have studied; and we shall find here, as in the case of the hydrocarbons, that the members of each group form an homologous series, with a general formula.

One of these groups is that of the *alcohols*, of which the well-known "wood alcohol" and ordinary alcohol are the most important members. These two alcohols will now be studied as typical of the group.

Formula of an Alcohol.—Neither of the commercial alcohols is quite pure, or free from water, but the anhydrous pure alcohols can be obtained from them. Pure wood alcohol is a liquid boiling at 66°. Its percentage composition is C = 37.46, H = 12.59, O = 49.95, and its vapor density is 1.106 (air = 1); hence the molecular formula is CH_4O. From the corresponding data for ordinary alcohol, its formula is found to be C_2H_6O. It is impossible, with tetravalent carbon, to write graphic formulas for these alcohols in which the oxygen is united by both of its valencies with a carbon atom. For CH_4O, only one graphic formula can be written, namely,  $\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$, in which the oxygen atom and one hydrogen atom form a hydroxyl group. For C_2H_6O there are two arrangements which account for the valencies,  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$ and  $H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H$. The first, containing an hydroxyl group, would seem the more probable, because of the similarities in the properties of the two alcohols. The matter can, however, be settled in the following manner: Anhydrous alcohol acts on sodium with the evolution of hydrogen and the formation of a compound whose formula is found to be C_2H_5NaO, in which sodium has replaced one atom of hydrogen in the alcohol molecule. As no other compound containing a larger proportion of sodium can in any way be produced from alcohol and sodium, we conclude that one of the six hydrogen atoms in alcohol stands in a different relation from the other five. This can only be accounted for by the first of the two possible formulas, and decides in its favor as the one which represents the constitution of alcohol. This conclusion is confirmed by the result of the reaction which alcohol undergoes with phosphorus chlorides:

$$C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$
$$3C_2H_6O + PCl_3 = 3C_2H_5Cl + H_3PO_3$$

The formula of the chlorine substitution product is determined in the usual way and shows that one atom of chlorine has taken the place of the oxygen and one hydrogen atom; and this clearly indicates that these two atoms were acting as the monovalent group hydroxyl. Wood alcohol gives exactly similar reactions, and therefore we consider these alcohols to be *alkyl hydroxides*. They can, in fact, be made by a reaction which this view of their character suggests, namely, by the reaction of the alkyl halides with potassium hydroxide in aqueous solution, or with silver hydroxide (p. 34):

$$CH_3I + KOH = CH_3OH + KI$$
$$C_2H_5Br + KOH = C_2H_5OH + KBr$$

(Compare these reactions with those which occur between the alkyl halides and potassium hydroxide in alcoholic solutions (p. 46).

Finally, all the facts that we know about these compounds agree with this conclusion that they are hydroxyl derivatives of the hydrocarbons, and all other such compounds are grouped with them as alcohols. The general formula of an alcohol is, therefore, $C_nH_{2n+1}OH$.

Methyl alcohol, CH_3OH, commercially known as "wood alcohol," is one of the products of the destructive distillation of wood. The process is carried out in iron retorts, and yields first a watery distillate called "pyroligneous acid," and then gases (methane, ethane, ethylene, carbon dioxide, etc.) and tar, leaving a residue of charcoal in the retort. The pyroligneous acid contains methyl alcohol, acetic acid, and acetone in aqueous solution, together with smaller amounts of many other substances. The yield of the various products depends on the kind of wood used, and also on the manner of heating. Quick heating to a high temperature gives the greatest amount of gas, and prolonged heating at lower temperatures increases the proportion of pyroligneous acid and tar. From birch, beech, and oak about 30 per cent. of the weight of the wood is obtained in the watery distillate. Of this about 10 per cent. is acetic acid, 1 per cent. methyl alcohol, and 0.1 per cent. acetone. On distilling the pyroligneous acid, the alcohol and acetone, whose boiling points are not very far apart and much lower than that of acetic acid, are separated from the latter, the separation being often made more complete by passing the vapors through milk of lime which fixes the acid as calcium acetate.

A second distillation from quicklime gives an alcohol of 99 per cent., which still contains some acetone. This is not objectionable for most of the commercial uses of the alcohol. The alcohol may be obtained in a state of purity as follows. By adding anhydrous calcium chloride to the impure alcohol a crystalline compound is formed in which the alcohol plays the part of "water of crystallization." When this is heated to 100°, the volatile impurities are driven off, and then, on adding water, the pure alcohol is distilled. Absolutely pure methyl alcohol may be obtained from the methyl ester of oxalic acid (p. 179), by boiling it with water. The disagreeable odor of most commercial wood alcohol is due to impurities; the pure alcohol has only a slight odor resembling that of ethyl alcohol.

Ethyl alcohol, $CH_3.CH_2OH$, commercially known as grain alcohol and ordinarily as "alcohol," is the chief product of the ordinary fermentation of certain sugars. This fermentation is brought about in the technical manufacture of alcohol by the addition of yeast, and it occurs naturally in the sweet juices of fruits, such as grapes, apples, etc., and in sugar solutions which are exposed to the air, because of the almost universal presence of yeast spores in the atmosphere. Much alcohol is produced from molasses (p. 213); and much has its source in the starch of various grains such as maize, rye, etc. in the United States, while in Europe the starch of potatoes is used. The starch is first converted into fermentable sugars, and yeast is then added to their solutions. Alcohol has also been made to some extent from saw-dust (cellulose) from which a fermentable sugar can also be obtained. The conversion of starch and cellulose into sugars and the fermentation of the latter are discussed in a later chapter. It is sufficient here to note that the fermentation requires a rather dilute solution of the sugars, and that the immediate product contains not more than about 12 per cent. of alcohol in aqueous solution, and in the case of cider, wines and beer, often much less. No alcoholic solution containing more than about 14 per cent. of alcohol can be obtained by fermentation alone, since alcohol of this strength inhibits the fermentation. When the purpose of the fermentation is to produce such beverages as those just named, no distillation is necessary; but for making liquors such as whiskey, brandy, rum, etc., or for the preparation of commercial alcohol, the dilute solution is distilled with the production of stronger alcoholic solutions.

The wines, beers, etc., are, therefore, dilute alcoholic solutions which contain various amounts of substances extracted from the materials out of which they are made, and which give them their "body," flavor, and color; while the distilled liquors are, of course, freed from all non-volatile substances, and are solutions containing 40–60 per cent. of alcohol, with minute amounts of volatile matters which impart an aroma and taste depending on the original material employed. In some instances, as in gin, a peculiar taste and odor are imparted by the addition of aromatic substances before the distillation. The distillates are all colorless, and the color which many liquors have is given them by standing in casks of charred wood as in the case of some whiskeys, or by addition of caramel, etc. Brandies are made by distilling wine or the fermented juices of various fruits, such as apples, peaches, etc.; whiskey is made from Indian corn or rye; rum, from molasses.

For the preparation of commercial alcohol, a more efficient apparatus is employed for the separation of the alcohol and water by distillation than that used in making the distilled liquors, with the result that there is only about 4 per cent. of water in the distillate. The rectification cannot go farther than this, since 96 per cent. of alcohol and 4 per cent. of water form a mixture which has a constant boiling point under ordinary pressure. Commercial alcohol is usually from 93–95 per cent.

In order to get *anhydrous alcohol* it is necessary to use some dehydrating agent. By allowing 95 per cent. alcohol to stand in contact with quicklime for some time and then distilling, most of the water is retained by the lime in the form of calcium hydroxide, and the distillate does not contain more than 0.5 per cent.

This is often called "absolute alcohol," though the name properly belongs only to a perfectly water-free product. The last amounts of water can be removed by means of anhydrous copper sulphate or by sodium or calcium. It is, however, very difficult to keep alcohol free from water, as it is very hygroscopic and takes up water from ordinary air. Traces of water are detected by the blue color which white anhydrous copper sulphate assumes when shaken with the alcohol, or by the yellow color imparted to the alcohol when barium oxide is added (barium oxide dissolves only in anhydrous alcohol).

Properties.—Methyl alcohol boils at 66°, ethyl alcohol at 78°. Both mix with water in all proportions and the mixing is attended with a rise in temperature and a contraction in volume. Both are solvents of wide application and burn with a hot, almost colorless flame. Both are intoxicating, and are poisonous, at least when pure or but slightly diluted. The poisonous character of methyl alcohol is much more pronounced than that of ethyl alcohol, and prolonged exposure to its vapor is attended with serious consequences, and has been followed by loss of sight. On this account ethyl alcohol is preferable as a solvent and has largely displaced wood alcohol in making shellac varnish since the introduction of the tax-free "denatured alcohol," which is ordinary alcohol rendered unfit for internal use by the addition of wood alcohol, benzene, and various other substances. "Proof spirit" contains 50 per cent. of alcohol by volume. The amount of alcohol in pure aqueous solutions is found by determining the density and using "alcohol tables" that give the percentages of alcohol corresponding to the densities.

Reactions.—Both alcohols are neutral substances. They undergo the following reactions. 1. The hydrogen of the hydroxyl group is replaced by sodium, which acts on the alcohols much more moderately than on water. The *alcoholates* thus formed are solid substances which crystallize with "alcohol of crystallization" (*e.g.*, $C_2H_5ONa.2C_2H_5OH$), which can be removed by heating. The alcoholates of sodium and potassium are decomposed by water·

$$C_2H_5ONa + HOH \rightleftarrows C_2H_5OH + NaOH$$

The reaction is reversible to some extent, and hence a solution of sodium hydroxide in alcohol, such as is employed in some organic reactions (*cf.* p. 46), contains some alcoholate. Since the alcohols react only with the most positive metals, and no alcoholates of such metals as zinc or silver can be made, these compounds cannot be regarded as salts in the proper sense of the term, but rather as mixed alkyl and metal oxides, and the names of sodium *methoxide* and *ethoxide* are therefore preferable to the salt-suggesting term alcoholate.

2. The alcohols show a certain analogy to the inorganic bases by reacting, as these do, with acids with the production of water and compounds in which the hydroxyl group of the alcohol is replaced by acid radicals:

$$C_2H_5OH + HCl \rightleftarrows C_2H_5Cl + H_2O$$
$$CH_3OH + H_2SO_4 \rightleftarrows CH_3.H.SO_4 + H_2O$$

Similar reactions take place between the alcohols and organic acids, and, since they are reversible reactions, are in all cases furthered by an excess of the acid or by the presence of some water-withdrawing substance. The compounds formed with acids, while not well-defined salts, show some marked analogies to salts, and are called "ethereal salts" or esters (*cf.* p. 119).

3. The characteristic action of the phosphorus halides on alcohols, resulting in the replacement of the hydroxyl group by the halogen, has been given (p. 32).

4. By means of water-absorbing agents, such as zinc chloride or concentrated sulphuric acid, the elements of water may be withdrawn from alcohols with the production of unsaturated

hydrocarbons or of ethers. Methyl alcohol, however, can yield no unsaturated hydrocarbon, though it gives an ether. When sulphuric acid is used, the alkyl sulphuric acid is first formed (*e.g.*, $C_2H_5.HSO_4$), and then this breaks up at 170° or 180° in the presence of a large excess (5:1) of concentrated acid into sulphuric acid and the alkene:

$$C_2H_5.HSO_4 = C_2H_4 + H_2SO_4$$

Under other conditions (130°–140° and a smaller proportion (1.5:1) of acid), ethers or alkyl oxides are formed (*cf.* p. 70):

$$C_2H_5.HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

similarly:

$$C_2H_5I + C_2H_5OH = (C_2H_5)_2O + HI$$

5. Alcohols are not only readily burned to carbon dioxide and water, but are also easily oxidized in dilute solution to intermediate compounds.[1]

By means of a mixture of dichromate of potassium and dilute sulphuric acid, for instance, ethyl alcohol is oxidized as follows:

$$C_2H_5OH + O \rightarrow C_2H_4O \text{ (aldehyde)}$$

and

$$C_2H_4O + O = C_2H_4O_2 \text{(acetic acid)}$$

The higher homologues of ethyl alcohol give similar reactions, but methyl alcohol is oxidized much more readily than the other alcohols so that the reaction hurries through the aldehyde to the acid and even to the end products, carbon dioxide and water. The vapor of methyl alcohol mixed with air is, however, partially oxidized to the corresponding aldehyde when brought in contact with a heated spiral of platinum wire. These reactions will be discussed in connection with our study of the aldehydes, ketones, and acids.

6. Chlorine acts on alcohols first as an indirect oxidizing agent

---

[1] The oxidizing agents usually employed in organic chemistry are nitric acid, chromic acid ($K_2Cr_2O_7 + H_2SO_4$), potassium permanganate, manganese dioxide and sulphuric acid, and, occasionally, chlorine or bromine.

with the production of aldehyde, and then replaces hydrogen (*cf.* p. 92).

Isomeric Alcohols.—It is evident from the principles of isomerism which we have studied, that beginning with propane, different hydroxyl derivatives of the hydrocarbons, or different alcohols, of the same molecular weight, are possible. We find here, as in the other cases, that the facts agree with the theory; there are two *propyl alcohols*,

$$CH_3.CH_2.CH_2OH \text{ and } CH_3.CHOH.CH_3;$$

four *butyl alcohols*,

$$CH_3.CH_2.CH_2.CH_2OH,$$

$(CH_3)_2{:}CH.CH_2OH$, $CH_3.CH_2.CHOH.CH_3$, and $(CH_3)_3{:}C.OH$; etc.

The formulas of these alcohols are, of course, arrived at by the consideration of the reactions of the various alcohols and by the manner in which they can be formed; and it will be noticed that the hydroxyl appears in three different groups:

$$-CH_2.OH, =CH.OH, \text{ and } \equiv COH,$$

and that these are all the varieties possible.

Ethyl alcohol and all those which on oxidation first yield aldehydes and then acids containing the same number of carbon atoms as the alcohol, are, in consequence, given formulas with the group $-CH_2OH$. In ethyl alcohol and its higher homologues, this group is united to an alkyl group; in methyl alcohol we assume, by analogy, the presence of the same alcohol group, here united with hydrogen. This difference probably explains the readier oxidation of methyl alcohol. Alcohols which give ketones as the first oxidation product, and then, on further oxidation break down into acids with a smaller number of carbon atoms, are characterized by the group $=CH.OH$; and, finally, those which are converted at once into ketones or acids of a less number of carbon atoms have $\equiv C-OH$ as their characteristic group. The first variety of alcohols, containing $-CH_2.OH$, are called *primary* alcohols; those with $=CH.OH$, united with two alkyl groups, *secondary;* and those with $\equiv C - OH$, with three alkyl groups, *tertiary* alcohols.

Some of the experimental evidence for the assignment of these groups will be given in Chapter VIII. Here we will only state that the primary and secondary alcohols can be formed by reduction (nascent hydrogen) of aldehydes and ketones, respectively.

Methods of Formation.—The principal laboratory methods for forming *primary* alcohols are:

1. Substitution of hydroxyl for a halogen atom or other acid radical in alkyl halides or other esters by the action of hydroxides of the metals or water (for the halides, moist silver oxide, which acts as silver hydroxide, is especially good; *cf.* p. 34).

2. From alkyl amine nitrites (*cf.* p. 131) on heating their aqueous solutions:

$$CH_3(NH_2).HNO_2 = CH_3OH + N_2 + H_2O$$

This reaction is analogous to that of ammonium nitrite when heated.

3. By reduction (with sodium amalgam) of aldehydes and ketones:

$$\underset{\text{Aldehyde}}{CH_3.CHO} + 2H = \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH}$$

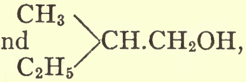
$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2H = \underset{\text{Sec. propyl alcohol}}{CH_3.CHOH.CH_3}$$

4. The Grignard reactions for secondary and tertiary alcohol.

It is not necessary to give here other special reactions for the formations of the three classes of alcohols. Although the alcohols are often spoken of as derivatives of the hydrocarbons, it must not be forgotten that the direct substitution of OH for H in a hydrocarbon is always impossible.

In some discussions, methyl alcohol is called "*carbinol*" and the other primary alcohols are considered as derivatives of it by the replacement of hydrogen by alkyl groups: thus ethyl alcohol is methyl carbinol; secondary butyl alcohol, $CH_3.CH_2.$-$CHOH.CH_3$, is methyl-ethyl-carbinol, etc.

Fusel oil, which is formed in small amounts in the fermentation which produces ethyl alcohol, is composed chiefly of two of the eight possible amyl alcohols: $(CH_3)_2\!:\!CH.CH_2.CH_2OH$, isoamyl alcohol, and



$$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CH.CH_2OH,$$

active amyl alcohol. The former comprises 70–80 per cent. of the fusel oil. The latter has the property of "optical activity" or power of rotating the plane of polarized light (*cf.* p. 169). Normal propyl alcohol and isobutyl alcohol—isopropylcarbinol—are also found in fusel oil. Fusel oil has a characteristic odor, and is poisonous. It distils with the ethyl alcohol, though having a much higher boiling point, and is, therefore, found in crude spirituous liquors, and is responsible in part for their specially disagreeable effects. It is destroyed more or less completely by the "aging" of the liquor.

Fusel oil is used as the source of iso-amyl alcohol and various esters derived from it, such as the acetate ("pear oil"), the isovalerate ("apple oil"), and the nitrite, which find a number of uses Amyl alcohol itself is employed occasionally as a solvent for alkaloids, etc. None of the other alcohols, except methyl and ethyl alcohols, are of any especial practical importance.

NORMAL PRIMARY ALCOHOLS

Name	Formula	Melting Point	Boiling Point		Specific Gravity	
Methyl	CH_3OH	−97.8	66.7°		0.812	At 0° and water at 0°
Ethyl	C_2H_5OH	−117.6	78.4		0.806	
Propyl	C_3H_7OH		97		0.817	
Butyl	C_4H_9OH		117		0.823	
Pentyl (Amyl)	$C_5H_{11}OH$		138		0.829	
Hexyl	$C_6H_{13}OH$		157		0.833	
Heptyl	$C_7H_{15}OH$		176		0.836	
Octyl	$C_8H_{17}OH$		195		0.839	
Nonyl	$C_9H_{19}OH$	−5°	213		0.842	
Decyl	$C_{10}H_{21}OH$	+7	231		0.839	At melting points and water at 0°
Dodecyl	$C_{12}H_{25}OH$	24	143	At 15 mm. pressure.	0.831	
Tetradecyl	$C_{14}H_{29}OH$	38	167		0.824	
Cetyl	$C_{16}H_{33}OH$	50	190		0.818	
Octadecyl	$C_{18}H_{37}OH$	59	211		0.813	
Myricyl	$C_{30}H_{61}OH$	86			0.808	

It will be noticed that the boiling points of these alcohols from ethyl alcohol to decyl alcohol increase with approximate regularity, the average increment being 19°. The boiling points of the last four are not comparable with those of the first ten since they are determined under reduced pressure, but when compared with each other it is seen that the differences are less. A similar decrease in boiling-point differences is observed in the normal paraffins (*cf.* table on page 17) and in other homologous series; and in general, in the higher members of a series, the uniform increase of molecular weight by the addition of CH_2 has less and less effect on the physical properties of the members. The difference between the boiling points of methyl and ethyl alcohols is 12 instead of 19, and the specific gravity of methyl alcohol is greater than that of ethyl alcohol instead of less as it should be to conform with the general changes in specific gravity of the other members. Such irregularities are found in other series, and correspond to the somewhat different chemical behavior often observed in the derivatives of methane as compared with their homologous compounds.

The effect of structure on the boiling point is shown in the following table of the amyl alcohols.

ISOMERIC AMYL ALCOHOLS

	Formula	Boiling Point
Primary	$CH_3.CH_2.CH_2.CH_2.CH_2OH$	138°
	$(CH_3)_2CH.CH_2.CH_2OH$	131
	$CH_3.CH(C_2H_5).CH_2OH$	128
Secondary	$CH_3.CH_2.CH_2.CHOH.CH_3$	119
	$(CH_3)_2CH.CHOH.CH_3$	112.5
	$CH_3.CH_2.CHOH.CH_2.CH_3$	117
Tertiary	$(CH_3)_2COH.CH_2.CH_3$	102

Unsaturated Alcohols

These are hydroxyl compounds in which a double or triple bond between two carbon atoms occurs. A number of alcohols of the general formula $C_nH_{2n-1}OH$ are known, but the first member of the series, **Vinyl alcohol,** CH_2:CHOH, has not been isolated—the reactions which should produce it resulting in the formation of acetaldyde, CH_3.CHO, which is isomeric with it. No simple alcohol, in fact, has a stable existence in which the carbon atom carrying the hydroxyl group is combined with another carbon atom by a double or triple bond. The first and best known of the unsaturated alcohols is **allyl alcohol,** CH_2:CH.CH_2-OH. It occurs in small amounts in crude wood alcohol, and can be made, mixed with other products, from glycerol and oxalic acid. The reaction, which is a somewhat complicated one, will be discussed under formic acid (p. 105). Allyl alcohol is a colorless liquid of very sharp odor, which boils at 96.6°, and mixes with water in all proportions. It gives reactions which are characteristic of a primary alcohol, and also such as belong to an unsaturated hydrocarbon.

Propargyl alcohol, $CH \equiv C.CH_2OH$, is the chief representation of alcohols with a triple bond, and which have the general formula, $C_nH_{2n-3}OH$. It is made by reactions of the kind which have been given for the production of members of the acetylene series and for the introduction of the hydroxyl group. It is a liquid boiling at 115° and gives reactions in accordance to the structure which is attributed to it.

Quite a number of alcohols with two double bonds have beer made in the laboratory and some representations of this grouı have been found in nature. The general formula of these alcohols is the same as that for the alcohols with a triple bond.

CHAPTER VI

THE ETHERS

Ethyl Ether.—Ordinary ether is obtained by the action of sulphuric acid on alcohol, and is often called "sulphuric ether" for that reason, though it contains no sulphur or sulphur-oxygen group. Alcohol and concentrated sulphuric acid are mixed in the proportion of about one to two, so that distillation begins at about 140°, and then alcohol is gradually added so that the boiling point is kept nearly constant. Some sulphur dioxide from the reduction of sulphuric acid, and other products from alcohol besides ether are formed at the same time. The ether formation, which, theoretically, should continue indefinitely, comes to an end when alcohol to the amount of about four times the weight of the sulphuric acid has been used. It will be recalled that a mixture of concentrated sulphuric acid and alcohol is used for the preparation of ethylene (p. 46). The chief product is seen to depend on the proportions of acid and alcohol and the temperature at which the reaction is carried on. This is an illustration of the greater flexibility of organic reactions as compared with the usual inorganic reactions.

The distillate contains water, alcohol, and some sulphur dioxide, mixed with the ether. The addition of sodium carbonate neutralizes and fixes the sulphurous acid, and renders the ether less soluble. The ether forms a layer on top of the solution, and, after separation from the aqueous solution, most of the water and some of the alcohol which is still mixed with it is absorbed by calcium chloride or quicklime, and the ether is distilled. It still contains small amounts of water and alcohol which may be removed by shaking it with shavings of bright sodium, and again distilling.

Properties.—Ether is a colorless, very thin liquid of the well-known characteristic odor. It is very volatile, giving a vapor which is two and a half times heavier than air; boils at 34.6° and has a specific gravity of 0.718 at 15.6°. It dissolves in about eleven times its volume of water at 25°, and in turn dissolves about 2 per cent. of its volume of water. It and its vapor are very easily inflammable and all operations with it must be conducted with great care to avoid its ignition. Chemically, it is a neutral substance and rather inert. Unlike alcohol, it is not acted on by sodium or potassium, nor by phosphorus chlorides in the cold. When heated with phosphorus pentachloride, ethyl chloride is formed.

Formula.—The molecular formula of ether derived from its analysis and vapor density is $C_4H_{10}O$. The formation of ethylene from alcohol was explained by the abstraction of the elements of one molecule of water from one molecule of alcohol. The ether reaction goes on at a lower temperature, and is hence presumably less drastic. The withdrawal of a molecule of water would presumably take place more readily from two molecules of alcohol than from one, and this would give us the formula of ether:

$$2C_2H_5OH - H_2O = C_4H_{10}O$$

Knowing that alcohol is the hydroxide of ethyl, the probable structure of ether is, therefore, $(C_2H_5)_2O$, or ethyl oxide. That it does not contain a hydroxyl group is shown by the failure of sodium to act on it.

The reaction is not, however, quite as simple as indicated by the above equation. Ethyl sulphuric acid is first formed and then reacts with a second molecule of alcohol:

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$

$$C_2H_5.HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

The constitution given to the ether molecule is confirmed by the other methods of its formation and by all of its chemical behavior. Thus, ether is formed when ethyl bromide or iodide reacts with certain oxides. The iodide and dry silver oxide react at once with evolution of heat:

$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI$$

A similar reaction with sodium oxide takes place at 180°, and ether is formed even when the iodide is sufficiently heated with a small amount of water. The temperature required for these last two reactions makes it necessary to carry them out in sealed tubes. Attention has been called to the fact that the reaction between alcohols and acids with the formation of esters and water is a reversible reaction. Now, when ethyl iodide (an ester) and water react, the first products are alcohol and hydrogen iodide:

$$C_2H_5I + H_2O \rightleftarrows C_2H_5OH + HI$$

and under proper conditions the alcohol and the still unchanged ethyl iodide form ether and hydrogen iodide:

$$C_2H_5OH + C_2H_5I \leftrightarrows (C_2H_5)_2O + HI$$

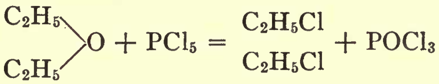
An excess of water would transform almost all of the iodide into alcohol, so only a small amount must be used if ether is to be produced.

Ether is also formed when sodium ethoxide and ethyl iodide are brought together in alcoholic solution:

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI$$

This synthesis of ether is of great historical importance, as it not only served to establish the structure of ether, but also had a far-reaching effect in clearing up the structural formulas of many other compounds. It was made by Williamson in 1850. The student should read his papers on etherification in the *Alembic Club Reports*, No. 16.

Reactions.—All the reactions of ether are in accordance with this view of its molecular structure. The production of ethyl chloride when ether is heated with phosphorus pentachloride shows that two chlorine atoms have replaced the one oxygen atom which unites two ethyl groups:



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \!\!>\! O + PCl_5 = \begin{matrix} C_2H_5Cl \\ C_2H_5Cl \end{matrix} + POCl_3$$

2. Ethyl halides are formed when the halogen acids react with ether, hydrogen iodide acting more readily than the others. At 0° hydrogen iodide produces ethyl iodide and ethyl alcohol:

$$(C_2H_5)_2O + HI = C_2H_5I + C_2H_5OH$$

but when heated with the strong acid the products are ethyl iodide and water:

$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O$$

3. Ether dissolves in cold concentrated sulphuric acid and can be separated unchanged from the solution by pouring the acid solution into water. When the solution of ether in the acid is warmed, however, ethyl sulphuric acid is formed:

$$(C_2H_5)_2O + 2H_2SO_4 = 2(C_2H_5)HSO_4 + H_2O$$

4. When heated with water containing a little sulphuric acid to 150–180° ether is hydrolyzed into alcohol:

$$(C_2H_5)_2O + H_2O = 2C_2H_5OH$$

5. Oxidation by means of nitric or chromic acid produces the same products as those obtained by the oxidation of alcohol — aldehyde and acetic acid:

$$(C_2H_5)_2O + 2O = 2CH_3.CHO + H_2O$$

$$(C_2H_5)_2O + 4O = 2CH_3.CO.OH + H_2O$$

6. Chlorine replaces the hydrogen step by step, with the final formation of $(C_2Cl_5)_2O$, a solid compound melting at 69° and having a penetrating camphor-like odor.

Uses.—Besides its use as a valuable anæsthetic, ether is much employed in the laboratory and in the arts and manufactures as an excellent solvent for many substances. These are readily recovered from their solutions in it, on account of its great volatility and low boiling point. Thus it is used for the extraction of fats, oils, etc., from mixtures. It not only dissolves many organic compounds, but also a number of inorganic substances, such as iodine, chromic acid, and chlorides of iron, mercury, and tin. In its rapid change into vapor, ether produces such a lowering of temperature that it has been used to manufacture ice; and in the form of a fine spray on the skin to produce local anæsthesia.

Other Ethers.—By methods similar to those which produce ethyl ether, many other ethers can be made whose reactions are like those of this ether and whose properties have the relationship and show the gradation which are familiar to us in compounds forming a homologous series. The general formula of an ether is $C_nH_{2n+2}O$, in which, however, n cannot be less than two. For if $n=0$, we have H_2O, and if $n=1$, CH_4O or methyl alcohol. Both of these substances may be considered of the ether type, since ether, water, and methyl alcohol are all oxides. But an ether is an *alkyl oxide*, while water is hydrogen oxide, and methyl alcohol, methyl-hydrogen oxide. The first ether, then, is methyl ether $(CH_3)_2O$.

Methyl and ethyl ether each contain two like alkyl groups. But from the methods of ether formation we should expect it possible to make ethers containing two dissimilar groups, and this can, in fact, be readily done. When a mixture of two alcohols is treated with sulphuric acid, as in the preparation of ethyl ether, a mixture of ethers results: from methyl and ethyl alcohols there is formed methyl ether, $(CH_3)_2O$; ethyl ether, $(C_2H_5)_2O$; and methyl-ethyl ether, $CH_3.O.C_2H_5$. A definite single mixed ether is obtained by the reaction of a sodium alkoxide and an alkyl iodide:

$$CH_3ONa + C_2H_5I = CH_3.O.C_2H_5 + NaI$$

This formation of a mixture of ethers and of single mixed ethers was used by Williamson to confirm his theory of the structure of ether and alcohol.

The ethers with two like alkyl groups are called *simple ethers*, the others *mixed ethers.* The first two ethers which correspond to the general formula, namely, $(CH_3)_2O$ and $CH_3.O.C_2H_5$, are gases at ordinary temperature. All the other ethers, except those of high molecular weights, are liquids, lighter than water.

A few unsaturated ethers are known, *e.g.*, *divinyl ether* $(CH_2:CH)_2O$, and *ethyl-propargyl ether*, $CH:C.CH_2.O.C_2H_5$.

ETHERS

Names	Formulas	Boiling Points	Specific Gravity
Dimethyl Ether	$(CH_3)_2O$	−23.6°	
Diethyl	$(C_2H_5)_2O$	34.6	0.731 (4°)
Dipropyl	$(C_3H_7)_2O$	90.7	0.763 (0°)
Dibutyl (normal)	$(C_4H_9)_2O$	141	0.784 (0°)
Dioctyl (normal)	$(C_8H_{17})_2O$	280–282	0.805 (17°)
Methyl-ethyl	$CH_3OC_2H_5$	11	....
Ethyl-propyl	$C_2H_5OC_3H_7$	63–64	0.739 (20°)
Ethyl-butyl (norm.)	$C_2H_5OC_4H_9$	92	0.769 (0°)
Ethyl-octyl (norm.)	$C_2H_5OC_8H_{17}$	182–184	0.794 (17°)

CHAPTER VII

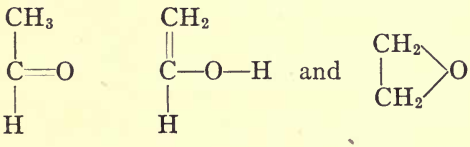
OXIDATION PRODUCTS OF ALCOHOLS ALDEHYDES AND KETONES

Aldehydes

Ethyl alcohol reacts readily with a dilute solution of chromic acid (potassium dichromate and sulphuric acid). Heat is developed and the first portions of the distillate contain a substance called aldehyde, which has a peculiar and suffocating odor. When separated from the water, alcohol, and small amounts of other substances with which it is mixed, the pure aldehyde is obtained as a liquid which boils at 21°. Its analysis and vapor density lead to the molecular formula, C_2H_4O. The oxidation of alcohol to aldehyde consists, therefore, in the removal of two hydrogen atoms from the alcohol molecule C_2H_6O, and it is from this fact that the name aldehyde—*al*cohol *dehyd*rogenatus—was given it:

$$CH_3.CH_2.OH + O = C_2H_4O + H_2O$$

There are three possible arrangements of the atoms in this formula:



$$\begin{array}{c} CH_3 \\ | \\ C{=}O \\ | \\ H \end{array} \qquad \begin{array}{l} CH_2 \\ \| \\ C{-}O{-}H \\ | \\ H \end{array} \quad \text{and}$$

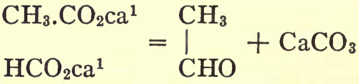
Two reactions will help us to decide which of these arrangements properly represents the structure of the alehyde molecule.

1. Phosphorus pentachloride acts on aldehyde with the pro-

duction of a compound whose formula is $C_2H_4Cl_2$, and whose structure must be $CH_2Cl.CH_2Cl$ or CH_3CHCl_2. This cuts out the second of the possible aldehyde formulas, which contains a hydroxyl group, and from which we should consequently expect phosphorus pentachloride to produce $CH_2 : CHCl$.

2. Aldehyde is readily oxidized to a monobasic acid, $C_2H_4O_2$, three of whose hydrogen atoms only can be replaced by chlorine by the direct action of this halogen, giving $C_2Cl_3HO_2$, which is still a monobasic acid. We may conclude, therefore, that in the acid, and in the aldehyde from which it is made, there is a CH_3 group. The structural formula of the aldehyde appears, therefore, to be the first one of the three, $CH_3.C\begin{smallmatrix}=O\\ \diagdown H\end{smallmatrix}$. All the reactions by which aldehyde is formed, and all of the reactions it gives, are in accord with this view of its structure.

Acetaldehyde, $CH_3.CHO$, is usually prepared by oxidizing alcohol in the way stated above. It is also produced when a mixture of calcium acetate and calcium formate is heated:



$$\begin{matrix} CH_3.CO_2ca^1 \\ HCO_2ca^1 \end{matrix} = \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} + CaCO_3$$

Acetaldehyde can also be formed from ethylidene chloride or bromide (p. 40) by heating with water in sealed tubes, or by boiling with alkalies:

$$CH_3CHBr_2 + H_2O = CH_3CHO + 2HBr$$

This reaction is of interest, but of no practical importance as a method of preparation, since these halides themselves are usually made from aldehyde by phosphorus halides.

Another method of formation of theoretical interest is from unsaturated hydrocarbons of the acetylene series, by the addition of the elements of water. This occurs when the hydrocarbon is

---

[1] For the sake of greater simplicity in the equation, ca = $\frac{1}{2}$ Ca.

dissolved in strong sulphuric acid which is then largely diluted and distilled:

$$CH \vdots CH + H_2O = CH_3CHO$$

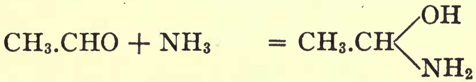
Properties and Reactions.—Acetaldehyde is a very volatile liquid which boils at 21°, and mixes with water in all proportions. It dissolves sulphur, phosphorus and iodine. It is easily inflammable and burns with a bright flame.

1. It is very readily oxidized to acetic acid, even in dilute solutions, and this change goes on slowly when it is in contact with air. Hence it is a powerful reducing agent. When warmed with an alkaline solution of copper sulphate (Fehling's Solution) it precipitates red cuprous oxide. Even very dilute solutions (1:4000) reduce ammoniacal solutions of silver nitrate, separating the silver in a finely divided state and giving to the solution a violet color. Stronger solutions precipitate most or all of the silver as a mirror on the walls of the vessel.

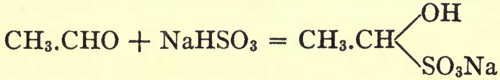
2. When sodium amalgam is put into its aqueous solution, aldehyde is "reduced" to alcohol by the direct addition of hydrogen:

$$CH_3.CHO + 2H = CH_3.CH_2.OH$$

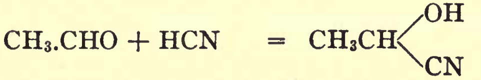
3. A number of other addition products are formed with various substances, in which, as in this instance, the double bond which unites oxygen to carbon in the CHO group is changed to a single bond so that the oxygen becomes a linking atom. Such reactions occur with ammonia, acid sodium sulphite, and hydrocyanic acid:



$$CH_3.CHO + NH_3 = CH_3.CH\left\langle\begin{matrix}OH\\NH_2\end{matrix}\right.$$



$$CH_3.CHO + NaHSO_3 = CH_3.CH\left\langle\begin{matrix}OH\\SO_3Na\end{matrix}\right.$$



$$CH_3.CHO + HCN = CH_3CH\left\langle\begin{matrix}OH\\CN\end{matrix}\right.$$

The ammonia addition product is precipitated in crystals when dry ammonia gas is led into a cold solution of aldehyde in anhydrous ether. It is very soluble in water. In air it slowly decomposes into resinous substances.

The sodium sulphite compound is also a solid crystalline substance which is obtained by shaking aldehyde with a saturated solution of the sulphite.

Aldehyde is recovered from both of these compounds when they are heated with dilute acids, and on this account they are sometimes made as a means of isolating and purifying aldehyde.

The hydrocyanic compound is the nitrile of lactic acid (p. 165), into which it is converted by hydrolysis.

4. With anhydrides of organic acids (*cf.* p. 117) addition products are also formed:

$$CH_3.CHO + (CH_3.CO)_2O = CH_3.CH(CH_3.CO.O)_2$$

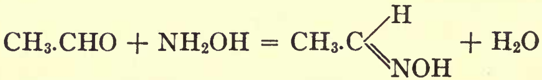
These compounds are decomposed by water into aldehyde and acid, or more readily by an alkali into aldehyde and a salt of the acid.

5. Another reaction which is common to the aldehydes is one in which they react with hydroxyl compounds with elimination of water. Thus, with alcohol, an *acetal* is formed:

$$CH_3.CHO + 2C_2H_5OH \rightleftarrows \underset{\text{Diethylacetal}}{CH_3.CH(OC_2H_5)_2} + H_2O$$

The reaction is aided by the presence of a little acetic acid as a catalyser. It is reversed when the acetals are boiled with acids and water.

6. With hydroxylamine (p. 122) aldehydes react to form *aldoximes:*



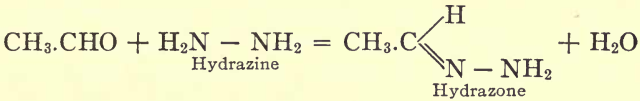
$$CH_3.CHO + NH_2OH = CH_3.C\begin{cases} H \\ NOH \end{cases} + H_2O$$

Acetoxime

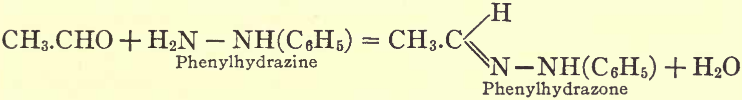
Similar products from ketones are called *ketoximes.*

Oximes from the lower members of the aldehyde and ketone series are liquids that can be distilled without decomposition. The hydrogen of their hydroxyl groups can be replaced by alkali metals, and with acids they form addition compounds such as, $CH_3.CH{:}N(OH)HCl$. On heating with acids they are hydrolyzed into hydroxylamine and the corresponding aldehyde or ketone. Energetic reduction (sodium amalgam in weak acid solution) converts them into primary amines.

7. A somewhat similar reaction occurs with hydrazine and hydrazine derivatives, with the formation of *hydrazones:*



$$CH_3.CHO + \underset{\text{Hydrazine}}{H_2N - NH_2} = \underset{\text{Hydrazone}}{CH_3.C\begin{cases} H \\ N - NH_2 \end{cases}} + H_2O$$



$$CH_3.CHO + \underset{\text{Phenylhydrazine}}{H_2N - NH(C_6H_5)} = \underset{\text{Phenylhydrazone}}{CH_3.C\begin{cases} H \\ N - NH(C_6H_5) \end{cases}} + H_2O$$

The hydrazones are hydrolyzed (the above reactions reversed) by boiling with dilute acids. The ready formation of oximes and hydrazones is so characteristic of compounds containing the carbonyl group, $=C=O$, that it serves as an excellent means for the identification of this group; and phenyl hydrazones have played an important part in the successful investigation of sugars (*cf.* p. 208).

8. With chlorine, aldehyde forms, in dilute solution, trichloraldehyde ("chloral" p. 91), but in strong solutions unless the hydrochloric acid which is formed is neutralized, this causes the production of "condensation" products such as

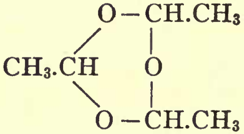
$$CH_3.CHCl.CCl_2.CHO.$$

9. Phosphorus halides, as has been already stated, replace the oxygen of aldehyde by two atoms of halogen:

$$CH_3.CHO + PCl_5 = CH_3.CHCl_2 + POCl_3$$

10. By the Grignard reaction aldehydes may be converted into secondary alcohols. Formaldehyde, however, yields primary alcohols (p. 37).

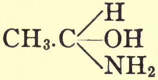
Polymerization. (*a*) The addition of a few drops of concentrated sulphuric acid to acetaldehyde causes it to become hot and boil violently. But instead of being all volatilized, the result is a colorless liquid which boils at 124°, and, when solidified by cold, melts at 10.5°. It is soluble in about eight parts of water. It shows none of the reactions characteristic of aldehyde, except the reaction with phosphorus halides. When boiled with dilute acids, it is converted into aldehyde again. Its empirical formula is the same as that of aldehyde, but its vapor density is three times as great, so that the molecular formula is $C_6H_{12}O_3$. This polymer of aldehyde is called *paraldehyde*. The fact that paraldehyde does not give aldehyde reactions shows that it does not contain the aldehyde group; and since it does not react with sodium, it has no hydroxyl group. A direct linkage of the three aldehyde molecules by carbon atoms is improbable, while all the additive reactions we have studied indicate that the oxygen in the aldehyde molecule readily shifts one of its double bonds to become a linking atom. Hence the formula which is given to paraldehyde is,



(*b*) At 0° a little hydrogen chloride, sulphur dioxide, or dilute sulphuric acid causes a crystallization to take place in aldehyde. Only part of the aldehyde is, however, transformed. This solid substance is insoluble in water, and when quickly heated it sublimes without melting, at about 112°, being partly reconverted at the same time into aldehyde. By continued slower heating or by distillation with a little dilute sulphuric acid, the conversion can be made complete. This substance is called *metaldehyde.* It is found to have the same molecular formula as paraldehyde, and is believed to be a "stereo-isomer" of it (*cf.* p. 166). Like the paraldehyde it gives ethylidene halides with phosphorus pentahalide.

(*c*) Acetaldehyde and other aldehydes, with the exception of formaldehyde, are converted into yellowish-brown resinous substances when warmed with alkalies. These aldehyde-resins are polymers of the aldehydes, but of unknown structure.

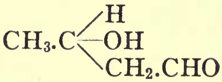
(*d*) *Aldol.*—When aldehyde is treated with a dilute solution of alkali or with certain salts (sodium acetate, zinc chloride) it is changed into a liquid called aldol, which has twice the molecular weight of aldehyde. Unlike the other polymers of aldehyde, aldol gives the aldehyde reactions, and it cannot be converted back into aldehyde. It also polymerizes readily. On oxidation it gives a hydroxy-butyric acid, $CH_3.CH.OH.CH_2.CO.OH$ (*cf.* p. 163), which has a chain of four carbon atoms. It appears, therefore, that aldol is an addition product of aldehyde to aldehyde of the type of the other addition products such as



$$CH_3.C\left\langle\begin{matrix}H\\OH\\NH_2\end{matrix}\right.$$

and in which a carbon atom of each of the two molecules is united.

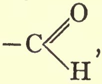
The formula would then be,



$$CH_3.C\left\langle\begin{matrix}H\\OH\\CH_2.CHO\end{matrix}\right.$$

According to this formula aldol would be an alcohol as well as an aldehyde, and this is found to be the case. The name aldol is based on this view, *ald*ehyde-alcoh*ol*. When heated, aldol loses the elements of water and becomes crotonic aldehyde: $CH_3.CH:CH.CHO$.

Other aldehydes undergo similar "aldol condensation," giving products which are useful in many organic syntheses.

The Aldehyde Series.—Acetaldehyde is a typical member of a series of saturated aldehydes, all of which contain the characteristic aldehyde group  $-C\begin{smallmatrix}O \\ H\end{smallmatrix}$, and have the general formula, $C_nH_{2n+1}CHO$, where n is any number or zero. All of them, except the first member, are formed by the same methods, and give the same reactions as acetaldehyde. On account of the readiness with which they react, and the variety of products that can be obtained from them, aldehydes are much employed in synthetic chemistry.

The first member of the series, formaldehyde, HCHO, differs from the other aldehydes in certain ways, which can be attributed to the fact that it alone contains no alkyl group, but only hydrogen united to the aldehyde group.

Nomenclature.—Aldehydes are usually named from the acids which they give on oxidation; thus, formaldehyde from formic acid, acetaldehyde from acetic acid, and propionic and butyric aldehydes from the acids of these names, etc. They are also named from the corresponding hydrocarbon by using the suffix *al*, thus methanal, ethanal, etc.

Formaldehyde, HCHO.—Methyl alcohol is so easily oxidized that the method used for the preparation of acetaldehyde is not a practical one for making formaldehyde. But when a mixture of methyl alcohol vapor and air are brought in contact with heated platinum or copper in the form of gauze or a spiral of fine wire, a flameless oxidation occurs with the formation of the aldehyde. Once started, the heat of the reaction is sufficient to maintain the temperature of the contact agent. By regulating the proportion of air and passing the products of oxidation through a condenser into water, a 30—40 per cent. solution of formaldehyde with some methyl alcohol may be obtained. This solution is sold under the name of "formalin." Formaldehyde is a gas (boiling point $-21°$), of very penetrating odor, and extremely irritating to the eyes. It is a powerful germicide, and is much used for disinfecting purposes, both as gas and in solution. Its solution is also used in small amounts as a food preservative, and as a preservative for anatomical preparations. Formaldehyde hardens albuminous substances and is hence used in histological work, and for rendering the gelatine films of photography hard and insoluble.

According to the general reaction for the formation of aldehydes by heating calcium salts with a formate, formaldehyde should be produced by heating calcium formate:

$$\begin{matrix} \text{H.CO.Oca} \\ \text{H.CO.Oca} \end{matrix} = \text{HCHO} + \text{CaCO}_3$$

But only a very small part of the theoretical amount can be obtained in this way, since, at the temperature necessary for the reaction, the aldehyde breaks up into carbon monoxide and hydrogen. For the same reason, its formation from methylene halide, CH_2Cl_2, and water, does not succeed.

Reactions.—Formaldehyde gives most of the reactions of the other aldehydes, but differs from them in the following ways:

It is oxidized more readily, and is therefore a more powerful reducing agent; not only reducing silver from the nitrate, but also forming mercurous choride and then mercury from mercuric chloride solutions. While its other addition products are similar to those of the other aldehydes, it reacts with ammonia to form *hexamethylene tetramine*, $(CH_2)_6N_4$, a weakly basic substance (p. 133). Formaldehyde in solution with sodium hydroxide gives sodium formate and methyl alcohol:

$$2\text{HCHO} + \text{NaOH} = \text{HCO.ONa} + \text{CH}_3\text{OH}$$

while other aldehydes with sodium hydroxide give aldols and resins. If hydrogen peroxide is added to an alkaline solution, formaldehyde is oxidized quantitatively to the alkali formate.

This is made the basis for determining the amount of formaldehyde in solution. A standard solution of sodium hydroxide is added in excess and then hydrogen peroxide. The alkali remaining after the reaction is then determined by titration with a standard acid, and from the result the amount of the formaldehyde is calculated. The reaction is:

$$HCHO + NaOH + H_2O_2 = HCO.ONa + 2H_2O$$

Formaldehyde with Grignard's reagents gives primary alcohols (p. 37).

Polymerization.—Formaldehyde polymerizes very readily when its solution is evaporated over sulphuric acid or by heat, and often on standing exposed to the air. Part of the aldehyde is given off as gas, but the greater part remains as a white solid, which can be sublimed, and after sublimation melts at 171°–172°. This is called *metaformaldehyde*, $(HCHO)_x$, of unknown molecular weight. It is only slightly soluble in ether and alcohol. In contact with water it slowly goes into solution, and this, when diluted, shows by the freezing-point method that the aldehyde is now in the monomolecular condition. The density of the vapor of metaformaldehyde corresponds to the simple formula, HCHO, but on cooling, it gradually polymerizes again. Metaformaldehyde is sold in the form of tablets and candles under the name of "paraform," and these are used as a source of formaldehyde for disinfecting purposes.

In the presence of dilute alkalies, formaldehyde polymerizes to substances from which it cannot be readily regenerated. From a solution saturated with calcium hydroxide and frequently shaken till the smell of the aldehyde has disappeared, a mixture of sweet, sugar-like substances is obtained from which Fischer isolated a substance called *acrose* which closely resembles natural sugars and has the same empirical formula as grape-sugar.

This laboratory synthesis of a sugar from formaldehyde is of especial interest in connection with the natural production of sugars and other carbohydrates in plants. Under the influence of sunlight and the chlorophyll of the leaves, it seems probable that the first product of the reduction of the carbon dioxide is formaldehyde: $CO_2 + H_2O = HCHO + O_2$, and that this immediately polymerizes: $6HCHO = C_6H_{12}O_6$.

Tests for Aldehydes.—The formation of a silver mirror or reduction of Fehling's solution together with the production of a resin on heating with a strong alkali indicate the probable presence of an aldehyde. The colorless solution formed by adding sulphurous acid to rosaniline (Schiff's reagent) is turned red-violet when an aldehyde is brought into it. Since formaldehyde is often used as a food preservative a simple test for its detection is of interest. Milk, for instance, may be tested for formaldehyde as follows: The milk is diluted with an equal amount of water and a few drops of a solution of ferric chloride are added. Concentrated sulphuric acid is now poured slowly into the inclined test tube so that it goes to the bottom as in the well-known test for nitric acid. If formaldehyde is present a violet ring appears where the two layers of liquid are in contact, when the tube is put into hot water. The color is the result of a reaction between a product formed in milk by the aldehyde and the reagents which are added, and any solution may be tested for formaldehyde in this way if milk is first added to it. The test is a very delicate one, showing the presence of the aldehyde in 200,000 parts of solution.

Unsaturated aldehydes may be formed by oxidation of unsaturated primary alcohols, or from saturated aldehydes by methods for producing the unsaturated condition (*cf.* p. 45). Some of the unsaturated aldehydes occur in "essential oils."

Acrylic aldehyde, *acroleïn*, $CH_2{:}\,CH.CHO$, is the first of the possible aldehydes with a double bond. It is formed by the oxidation of allyl alcohol (p. 69), but is made more readily by the withdrawal of the elements of water from glycerol (p. 159), as by heating it with potassium hydrogen sulphate:

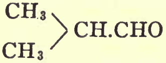
$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} - 2H_2O = \underset{\text{Acroleïn}}{CH_2{:}\,CH.CHO}$$

Acrylic aldehyde is a liquid boiling at 52.4°. It has a penetrating odor which brings tears to the eyes. Small amounts of it are formed when fats and oils (which are glyceryl esters) are heated, and it is partly responsible for the odor they give. Acrylic aldehyde gives all the reactions of an aldehyde and of an unsaturated hydrocarbon, with some modifications. For instance , with ammonia it reacts to form C_6H_9NO, a glue-like substance, and H_2O, instead of the usual addition product of an aldehyde; and it combines additively with two molecules of sodium bisulphite instead of with but one.

Crotonic aldehyde, $CH_3.CH: CH.CHO$, is formed by heating aldol (p. 82).

Geranial or **citral,** $(CH_3)_2C: CH.CH_2.CH_2.C(CH_3): CH.CHO$, is an aldehyde with two double bonds, which is found in various essential oils, such as those of orange peel and citron. It is a liquid which can be distilled without decomposition only under reduced pressure. It is used in the manufacture of *ionone*, a cyclic compound, which is the artificial oil of violets. The corresponding alcohol, geraniol, occurs in the oils of geranium (hence the name) and of roses.

ALDEHYDES

		Boiling Point	Specific Gravity
Formaldehyde	$HCHO$	−21°	0.8153 (−20°)
Acetaldehyde	$CH_3.CHO$	20.8	0.780 (20°)
Propionic	$CH_3.CH_2.CHO$	49	0.807 (20°)
Butyric	$CH_3.CH_2.CH_2.CHO$	74	0.817 (20°)
Isobutyric	 $\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle CH.CHO$	63	0.794 (20°)
Valeric	$CH_3.CH_2.CH_2.CH_2.CHO$	103	0.818 (11.2°)
Isovaleric	 $\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle CH.CH_2.CHO$	92	0.798 (20°)
Caproic	$CH_3(CH_2)_4.CHO$	128	0.834 (20°)
Acroleïn	$CH_2:CH.CHO$	54.2	....
Crotonic	$CH_3.CH:CH.CHO$	103	0.856 (17°)
Geranial (citral)	$C_9H_{15}.CHO$	224–228	....
Chloral	$CCl_3.CHO$	97	1.512 (20°)

KETONES

Name	Formula	Boiling Point °	Specific Gravity
Acetone	$CH_3.CO.CH_3$	56.	0.812 (0°)
Methyl-ethyl Ketone	$CH_3.CO.C_2H_5$	79.6	0.825 (0°)
Diethyl Ketone	$C_2H_5.CO.C_2H_5$	102.7	0.833 (0°)
Methyl-propyl (n) Ketone	$CH_3.CO.C_3H_7$	102	0.808 (20°)
Methyl-isopropyl Ketone	$CH_3.CO.CH(CH_3)_2$	94–96	0.815 (15°)
Methyl-butyl (n) Ketone	$CH_3.CO.C_4H_9$	127–128	0.830 (0°)
Methyl-butyl (iso) Ketone	$CH_3.CO.CH_2.CH(CH_3)_2$	116	0.819 (0°)
Methyl-butyl(ter.) Ketone	$CH_3.CO.C(CH_3)_3$	106	0.826 (0°)
Ethyl-propyl (n) Ketone	$C_2H_5.CO.C_3H_7$	122–124	0.833 (0°)
Ethyl-propyl (iso) Ketone	$C_2H_5.CO.CH(CH_3)_2$	117–119	0.830 (0°)
Dipropyl (n) Ketone	$C_3H_7.CO.C_3H_7$	144	0.820 (20°)
Methyl-amyl (n) Ketone	$CH_3.CO.C_5H_{11}$	155–156	0.813 (0°)
Ethyl-butyl (iso) Ketone	$C_2H_5.CO.C_4H_9$	135	0.829 (0°)

Ketones

Ketones are the first oxidation products of secondary alcohols. The simplest ketone possible, therefore, is that derived from isopropyl alcohol, $CH_3.CH.OH.CH_3$ and has the molecular formula, C_3H_6O. From our knowledge of the structure of secondary alcohols and the discussion of the structural formula of aldehyde, we should naturally give this ketone the formula, $CH_3.CO.CH_3$. This is determined to be the correct formula by its reactions, especially that with phosphorus pentachloride which substitutes two atoms of chlorine for one of oxygen. Other ketones give similar reactions; hence the characteristic group of a ketone is the divalent group $=C=O$ uniting two alkyls, and the general formula for simple ketones of this series is $C_nH_{2n+2}CO$, in which n is not less than two. The group $=CO$ is called *carbonyl.*

It should be noticed that the carbonyl group is common to both ketones and aldehydes, the only difference in their formulas being that in the ketones carbonyl unites two alkyls, and in the aldehydes, an alkyl and a hydrogen atom.

Acetone, $CH_3.CO.CH_3$, is the first member of the series of saturated ketones and is typical of all the others. It is obtained commercially from the products resulting from the distillation of wood (p. 59), and also from calcium or barium acetate. Pure acetone is made by distilling the crystalline addition product it forms with sodium sulphite with a solution of sodium carbonate. It is a colorless liquid of a characteristic and not unpleasant odor. It mixes in every proportion with water and can be separated from water by fractional distillation. It boils at 56.5°. Acetone is a good solvent for many organic compounds, and for gums, resins, etc. It is used as a solvent, and also in the preparation of chloroform, iodoform, sulphonal (p. 240), and other compounds used in medicine. Acetone occurs in normal urine in small amounts, and is present in larger quantities in certain diseases, especially in diabetes.

Acetone and other ketones can be formed: 1. From the corresponding alkyl dihalides, as the aldehydes are:

$$CH_3.CCl_2.CH_3 + H_2O = CH_3.CO.CH_3 + 2HCl$$

2. From acid chlorides (p. 114) by zinc alkyls or magnesium alkyl halides:

$$\underset{\text{Acetyl chloride}}{2CH_3.CO.Cl} + 2C_2H_5MgI = \underset{\text{Methyl-ethyl ketone}}{2CH_3.CO.C_2H_5} + MgCl_2 + MgI_2$$

This reaction gives a method by which mixed ketones, containing two different alkyl groups can be made.

3. By oxidation of secondary alcohols (p. 66):

$$CH_3.CHOH.CH_3 + O \rightarrow CH_3.CO.CH_3 + H_2O$$

4. From calcium salts of organic acids by distillation:

$$\begin{array}{l} CH_3.CO.Oca \\ CH_3.CO.Oca \end{array} = CH_3.CO.CH_3 + CaCO_3$$

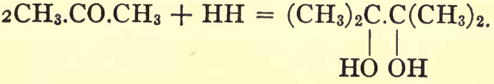
$$\begin{array}{l} CH_3.CO.Oca \\ C_2H_5CO.Oca \end{array} = CH_3.CO.C_2H_5 + CaCO_3$$

But in the second reaction the two simple ketones, acetone $CH_3.CO.CH_3$, and diethylketone $C_2H_5.CO.C_2H_5$, are also formed.

We have seen that when calcium formate is heated with the salt of a higher acid, the chief product is an aldehyde (p. 77). Aldehydes may, indeed, be viewed as mixed ketones in which hydrogen replaces one of the alkyl groups. In fact, the first substance corresponding to the general formula $C_nH_{2n+2}CO$ is $CH_4CO = CH_3.CHO$ or acetaldehyde. The general formulas for ketones and for aldehydes show that these compounds, when the number of carbon atoms is the same, are isomeric, both being $C_nH_{2n+2}CO$, and are only distinguished by formulas containing the groups characteristic of each.

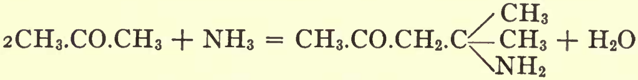
Nomenclature.—Acetone was the first ketone known and its name indicated its relation to the acetates. The individual ketones are named descriptively from the alkyl groups they contain—thus acetone is dimethyl ketone; $CH_3.CO.C_2H_5$, methylethyl ketone, etc. Ketones are also systematically named by adding *on* to the name of the hydrocarbons from which they are theoretically derived: thus $CH_3.CO.CH_3$ is *propanon*, $CH_3CO.C_2H_5$, *butanon*, etc.

The reactions of acetone and the other ketones are not as varied as those of the aldehydes. Like the aldehydes, their oxygen atom is replaced by two atoms of chlorine or bromine through the action of phosphorus pentahalides; they form addition products with hydrocyanic acid and acid sodium sulphite (but only when they contain the group $CH_3.CO$), and with nascent hydrogen (giving secondary alcohols); with Grignard's reagent they yield tertiary alcohols (p. 37); and they react with hydroxylamine and hydrazines, forming ketoximes and hydrazones. But unlike the aldehydes, the ketones are not easily oxidized, and hence are not reducing agents. When oxidation occurs, acids of a less number of carbon atoms are formed, the chain of carbon atoms breaking at the carbonyl group. When reduced by sodium amalgam, together with the secondary alcohol appreciable amounts of dihydroxyl tertiary alcohols are formed, called *pinacones:*



$$2CH_3.CO.CH_3 + HH = (CH_3)_2\underset{\substack{| \\ HO}}{C}.\underset{\substack{| \\ OH}}{C}(CH_3)_2.$$

Ketones give no addition product with ammonia, but form a number of complex condensation products from reaction between two or more molecules and ammonia, *e.g.*:



$$2CH_3.CO.CH_3 + NH_3 = CH_3.CO.CH_2.C\begin{array}{l}\diagup CH_3\\ - CH_3\\ \diagdown NH_2\end{array} + H_2O$$

Diacetonamine

Ketones do not react with alcohols and acid anhydrides as aldehydes do, they do not polymerize, nor do they give resins with alkalies.

The agreements in the reactions of ketones and aldehydes are conditioned by the presence of the carbonyl group, $=C=O$, which is common to both classes of compounds; the differences are due to the fact that in ketones both valencies of this group are united to alkyl groups, while in aldehydes (except formaldehyde which shows individual peculiarities), one valence is satisfied with hydrogen and the other with an alkyl group.

Identification.—Ketones are identified by the formation of an oxime (ketoxime) or phenylhydrazone, or a crystalline additive product with acid sodium sulphite (if they contain the $CH_3.CO$ group), while they do not reduce Fehling's solution, or silver nitrate, or produce an immediate color with Schiff's reagent.

Halogen Derivatives of Aldehydes and Ketones

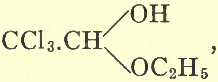
Chloral, $CCl_3.CHO$ (trichloraldehyde), and **chloral hydrate,** $CCl_3.CHO.H_2O$, are the most important of the halogen derivatives of the aldehydes. Chloral can be made by the direct action of chlorine on aldehyde in dilute solution; but the best method for its preparation is by leading chlorine into alcohol. The alcohol is at first kept cool and afterward warmed to about 60°, and the current of chlorine is continued until it is no longer absorbed, the operation lasting several days. The product, when cool, forms a crystalline mass from which, on treatment with concentrated sulphuric acid, the chloral separates as an oil, and is purified by distillation from calcium carbonate.

The action of the chlorine on alcohol is first that of an oxidizing agent, producing aldehyde:

$$CH_3.CH_2OH + Cl_2 = CH_3.CHO + 2HCl$$

Then the chlorine replaces hydrogen in the methyl group:

$$CH_3.CHO + 3Cl_2 = CCl_3.CHO + 3HCl$$

Secondary reactions, however, occur, so that the product contains *trichloracetal*, $CCl_3.CH(OC_2H_5)_2$, from reactions of aldehyde and chlorine with unchanged alcohol; *ethyl chloride*, C_2H_5Cl, and *chloral alcoholate*,  $CCl_3.CH\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}$, from decomposition of trichloracetal by the hydrochloric acid which is formed; and *chloral hydrate* by union of chloral with the water present. The sulphuric acid which is added sets chloral free from its compounds.

Properties and Reactions.—Chloral is an oily liquid of penetrating odor; it boils at 97.7° and its specific gravity is 1.513 (20°). It does not dissolve in water, but reacts with it with the development of much heat and the formation of the hydrate. Chloral hydrate, which is the form in which chloral is usually employed, is given the formula, $CCl_3.CH(OH)_2$, indicating that it is not properly a hydrate, or compound with water of crystallization, but a definite compound with two hydroxyl groups. In support of this view are the facts of the heat produced in its formation, and that it does not give the aldehyde reaction with Schiff's reagent (p. 86).

Chloral hydrate forms large crystals, which melt at 57°. At 96–98° it boils with decomposition into chloral and water. It is well known as a soporific.

Chloral and chloral hydrate are oxidized by nitric acid to trichloracetic acid, $CCl_3.CO.OH$; and when treated with alkalies give chloroform and a formate:

$$CCl_3.CHO + KOH = CHCl_3 + HCO.OK$$

Chloral is probably formed as an intermediate step in the manufacture of chloroform from alcohol by means of bleaching powder. The course of this reaction is commonly represented as follows: (1) Oxidation of alcohol to aldehyde, (2) chlorination of aldehyde to chloral, and (3) reaction of the chloral with the calcium hydroxide present in bleaching powder with the formation of chloroform and calcium formate:

$$
\begin{aligned}
&1.\ 2CH_3.CH_2OH + Ca(OCl)_2 = 2CH_3.CHO + CaCl_2 + 2H_2O \\
&2.\ 2CH_3.CHO + 3Ca(OCl)_2 = 2CCl_3.CHO + 3Ca(OH)_2 \\
&3.\ 2CCl_3.CHO + Ca(OH)_2 = 2CHCl_3 + (HCO.O)_2Ca
\end{aligned}
$$

Halogen derivatives of ketones are readily made by direct substitution; but here, as generally in direct replacements of hydrogen in compounds containing two or more carbon-hydrogen groups, it is impossible to obtain all of the possible chlorine or bromine derivatives by the action of these elements on the ketone. Symmetrical dichloracetone, $CH_2Cl.CO.CH_2Cl$, is not formed in this way, though the isomeric compound, $CH_3.CO.CHCl_2$, is readily made.

Trichloracetone is decomposed by alkalies into chloroform and an acetate, and this reaction is probably the last step in the preparation of chloroform from acetone by the action of bleaching powder:

$$
\begin{aligned}
&2CH_3.CO.CH_3 + 3Ca(OCl)_2 = 2CCl_3.CO.CH_3 + 3Ca(OH)_2 \\
&2CCl_3.CO.CH_3 + Ca(OH)_2 = 2CHCl_3 + (CH_3.CO.O)_2Ca
\end{aligned}
$$

CHAPTER VIII

SIMPLE MONOBASIC ACIDS

Acetic acid is one of the best-known organic acids, and since it is one of the simplest in composition and structure we will begin our discussion of the organic acids by considering its properties and reactions. Both the acid and its salts occur in small amounts in certain plants. Vinegar, of which acetic acid is the chief acid constituent, has been known from the earliest times. The two chief sources of acetic acid are alcohol and wood. The acid is obtained in many instances from ethyl alcohol as the result of an oxidation effected by means of a bacterial ferment (*Bacterium aceti*). These bacteria are usually present in the air, and, consequently, dilute solutions of alcohol such as cider, wines, etc., produced by the alcoholic fermentation of fruit juices, usually become sour after a time from the conversion of their alcohol into acetic acid, and are thus changed into vinegar. The slimy substance which is found in vinegar barrels contains the bacteria and is called "mother-of-vinegar." The oxygen necessary for the change is supplied by the air. Solutions containing more than about 10 per cent. of alcohol do not ferment, nor does fermentation occur in dilute solutions unless they contain small amounts of certain substances—phosphates and nitrogen compounds—which are essential for the growth of the organisms. This method of making acetic acid is carried on commercially by the so-called "quick vinegar process." In this, dilute alcohol, mixed with vinegar, and to which malt or beer is often added, is allowed to trickle slowly through tall vats nearly filled with beech-wood shavings which have been covered with the necessary bacteria by previous soaking in vinegar. The heat produced by the oxidation of the alcohol causes a current of air to enter by perforations in the bottom, and draw up through the vats; and the temperature, which should be about 30°, is regulated by controlling the temperature of this entering air. The solutions are usually passed through several vats in succession, the operation taking eight to twelve days, until most of the alcohol is changed into acid. A little alcohol is, however, always left unchanged, because with its total disappearance the acetic acid would begin to be itself oxidized into carbon dioxide and water.

The vinegar thus obtained usually contains from 4 to 6 per cent. of acid, though it is sometimes a little stronger. It is used as table vinegar, and to some extent in making white lead by the Dutch process. Table vinegar contains various substances besides acetic acid, which give it its aroma and flavor and which vary with the source. Thus cider vinegar, wine vinegar, and malt vinegar, each have distinctive qualities. Spirit vinegar, made from dilute alcohol, is often colored with caramel and given its odor and flavor by adding certain esters.

Acetic acid for other uses than the above is mostly obtained from the "pyroligneous acid" produced in the dry distillation of wood. The acid in the distillate is first converted into calcium acetate, and from this the commercial acid is obtained by distillation with sulphuric acid from cast iron retorts, or with concentrated hydrochloric acid from copper retorts. An excess of hydrochloric acid must be avoided so that none of it shall distil with the acetic acid. The acid thus obtained is purified by redistillation from a little potassium dichromate (to oxidize impurities) and by filtering through charcoal. The ordinary commercial acid contains about 30 per cent. of the pure acid.

For the purpose of preparing the pure anhydrous acid, sodium acetate is made, purified by recrystallization, heated to drive off its water of crystallization, and then mixed with concentrated sulphuric acid and distilled. A nearly anhydrous acid is thus obtained, and from it an acid entirely free from water is prepared by crystallization. Its molecular formula is found to be $C_2H_4O_2$.

Uses.—Acetic acid is used in making white lead, as stated above, in the dye-stuff industry, and for making a number of salts of practical value: lead acetate or "sugar of lead," "verdigris," a basic acetate of copper, "Paris green," a double salt of copper acetate and arsenite, and the acetates of iron, chromium, and aluminium, which are extensively used as mordants in dyeing and calico printing.

In the laboratory the pure acid is used as an excellent solvent for many carbon compounds.

Properties of Acetic Acid.—Pure anhydrous acetic acid is a colorless liquid at temperatures above 16.675°, which is the melting point of the crystalline solid formed at lower temperatures. From the resemblance of the solid acid to ice the anhydrous acid is often called "glacial" acetic acid. The boiling point is 118°. The anhydrous acid and mixtures with small amounts of water show in a pronounced degree, the phenomenon of supercooling, which is common to many liquids and solutions. The addition of a crystal of the acid is usually necessary to cause the crystallization to take place, and when it occurs the temperature rises to the "freezing point." The freezing point of mixtures of acid and water (the temperature at which some separation of solid occurs) is lower as the proportion of water increases, until with 40 per cent. of water a minimum is reached at $-26.75°$. From solutions less dilute than this, the anhydrous acid separates at the freezing point, while from more dilute solutions ice is formed. From the mixture containing 40 per cent. of water, acid and water crystallize together and the temperature remains unchanged till the whole is solid.[1] When the anhydrous acid is mixed with

---

[1] See a Physical Chemistry for discussion of cryohydrates.

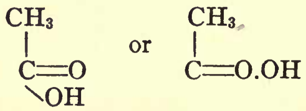
water there is contraction of volume and the temperature rises. The specific gravity increases as the acid is diluted, until (at 15°) with 77–80 per cent. of acid a maximum is reached. A solution containing 43 per cent. has the same specific gravity at 15° as the anhydrous acid; and there are two solutions of different strengths for all specific gravities between this (1.055) and the maximum (1.075).

Acetic acid does not form a constant boiling-point mixture with water as the halogen acids (and formic acid) do, but the distillate becomes more and more dilute, while a stronger and stronger acid remains in the flask.

Glacial acetic acid blisters the skin, and has a penetrating and characteristic odor. It is not inflammable until heated nearly to the boiling point, when the vapor burns with a pale blue flame. The acid mixes with water, alcohol and ether in all proportions, and its aqueous solutions are sharply acid. Acetic acid dissolves very many organic compounds (without acting on them chemically) and some inorganic substances which are insoluble in water, as, for instance iodine and sulphur.

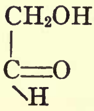
It acts on certain metals and dissolves the hydroxides of metals, readily forming acetates. Acetic acid is an unusually stable organic compound. Its vapor is hardly decomposed when led through a red-hot tube; it withstands oxidizing agents to a remarkable degree, and is hence a frequent product of the oxidation of more complicated compounds. On this account it may be employed as a solvent for chromic acid when this is to be used to oxidize a substance insoluble in water.

Structure of Acetic Acid.—From the molecular formula of acetic acid, $C_2H_4O_2$, we can make three simple structural formulas:



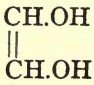
1

,



2

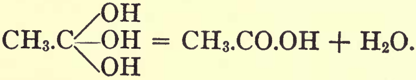
, and



$$\begin{array}{c} CH.OH \\ \| \\ CH.OH \end{array}$$

3

The third formula is that of an unsaturated dihydroxyl alcohol, and the second is a mixed alcohol and aldehyde. Acetic acid shows none of the properties of such compounds: it does not give the reactions peculiar to unsaturated compounds, it has no alcohol characteristics, and it is not a reducing agent as it should be if it contained an aldehyde group. As it is formed by the oxidation of ethyl alcohol, $CH_3.CH_2OH$, or of its first oxidation product aldehyde, $CH_3.CHO$, the first formula is the one naturally suggested. 1. Analysis of its salts show that it is a monobasic acid, which means that one hydrogen atom is differently combined from the other three. 2. Chlorine replaces, one after the other, three and only three of the hydrogen atoms. This indicates the methyl group, CH_3. 3. Phosphorus chlorides substitute one chlorine atom for one atom each of hydrogen and oxygen; hence an hydroxyl group is present. The only possible structure with a methyl and a hydroxyl group is $CH_3.C{=}O.OH$. Further, acetic acid may be made by the action of potassium hydroxide in alcoholic solution on trichlor-ethane, $CH_3.CCl_3$. We may picture this reaction as first giving $CH_3.C(OH)_3$ followed by the breaking down of this unstable compound into acetic acid and water:



$$CH_3.C\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix} = CH_3.CO.OH + H_2O.$$

This structure accords with all the reactions of acetic acid and all the methods of its formation. The monad group $-C{=}O.OH$ which contains the acid hydrogen atom of acetic acid is called the carboxyl group (*car*bonyl and hydr*oxyl*) and is the characteristic group of all organic acids.

Laboratory Methods for the Formation of Acetic Acid and its Homologues.—The most important reactions which result in the formation of acetic acid and which are also general reactions for the formation of its homologues, are:

1. Oxidation of the primary alcohols or aldehydes (already described).

2. Hydrolysis of an alkyl cyanide (acid nitrile) (p. 153):

$$\underset{\text{Methyl cyanide}}{CH_3.CN} + 2H_2O = \underset{\text{Acetic acid}}{CH_3.CO.OH} + NH_3$$

The alkyl cyanides are produced by the action of potassium cyanide and alkyl iodides:

$$CH_3I + KCN = CH_3.CN + KI$$

The hydrolysis of the alkyl cyanide is effected most rapidly by boiling the cyanide with dilute sulphuric or hydrochloric acid, or a dilute alkali (*cf.* the formation of formic acid p. 102).

3. From esters by hydrolysis with water or caustic alkalies:

$$\underset{\text{Ethyl acetate}}{CH_3.CO.OC_2H_5} + H_2O \rightleftarrows CH_3.CO.OH + C_2H_5OH$$

$$CH_3.CO.OC_2H_5 + KOH = CH_3.CO.OK + C_2H_5OH$$

In the second reaction the acetate is of course obtained, from which the acid is readily set free by hydrochloric or sulphuric acid.

4. From trihalides by hydrolysis (p. 41a):

$$CH_3.CCl_3 + 4KOH \rightarrow CH_3.CO.OK + 3KCl + 2H_2O$$

5. By heating dibasic acids which contain two carboxyl groups united to the same carbon atom:

$$\underset{\text{Malonic acid}}{CH_2:(CO.OH)_2} = CH_3.CO.OH + CO_2$$

6. From alkyl halides by the Grignard reaction (p. 37).

Reactions of Acetic Acid.—The hydrogen of the hydroxyl group can be replaced:

1. By metals with the formation of salts.

2. By alkyl groups, giving esters,

$$CH_3.CO.OH + C_2H_5OH \rightleftarrows \underset{\text{Ethyl acetate}}{CH_3.CO.OC_2H_5} + H_2O$$

3. The hydroxyl group may be replaced by chlorine or bromine (by phosphorus halides) giving the acid halides:

$$3CH_3.CO.OH + 2PCl_3 = 3CH_3.CO.Cl + 3HCl + P_2O_3$$

$$CH_3.CO.OH + PCl_5 = \underset{\text{Acetyl chloride}}{CH_3.CO.Cl} + POCl_3 + HCl$$

4. The hydrogen of the methyl group can be directly replaced by chlorine or bromine, yielding mono-, di-, and tri-halogen acetic acids:

$$CH_2Cl.CO.OH,\ CHCl_2.CO.OH,\ CCl_3.CO.OH$$

Reactions of Acetates.—Among the important reactions into which acetates enter are:

1. The formation of the acid amide (p. 137) by heating ammonium acetate:

$$CH_3.CO.ONH_4 = \underset{\text{Acetamide}}{CH_3.CO.NH_2} + H_2O$$

By distillation of the acid amide with phosphorus pentoxide the nitrile of the acid (an alkyl cyanide) is formed:

$$CH_3.CO.NH_2 \xrightarrow{P_2O_5} CH_3.CN + H_2O$$

2. The formation of aldehyde by heating a mixture of calcium acetate and formate; or of a ketone when calcium acetate is heated alone or with homologous calcium salts of higher atomic weights (pp. 77, 89).

3. The formation of methane by replacement of the carboxyl group with hydrogen, when sodium acetate is heated with sodium hydroxide or soda-lime (p. 26):

$$CH_3.CO.ONa + NaOH = CH_4 + Na_2CO_3$$

4. The formation of ethane by electrolysis (p. 29).

Other Acids of the Type of Acetic Acid.—A large number of organic acids are known, in each of which one carboxyl group is united to an alkyl group (or hydrogen). They form an homologous series, whose general formula is $C_nH_{2n+1}CO.OH$.

General Properties of the Acids.—The acids of this series, which contain less than ten atoms of carbon, are liquids at ordinary temperatures, and those of greater molecular weight solids. As the molecular weight increases, the liquid acids become oily and less soluble in water, and the specific gravity decreases. All except the first three are lighter than water. The solid acids have a waxy or fatty consistency and are insoluble in water but are all soluble in alcohol and in ether. All except the highest boil without decomposition, and the boiling points are higher with greater molecular weights. The melting points of the acids exhibit an interesting periodicity, alternately rising and sinking as the molecular weights become larger; the acids with an even number of carbon atoms always having higher melting points than the acids containing an odd number of carbon atoms which are next above them in the series. The acids containing from four to nine carbon atoms have a disagreeable odor like that of rancid butter. The acid character becomes less and less pronounced as the molecular weight is greater, and the higher members of the series show that they are acids only by the formation of salts. The salts of the lower members are all soluble in water, but with the higher members only the alkaline salts dissolve.

Their reactions are similar to those of acetic acid and the acetates. It should be remarked, however, that chlorine and bromine replace the hydrogen nearest the carboxyl group, thus giving α-substitution products.

NORMAL MONOBASIC ACIDS

Name	Radical with CO. OH group	Melting Point	Boiling Point		Specific Gravity
Formic	H	8.6°	101°		1.231 (10°)
Acetic	CH_3	16.7	118.5		1.0515 (15°)
Propionic	C_2H_5	−22	141		0.9985 (14°)
Butyric	C_3H_7	− 7.9	162		0.9599 (19.1°)
Valeric	C_4H_9	−58.5	186		0.9560 (0°)
Caproic	C_5H_{11}	− 1.5	205		0.9450 (0°)
Heptylic	C_6H_{13}	−10.5	223		0.9186 (17.2°)
Caprylic	C_7H_{15}	16.5	237.5		0.9100 (20°)
Pelargonic	C_8H_{17}	12.5	254		0.9110 (m.p.)
Capric	C_9H_{19}	31.4	269		......
Lauric	$C_{11}H_{23}$	48	225	At 100 mm. pressure	......
Palmitic	$C_{15}H_{31}$	62.6	268		0.8527 (m.p.)
Margaric	$C_{16}H_{33}$	60	277		......
Stearic	$C_{17}H_{35}$	69.3	287		0.8454 (m.p.)
Cerotic	$C_{26}H_{53}$	78°	...		......

All the normal acids up to $C_{19}H_{39}.CO.OH$ are known. The acid of largest molecular weight which is known is $C_{33}H_{67}.CO.OH$. Isomeric acids corresponding to the isomeric primary alcohols can all be made.

Nomenclature.—The usual names of the acids of this series are the original names which are often suggested by the sources from which the acids were first obtained. Thus formic acid from ants (*formicæ*), acetic from vinegar (*acetum*), butyric from butter, palmitic from palm oil, stearic from tallow (ςτέαρ), oleïc from oils, etc. A systematic method of naming which is often employed, and which has the advantage of being descriptive of the structure, is one which regards them (except formic acid) as derivatives of acetic acid: thus propionic acid, $CH_3.CH_2.CO.OH$, is methyl acetic acid; normal butryic acid, $CH_3.CH_2.CH_2.CO.OH$ is ethyl acetic acid; and iso-butyric acid $(CH_3)_2CH.CO.OH$, is dimethyl acetic acid. Another systematic nomenclature changes the name of the hydrocarbon of the same number of carbon atoms, of which the acid is a theoretical derivative, by substituting *oic* for the final *e*; thus acetic acid is *ethanoic acid*, etc. The name of *fatty acids* is often given to the series, from the fact that esters of some of the higher members occur in the fats, and many of the acids themselves resemble fats.

Formic acid, $HCO.OH$, the first member of the series, is found in ants (*formicæ*), bees, and in stinging nettles. The irritation from the sting of these is probably due to the formic acid which they deliver. Formic acid occurs also in many insects and plants, and is frequently one of the products formed in the destructive distillation and oxidation of many organic substances. Formic acid, or its alkaline salts (from which the acid is readily set free by hydrochloric acid) can be made in the laboratory by many reactions. Some of them are:

1. By the oxidation of a solution of methyl alcohol.

2. By the hydrolysis of hydrocyanic acid by means of dilute alkalies or acids:

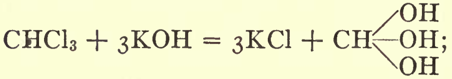
$$HCN + 2H_2O = H.CO.OH + NH_3$$

If an acid is employed the products are formic acid and the ammonium salt of the acid; with an alkali, the alkaline formate and ammonia are produced.

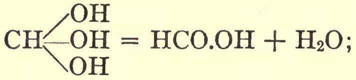
3. By warming chloroform with an alkali,

$$CHCl_3 + 4KOH = H.CO.OK + 3KCl + 2H_2O$$

This reaction may be regarded as taking place in three steps:



$$CHCl_3 + 3KOH = 3KCl + CH\begin{array}{l}\diagup OH\\ - OH;\\ \diagdown OH\end{array}$$



$$CH\begin{array}{l}\diagup OH\\ - OH\\ \diagdown OH\end{array} = HCO.OH + H_2O;$$

$$HCO.OH + KOH = HCO.OK + H_2O.$$

Two further reactions by which salts of formic acid can be formed from the elements are of special interest. These are:

4. By the action of moist carbon monoxide on solid potassium or sodium hydroxide at a temperature of about 200°:

$$CO + NaOH = HCO.ONa$$

This reaction is employed in the commercial preparation of sodium formate, the carbon monoxide from generator gases being used under pressure.

5. Moist carbon dioxide acts slowly on potassium, forming a mixture of the acid carbonate and the formate:

$$2CO_2 + 2K + H_2O = HCO.OK + KHCO_3$$

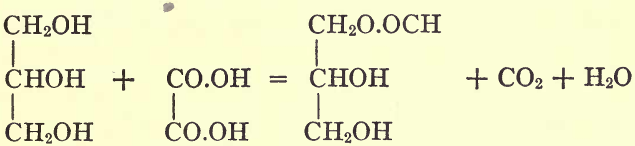
6. Formates are also produced by the reduction of solutions of ammonium carbonate or of acid carbonates by means of sodium amalgam.

Preparation.—None of the above reactions are, however, usually employed for laboratory preparation of formic acid; but the acid is made by distilling a mixture of glycerol (glycerine) and oxalic acid. Oxalic acid when heated alone gives a small amount of formic acid together with carbon dioxide:

$$\mathrm{C_2H_2O_4 = HCO.OH + CO_2}$$

but most of the oxalic acid sublimes unchanged. When mixed with glycerol, however, the reaction goes on quite readily and completely. The glycerol prevents the sublimation of the oxalic acid through the formation of a formic acid ester of glycerol, which then breaks down through hydrolysis with the water present into formic acid and glycerol.

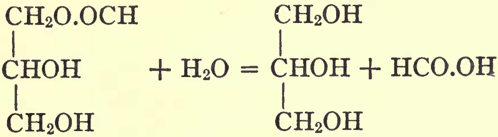
The reactions which occur at about 120° with a mixture of equal parts of glycerol and crystallized oxalic acid are:



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + \begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CO.OH} \end{array} = \begin{array}{l} \mathrm{CH_2O.OCH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{CO_2} + \mathrm{H_2O}$$

Glycerol　Oxalic acid　Glyceryl monoformate

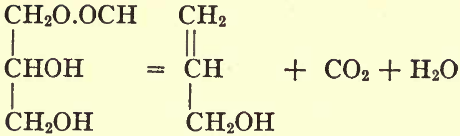
Very little formic acid distils until another portion of oxalic acid is added, when by the reaction between the monoformate and the crystallization water of the oxalic acid formic acid is set free and at the same time the monoformate is reproduced:



$$\begin{array}{l} \mathrm{CH_2O.OCH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{H_2O} = \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{HCO.OH}$$

By adding fresh portions of oxalic acid from time to time the production of formic acid goes on indefinitely.

When oxalic acid and four times its weight of glycerol are heated and the temperatures brought up to 220°–260°, a deeper-seated decomposition of the formic acid ester occurs with the formation and distillation of allyl alcohol (p. 69):

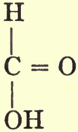


$$\begin{array}{l} CH_2O.OCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + CO_2 + H_2O$$

Glycerol monoformate Allyl alcohol

Anhydrous formic acid cannot be obtained by distillation. It can be prepared from anhydrous lead formate by the action of hydrogen sulphide; but more conveniently by using anhydrous oxalic acid as a dehydrating agent.

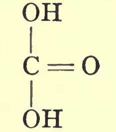
The structure shown by the formula which has been used in the description of the methods for making formic acid is directly indicated by some of these reactions, and is in accord with all the known facts about the acid. The characteristic acid group, — CO.OH, is here combined with hydrogen instead of an alkyl group as in acetic acid and the other acids of this series, and in this fact we have an explanation of some methods of formation and some reactions which differ from those of the other acids of this series. Attention is called especially to the presence of the aldehyde group shown in the structural formula,



$$\begin{array}{l} H \\ | \\ C = O \\ | \\ OH \end{array}$$

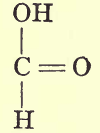
Formic acid is thus both an acid and an aldehyde.

Properties.—Formic acid is a colorless liquid which fumes slightly in the air and is hygroscopic. It is heavier than water, solid below 8.6° and boils at 101°. When mixtures of the acid and water are distilled, they behave like solutions of hydrochloric acid, —both strong and weak solutions giving finally a mixture whose boiling point (about 107°) and composition (about 77 per cent. acid) are constant while the pressure remains unchanged. The acid has an irritating odor, and the pure acid in contact with the skin causes blisters and painful wounds. It mixes with water and with alcohol in all proportions, and its solutions show a strong acid reaction with litmus. Formic acid is, in fact, the strongest of the organic acids. The liquid acid does not burn, but its vapor burns readily with a blue flame into water and carbon dioxide; and solutions of the acid are easily oxidized by various agents and yield the same products. Formic acid is, therefore, a strong reducing agent. It precipitates silver and mercury when warmed with neutral solutions of their salts. This reducing power, which is not shown by the other acids of this series, is like that shown by the aldehydes (p. 78); and as has been pointed out, the acid contains an aldehyde group united with hydroxyl. Formic acid, from this point of view, may be regarded as an aldehyde derivative of carbonic acid:



$$\begin{array}{l} OH \\ | \\ C=O \\ | \\ OH \end{array}$$

Carbonic acid



$$\begin{array}{l} OH \\ | \\ C=O \\ | \\ H \end{array}$$

Formic acid

The production of formates by the reduction of carbonates (p. 103) agrees with this view, since the aldehydes may be regarded as derived from the corresponding acids by the withdrawal of an atom of oxygen.

Reactions.—Formic acid is decomposed into carbon dioxide and hydrogen when heated to 160° in a closed vessel; and with concentrated sulphuric acid the acid (and of course, its salts) decompose readily into carbon monoxide which is evolved, and water which is held by the sulphuric acid. Some contact agents such as finely divided rhodium, cause a spontaneous decomposition of the same sort.

The salts of formic acid—the formates—are all soluble in water, though some, such as the silver and lead formates, do not dissolve very freely.

Formates are decomposed by heating. The alkali salts when carefully heated, and the salts of the alkaline earths under all conditions, give carbonates:

$$\begin{array}{l}HCO.ONa\\HCO.ONa\end{array} = Na_2CO_3 + H_2 + CO$$

though by rapidly raising the temperature to 400°, in the absence of air, the alkali formates yield oxalates and hydrogen:

$$\begin{array}{l}HCO.ONa\\HCO.ONa\end{array} = C_2O_4Na_2 + H_2$$

Ammonium formate gives neither carbonate nor oxalate when heated, but at 230° loses the elements of water with the production of formamide $HCO.NH_2$.

Formic acid and formates may be identified by the reactions with concentrated sulphuric acid, and with an ammoniacal solution of silver nitrate. Either alone is inconclusive, because given by other substances, but if in the first the substance does not blacken and a gas is obtained which burns with a blue flame; and silver is precipitated in the second, formic acid or a formate is present.

Higher Fatty Acids

These may be made by the general methods which have been given. The three normal acids which follow acetic acid in the series are also formed by processes of fermentation.

Propionic Acid, $CH_3.CH_2.CO.OH$ (methyl acetic acid or propanoic acid).—The original name of this acid was given it as the first or the series which showed fat-like properties (*πρῶτος* and *πιον*). It is found in small quantities in wood vinegar, and is formed in a fermentative process which takes place in solutions of the calcium salts of malic and lactic acids. It is also a reduction product of lactic, glyceric, acrylic and propargylic acids.

Butyric Acids.—*Normal butyric acid*, $CH_3.CH_2.CH_2.CO.OH$, ethyl acetic acid, is found in rancid butter. Its glyceryl ester forms about 5 per cent. of butter fat, which is made up of this and of esters of several other acids of this series. The acids may be set free from these esters by hydrolysis; but on account of the difficulty of separation this is not a favorable method for obtaining butyric acid.

It is produced by the action of a special ferment (butyric ferment) contained in old Limburger cheese (which also contains the acid), on sugars, lactic acid, and other substances. This fermentative process is the one usually employed for its preparation.

Isobutyric acid $(CH_3)_2:CH.CO.OH$, dimethyl acetic acid, is apparently not formed by fermentation. It occurs in considerable quantities in the juices of "St. John's bread," the fruit of the carob tree, and can be obtained from this source by distillation with water.

Both the acid and an ester occur in aconite root, and in some other substances. Isobutyric acid is much less soluble in water than the normal acid, and, as is the rule with iso-compounds, its boiling point is lower.

Valeric Acid.—There are four valeric acids, $C_4H_9.CO.OH$, known, all that are structurally possible. The normal acid is in wood vinegar in small amounts and is formed in a fermentation of calcium lactate solution. One of the iso-acids is found in the roots of valerian (hence the name), and angelica, and may be obtained from these by distillation with water. It is optically active.

Palmitic Acid, $C_{15}H_{31}CO.OH$, and Stearic Acid, $C_{17}H_{35}CO.OH$.—Glyceryl esters of the normal acids, together with that of oleïc acid (p. 110), are the chief constituents of animal fats, and are contained in many vegetable fats and oils. The acids are obtained from these sources, commercially, by hydrolysis of the esters (p. 124). After the crystallization of the two solid acids, the liquid oleïc acid is removed from them by hydraulic pressure. The mixture of palmitic and stearic acids thus obtained is known by the trade name of "stearin" (not to be confused with *stearin* as used in chemistry, which is the name given to the glyceryl ester of stearic acid). This "stearin," mixed with paraffin to prevent crystallization and consequent brittleness, is largely used for making candles.

Palmitic and stearic acids are colorless, waxy solids which melt at 63° and 69° respectively, and can be distilled without decomposition only in a partial vaccuum.

Soaps.—The salts of the three acids whose esters form the fats are called soaps, though in the common use of the word, only the alkali salts are meant. Soap is made by the decomposition of the esters (fats) by solutions of the alkalies, the alkali salts and glycerol being produced in equivalent amounts:

$$\underset{\text{Stearin}}{(C_{17}H_{35}CO.O)_3C_3H_5} + 3KOH = \underset{\text{Potassium stearate}}{3C_{17}H_{35}CO.OK} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}.$$

When potassium hydroxide is used, the salts with the glycerol form a jelly-like mass which is known as soft-soap; when the fats are boiled with sodium hydroxide, a hard soap is formed, which is precipitated from the solution by adding common salt and cooling, while the glycerol is left in solution. Transparent soaps are made by dissolving a hard soap in alcohol and evaporating the clear solution. Common soaps are made from many different materials and often contain various additions. Pure soaps are soluble in alcohol, and dissolve in water with some hydrolysis or separation into alkali and insoluble acid. The soaps of the alkaline earths and of other metals are insoluble; hence a precipitate of calcium and magnesium salts is produced when soap is used with hard water and the formation of a lather is prevented until the precipitation is complete. The method for determining the hardness of a water is based on this reaction—a soap solution of known strength being added to a measured quantity of water, till a permanent lather is produced on shaking. The cleansing action of soap has been the subject of such dispute. It appears to be due chiefly to the power which soap solutions have of emulsifying oily substances, of wetting and penetrating into oily textures, and of lubricating texture and impurity so that the impurity is readily removed.[1]

Unsaturated Acids

Oleïc acid, whose glyceryl ester occurs in fats and oil, is an unsaturated acid with a double bond between two of its carbon atoms:

$$C_{17}H_{33}.CO.OH, \text{ or } CH_3(CH_2)_7CH:CH(CH_2)_7CO.OH.$$

The position of the double bond is indicated by the study of the compounds (acids) obtained by its oxidation, on the assumption that the break caused by oxidation occurs at this place.

Oleïc acid is an oily, odorless liquid, insoluble in water. When cooled it crystallizes, and melts at 14°. It readily oxidizes in contact with air, becoming brown and rancid.

Both oleïc acid and its glyceryl ester are changed into solids by a small amount of nitrous acid. These solids have the same composition as the original substances, and are called *elaïdic acid* and *elaïdin*, respectively. The reaction is used in the examination of oils as an indication of the amount of oleïn they contain.

Acrylic acid, $CH_2 : CH.CO.OH$, is to be regarded as the oxidation product of allyl alcohol (p. 69) or of acrylic aldehyde (acroleïn, p. 86). It is the first acid of the series of acids with a double bond, as allyl alcohol is the first alcohol. It can be formed from the corresponding saturated acid, propionic acid, by substituting a halogen atom or a hydroxyl group for hydrogen, and then employing the reactions used for making the unsaturated hydrocarbons from similar substitution products (p. 45):

$$CH_2I.CH_2.CO.OH + KOH = CH_2:CH.CO.OH + KI + H_2O.$$

$$CH_2OH.CH_2.CO.OH - H_2O = CH_2:CH.CO.OH$$

In the first reaction the potassium hydroxide must be used in alcoholic solution; the second occurs on distillation. Since the

---

[1] See Journal of American Chemical Society, XXV, 511.

corresponding nitrile, $CH_2:CH.CN$, does not exist, the general reaction for making acids from their nitriles cannot be employed in this case.

Acrylic acid is not unlike acetic acid in many of its properties, but it gives the reactions which are characteristic of an unsaturated compound, uniting directly with chlorine and bromine, with halogen acids, and with hydrogen (nascent) to form saturated compounds. When oxidized, it breaks at the double bond. The structural formula given it is based on a study of the methods of its formation and its reactions.

Crotonic acids, $C_3H_5CO.OH$. Four acids of this formula are known, two of which have a special theoretical interest, since they have the same constitutional formula, and yet differ widely in their physical characteristics.

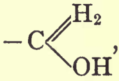
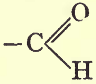
Crotonic acid (first obtained from croton oil) is a solid, melting at 72° and boiling at 181°, and resembles acrylic acid in its general behavior. *Isocrotonic acid* is an oily liquid boiling at 172°, with an odor which recalls that of butyric acid. Both acids are present in crude wood vinegar and both can be made synthetically. Both can be converted into butyric acid by addition of hydrogen halides followed by reduction with nascent hydrogen; and isocrotonic acid is transformed into crotonic acid by continued heating to 170–180°. The constitutional formula given to these acids is $CH_3.CH:CH.CO.OH$, and the differences in the two acids is explained as the result of so-called *geometrical isomerism* which will be discussed later (p. 186).

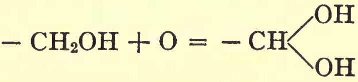
Propiolic acid, $CH:C.CO.OH$, is an illustration of a small group of acids which have a triple bond. It is related to propargyl alcohol (p. 69) as acetic acid is to ethyl alcohol, but cannot be made from this by oxidation. It is a liquid. When cooled it freezes, and the crystalline solid melts at 6°. It is partly decomposed when distilled under ordinary pressure, but distils unchanged in a partial vacuum. It unites the properties of an organic acid with those which are characteristic of acetylene, and in every way justifies the structural formula given it.

Acids with Two or More Double Bonds.—Very few acids of these classes are known. An acid with two double bonds is *sorbic acid*, $CH_3.CH:CH.CH:CH.CO.OH$, which is found in the unripe berries of the mountain ash. It is an odorless, crystalline solid, melting at 134.5°. *Linolic acid*, $C_{17}H_{31}.CO.OH$, whose glyceryl ester is an important constituent of several "drying oils" (*cf.* p. 160a), has also probably two double bonds. Two acids with three double bonds are *linolenic* and *isolinolenic acids*, $C_{17}H_{29}.CO.OH$, whose glyceryl esters are in linseed oil.

Further Study of Oxidation

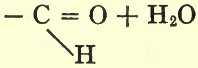
We have learned that the saturated hydrocarbons are not oxidized easily, and that oxidation, when it takes place, usually results in producing the end products, carbon dioxide and water, without such intermediate compounds as alcohols, aldehydes, and acids. When, however, the hydroxyl group is present, as in alcohols, oxidation is easily effected and controlled, so that these compounds may be prepared.

How shall we picture the progress of these oxidations? When alcohol is oxidized into aldehyde, the net result is the removal of two atoms of hydrogen from the primary alcohol group,  $-C\begin{smallmatrix}H_2\\OH\end{smallmatrix}$, with the formation of water and the aldehyde group, $-CHO$. The first suggestion is that the two atoms of hydrogen united to the carbon atom have been simply burned out of the group. This, however, would leave $\equiv C—O—H$, a group still containing hydroxyl, while in the aldehyde group,  $-C\begin{smallmatrix}O\\H\end{smallmatrix}$, the hydrogen and oxygen are both united directly with a saturated carbon atom. An explanation is found in the view that the first action of the oxygen is to form an additional hydroxyl group:



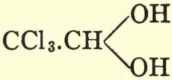
$$-CH_2OH + O = -CH\begin{matrix}OH\\OH\end{matrix}$$

and that this arrangement, being unstable, breaks down at once into

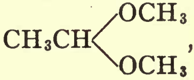


$$-\underset{\diagdown \mathrm{H}}{\mathrm{C}} = \mathrm{O} + \mathrm{H_2O}$$

This view of the "mechanism" of oxidation gains force from the fact that, while very few compounds with two hydroxyl groups united to the same carbon atom are known, the compound whose structural formula is



$$\mathrm{CCl_3.CH}\begin{matrix}\diagup \mathrm{OH} \\ \diagdown \mathrm{OH}\end{matrix}$$

(chloral hydrate) is a well known and comparatively stable substance; and a number of compounds of the type  $\mathrm{CH_3CH}\begin{matrix}\diagup \mathrm{OCH_3} \\ \diagdown \mathrm{OCH_3}\end{matrix}$, the acetals, are known, in which alkyl groups are in the place of the hydrogen of the double hydroxyl compound. According to this view, the formation of a ketone from a secondary alcohol would involve the reactions:

$$\mathrm{CH_3.CH.OH.CH_3} + \mathrm{O} \rightarrow \mathrm{CH_3.C(OH)_2CH_3} \rightarrow$$
$$\mathrm{CH_3.CO.CH_3} + \mathrm{H_2O}$$

while the oxidation of an aldehyde into an acid evidently consists simply in the formation of a hydroxyl group in the manner just described:

$$-\mathrm{CO.H} + \mathrm{O} = -\mathrm{CO.OH}$$

Further, unsaturated hydrocarbons, which are readily oxidized, yield hydroxyl derivatives. This is the view of the course of oxidation which is generally accepted, and it is applicable to all oxidations of organic substances. We may sum the matter up as follows: 1. Saturated hydrocarbons are not readily oxidized except into the end products, carbon dioxide and water. Unsaturated hydrocarbons, on the contrary, are easily oxidized and give hydroxyl derivatives. 2. Saturated compounds already containing oxygen in a hydroxyl group, or an aldehyde group, are easily oxidized, and the oxidation affects first the hydrogen atoms united to the carbon atom already in combination with oxygen. 3. The immediate result of the oxidation is the formation of hydroxyl groups. 4. If two hydroxyl groups are united to a single carbon atom, the system is unstable, and breaks down into oxygen, which remains combined with the carbon by both valencies, and water.

CHAPTER IX

ACID CHLORIDES; ANHYDRIDES; ESTERS

Acyl Chlorides

When phosphorus trichloride is mixed with glacial acetic acid and the mixture gently heated, hydrogen chloride is copiously evolved, and on distillation of the remaining liquid a compound is obtained which boils at 51° and has the molecular formula, C_2H_3OCl. It reacts readily with water, forming acetic and hydrochloric acids. It appears from these reactions that the hydroxyl group of acetic acid is replaced by chlorine, and then restored; so that the structure of the compound first formed is $CH_3.CO.Cl$. This is *acetyl chloride*—the group, $CH_3.CO$ being named the *acetyl group*. With the exception of formic acid, similar compounds can be obtained from all organic acids, and are called, generally, *acyl chlorides*, *acyl* being a general name for the organic acid radical or group, $C_nH_{2n+1}CO$. All attempts to make formyl chloride have failed, as it breaks up at once into carbon monoxide and hydrogen chloride:

$$HCO.Cl = CO + HCl.$$

The general formula for the acid chlorides of the acetic acid series is $C_nH_{2n+1}CO.Cl$.

Preparation.—1. The reaction by which acetyl chloride is prepared, as above, is:

$$3CH_3.CO.OH + 2PCl_3 = 3CH_3.CO.Cl + 3HCl + P_2O_3.$$

2. Phosphorus pentachloride gives the same product together with phosphorus oxychloride:

$$CH_3.CO.OH + PCl_5 = CH_3.CO.Cl + POCl_3 + HCl.$$

These are general reactions for making the acid chlorides. For the lower members of the acetic acid series the reaction with phosphorus trichloride is preferred, since it avoids the formation of the phosphorus oxychloride (boiling point 107°) from which the acyl chloride is separated with some trouble.

Other general reactions for the formation of acid chlorides are the following: 3. By the action of phosphorus chlorides or oxychloride on the sodium salts of the acids, and 4. By withdrawal of the elements of water from a mixture of the acid and hydrogen chloride, which is effected by leading hydrogen chloride into a mixture of the acid and phosphorus pentoxide:

$$CH_3.CO.OH + HCl \overset{P_2O_5}{=} CH_3.CO.Cl + H_2O$$

In the commercial preparation of acetyl chloride (for laboratory use) a mixture of sulphur dioxide and chlorine is passed over anhydrous sodium acetate. Sulphuryl chloride, SO_2Cl_2, appears to be first formed, and this reacts with the acetate as follows:

$$2CH_3.CO.ONa + SO_2Cl_2 = 2CH_3.CO.Cl + Na_2SO_4$$

Properties and Reactions.—The lower members of the series are liquids of penetrating odor, which fume in the air, because of the hydrogen chloride formed by the aqueous vapor present. The boiling points of the acyl chlorides are lower than those of the corresponding acids, an effect of the substitution of chlorine for hydroxyl like that found in the boiling points of alcohols and the corresponding alkyl chlorides. The acyl chlorides react readily with hydroxyl and amido compounds, and acetyl chloride is frequently employed as an organic reagent (*cf.* pp. 124, 138, 329, etc.).

1. The acyl chlorides are insoluble, as such, in water, but are decomposed by it with the formation of the organic acid and hydrochloric acid:

$$CH_3.CO.Cl + H_2O = CH_3.CO.OH + HCl$$

This reaction occurs very readily and violently in cold water with acetyl chloride and a few of the next higher homologues, but more slowly as the molecular weight increases. Similar reactions take place with other hydroxyl compounds.

2. With sodium hydroxide the acetate and chloride of sodium are formed.

3. With alcohols, an ester and hydrogen chloride are formed:

$$CH_3.CO.Cl + C_2H_5OH = CH_3.CO.OC_2H_5 + HCl$$

This reaction with acetyl chloride is a valuable one for determining whether a compound contains the hydroxyl group of an alcohol.

The facility with which these reactions of the acyl chlorides with water and alcohols take place stands in sharp contrast with the behavior of the alkyl chlorides.

4. With organic acids a reaction occurs which is slow and incomplete, but their salts react readily with the formation of simple or mixed acid anhydrides (p. 117):

$$CH_3.CO.Cl + CH_3.CO.OK = (CH_3CO)_2O + KCl$$

5. With ammonia the acid chloride reacts easily with the formation of acid amides (p. 137), and similar reactions occur with substituted ammonias, such as aniline:

$$CH_3.CO.Cl + NH_3 = CH_3.CO.NH_2 + HCl$$

The acyl chlorides, unlike the alkyl chlorides, do not react directly with sodium or other metals.

The acid bromides and iodides are of much less importance than the chlorides. The bromides are sometimes used in preparing bromine substituted acids, as *α*-brompropionic acid, $CH_3.CH.Br.CO.OH$, since replacement by bromine occurs more readily in the acid bromide than in the acid. They can be made by the action of the phosphorus bromide (red phosphorus and bromine) on the acids or their salts.

ACID CHLORIDES AND ANHYDRIDES

Name of Acid	Formula of Radical	Acid Chloride : RCl			Acid Anhydride : R_2O	
		Melting Point	Boiling Point		Melting Point	Boiling Point
Acetic	$CH_3.CO$		51°			136°
Propionic	$C_2H_5.CO$		78			167
Butyric (norm.)	$C_3H_7.CO$		101			192
Butyric (iso)	$C_3H_7.CO$		92			182
Valeric (iso)	$C_4H_9.CO$		115			215
Heptylic	$C_6H_{13}.CO$					268–271
Caprylic	$C_7H_{15}.CO$		83	At 15 mm. pressure		
Pelargonic	$C_8H_{17}.CO$		98		5°	
Capric	$C_9H_{19}.CO$		114			
Palmitic	$C_{15}H_{31}.CO$	12°	192.5		64	
Stearic	$C_{17}H_{35}.CO$	23	215			

Acid Anhydrides

We have seen that by the action of acetyl chloride on sodium acetate a compound is produced with the formula $(CH_3.CO)_2O$. This is the anhydride of acetic acid, which may be regarded as two acid radicals united by oxygen, and derived from two molecules of the acid by the withdrawal of the elements of water. It corresponds, therefore, to the inorganic anhydrides, SO_3, N_2O_5, etc. This view of its constitution follows immediately from the method of its formation, since we know the structure of the acid chloride and of the sodium acetate. In confirmation of this formula is the fact that it is formed (though not readily and only in small amounts) by the action of phosphorus pentoxide on glacial acetic acid:

$$2CH_3.CO.OH + P_2O_5 = (CH_3.CO)_2O + 2HPO_3$$

Similar compounds are obtained corresponding to the other acids of this series, except in the case of formic acid. Formic anhydride $(HCO)_2O$, like its chloride, is too unstable to exist.

Formation.—In addition to the methods already given, the anhydrides can be formed by the action of the acid chlorides on the anhydrous acids; but the reaction, like that of the direct withdrawal of water from the acid, is slow and incomplete. The anhydrides can also be formed from the salts of the acids by heating them with carbonyl chloride:

$$2CH_3.CO.ONa + COCl_2 = (CH_3CO)_2O + CO_2 + 2NaCl$$

They are almost always prepared, however, by the interaction of the sodium salt of the acid and its chloride.

Properties.—Acetic anhydride, or acetyl oxide, and its next homologues are liquids whose boiling points are higher than those of the acids from which they are derived. The anhydrides of greater molecular weight are solids. They are all insoluble in water, but soluble in ether. Acetic anhydride is the most important of this group.

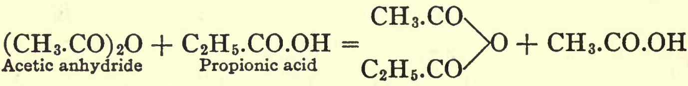
Reactions.—The anhydrides react with hydroxyl compounds in a manner similar to the acid chlorides, but less vigorously, and, like the chlorides, they are much used to identify the alcoholic hydroxyl group.

1. Like the inorganic anhydrides, the organic anhydrides are converted into acids by water. The reaction, however, even with acetic anhydride, is very slow in cold water; and some of the higher anhydrides can be boiled in water for a considerable time without being completely changed. With solutions of alkalies the reaction takes place easily with the formation of the salt of the acid.

2. With alcohols, the anhydrides give an ester and the acid:

$$(CH_3.CO)_2O + C_2H_5OH = CH_3.CO.OC_2H_5 + CH_3.CO.OH$$

3. With organic acids, the anhydrides act only when heated, and then slowly. This reaction gives a method for making mixed anhydrides, for instance, with propionic acid:



$$\underset{\text{Acetic anhydride}}{(CH_3.CO)_2O} + \underset{\text{Propionic acid}}{C_2H_5.CO.OH} = \begin{matrix} CH_3.CO \\ C_2H_5.CO \end{matrix}\!\!>O + CH_3.CO.OH$$

Such mixed anhydrides are decomposed by distillation into the simple anhydrides.

4. With hydrochloric acid, a reaction of the same kind occurs:

$$(CH_3.CO)_2O + HCl = CH_3.CO.Cl + CH_3.CO.OH$$

Acetyl chloride may be thus regarded as a mixed anhydride of acetic and hydrochloric acids.

5. With ammonia, acid amides are formed:

$$(CH_3.CO)_2O + 2NH_3 = \underset{\text{Acetamide}}{2CH_3CO.NH_2} + H_2O$$

6. Chlorine and bromine act very readily on the anhydrides, substituting for one hydrogen atom, while the hydrogen halide which is formed reacts on the substituted anhydride, so that the final products are the acyl halide, and the monohalogen substituted acid; *e.g.*, $CH_3.CO.Cl$ and $CH_2Cl.CO.OH$.

7. Nascent hydrogen (sodium amalgam) reduces anhydrides to aldehydes and alcohols, but the reaction yields other products as well.

The student should compare the reactions of the anhydrides with those of the acyl halides (and esters) and decide how an anhydride may be identified.

Esters of Inorganic Acids

Both inorganic and organic acids react with alcohol with the formation of compounds which are called esters.

Esters of Sulphuric Acid.—When concentrated sulphuric acid is mixed with ethyl alcohol and the mixture heated for some time on a water bath, an acid compound is formed which gives with barium carbonate a soluble barium salt, and thus may be separated from any unchanged sulphuric acid. If just enough sulphuric acid is added to the solution of this barium salt to exactly precipitate the barium, there is obtained, on evaporation of the filtrate, a thick acid liquid which cannot be distilled without decomposition into ethylene and sulphuric acid. Most of the salts of this acid compound are soluble in water and can be obtained pure by crystallization. Analysis of these salts shows that they may be regarded as derived from an acid whose composition is $H(C_2H_5)SO_4$, *ethyl hydrogen sulphate*. The *normal ethyl sulphate* or diethyl sulphate, may be made by the reactions of silver sulphate and ethyl iodide:

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI$$

This reaction gives conclusive evidence as to the structure of this compound.

It is a liquid of pleasant peppermint-like odor, which boils at 208° with only slight decomposition.

Ethyl hydrogen sulphate, or *ethyl sulphuric acid*, is an intermediate product in the reactions by which ethylene and ether are prepared (pp. 46 and 70). Although the final result of these reactions may be expressed as due to the withdrawal of the elements of water from one or from two molecules of alcohol, the actual progress of the reactions is represented by the following equations.

For ethylene:

$$C_2H_5OH + H_2SO_4 \leftrightarrows H(C_2H_5)SO_4 + H_2O$$

and

$$H(C_2H_5)SO_4 = CH_2{:}CH_2 + H_2SO_4$$

In the ether formation, ethyl sulphuric acid is formed as above, and then reacts with another molecule of alcohol:

$$H(C_2H_5)SO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

The course of the principal reaction is determined, as has been stated, by the proportions of acid and alcohol which are used, and the temperature.

Ethyl sulphuric acid is also formed when ethylene is led into the concentrated acid. This gives an interesting method for making ethyl alcohol from inorganic materials. For from calcium carbide (lime and coke), acetylene is obtained by the action of water, and acetylene is readily converted into ethylene by hydrogen in the presence of platinum black.

When heated with water, ethyl sulphuric acid is converted into alcohol and sulphuric acid:

$$H(C_2H_5)SO_4 + H_2O \rightleftarrows C_2H_5OH + H_2SO_4$$

Ethyl sulphuric acid or its salts are frequently used in preparing other ethyl compounds by such reactions as:

$$K(C_2H_5)SO_4 + KBr = C_2H_5Br + K_2SO_4$$

$$K(C_2H_5)SO_4 + KCN = C_2H_5CN + K_2SO_4$$

Sulphuric acid esters containing other alkyl groups may be obtained by the methods given for making the ethyl compounds, and resemble these in their properties.

Esters of Other Inorganic Acids.—The hydrogen of other inorganic acids may be replaced by alkyl groups with the formation of esters. These esters are mostly oily liquids which are more or less easily hydrolyzed into alcohol and acid by water, and are in all cases decomposed by boiling solutions of alkalies into alcohols and salts.

The normal esters are insoluble or only slightly soluble in water, but the acid esters are soluble; an illustration of the influence of the presence of the hydroxyl group on solubility in water. (Compounds containing this group are mostly more or less soluble in water, while those in which the group is absent are usually insoluble or nearly insoluble. Among the compounds we have so far considered this is seen to be true, except in the case of the aldehydes and ketones.)

In the formation of the esters by the direct action of the acids on the alcohols, the reaction is never complete, and when the acid is polybasic an *acid ester* (or alkyl acid) is formed. The best general method for making the *normal esters* is by the reaction between the silver salt of the acid and the alkyl halide as in the case of ethyl sulphate. For instance:

$$Ag_3AsO_3 + 3C_2H_5I = (C_2H_5)_3AsO_3 + 3AgI$$

The acid esters are, as a rule, less stable than the normal ones. They are odorless and decompose when distilled. Their salts, however, are more stable than the esters themselves.

The normal esters often have a pleasant fruity odor, and can usually be distilled without decomposition.

The *nitric* and *nitrous esters* of methyl and ethyl are readily hydrolyzed to acid and alcohol; the nitric esters are converted by nascent hydrogen (tin and hydrochloric acid) into hydroxylamine and alcohol:

$$C_2H_5ONO_2 + 6H = \underset{\text{Hydroxylamine}}{NH_2OH} + C_2H_5OH + H_2O.$$

The nitric ester of glycerol, a polyhydroxyl alcohol, is described on page 159.

Ethyl nitrite, C_2H_5ONO known in alcoholic solution as "sweet spirit of nitre," and isoamyl nitrite are used in medicine.

The alkyl halides are esters of the halogen acids, but on account of their importance in various reactions and the fact that many of them can be made directly from the hydrocarbons by the action of halogens, have been already discussed (p. 31).

ESTERS

	Nitrite B.p.	Nitrate B.p.	Sulphate (neutral) B.p.	Acetate B.p.
Methyl	−12°	66°	187°	57.3°
Ethyl	17	87	208	77.5
Propyl	57	110.5		101.8
Isopropyl	45	101.5		c. 90
Butyl (norm.)	75	.....		124.5
Isobutyl	67	123		116.3

ETHYL ESTERS

	Boiling Point		Boiling Point
Formic acid	55°	Caproic	166.6°
Acetic	77.5	Heptylic	187.1
Propionic	98.8	Caprylic	205.8
Butyric (norm.)	120.9	Pelargonic	227–228
Butyric (iso.)	110.1	Capric	243–245
			Melting Point
Valeric (norm.)	144.7	Palmitic	24°
Valeric (iso.)	134.3	Stearic	34–34

Esters of Organic Acids

Ethyl acetate, which makes its presence known, when ethyl alcohol and acetic acid or an acetate are heated with sulphuric acid, by the agreeable fruity odor which serves as a test for the acetic acid radical, is a typical member of a large group of similar compounds. Several reactions into which it enters have already been given (pp. 35 and 99).

It is formed when alcohol and acetic acid are mixed and heated; but the reaction goes on very slowly and, as it is rather readily reversible, an equilibrium is established far short of completion. An excess of either acid or alcohol causes a larger proportion of the one present in smaller amount to be changed into the ester; and in the presence of a water-withdrawing agent the conversion may be nearly complete. When the ester, already made, is mixed with water it is slowly transformed into acid and alcohol. The reaction by which it is formed appears, thus, to consist in the separation of the elements of water from acid and alcohol:

$$\underset{\text{Acetic acid}}{CH_3.CO.OH} + \underset{\text{Alcohol}}{C_2H_5OH} \rightleftarrows H_2O + \underset{\text{Ethyl acetate}}{CH_3.CO.OC_2H_5}$$

and (since the formulas of the acid and alcohol are known), the formula given in the above equation for the ester is plainly indicated. This is proved to be the right formula by other reactions in which the ester is made from substances with known formulas, as from acetic acid or an acetate with ethyl halide, or from acetyl chloride with sodium ethoxide.

$$CH_3.CO.ONa + C_2H_5I = CH_3.CO.OC_2H_5 + NaI$$

$$CH_3.CO.Cl + C_2H_5ONa = CH_3.CO.OC_2H_5 + NaCl$$

In the usual method for the preparation of ethyl acetate from alcohol and acetic acid with the addition of sulphuric acid, ethyl sulphuric acid is first formed, and then reacts with the acetic acid:

$$H(C_2H_5)SO_4 + CH_3.CO.OH \rightleftarrows CH_3.CO.OC_2H_5 + H_2SO_4$$

In another procedure hydrogen chloride is led into the mixture of acid and alcohol. One explanation of the effect of the hydrogen chloride is that it acts as a water-withdrawing substance, while according to another interpretation of the reaction, acetyl chloride is an intermediate product which then reacts as follows:

$$CH_3.CO.Cl + C_2H_5OH \rightleftarrows CH_3.CO.OC_2H_5 + HCl$$

Ethyl acetate is also formed from alcohol and acetic anhydride (p. 118).

Properties and Reactions.—Ethyl acetate is a liquid which boils at 77° and is soluble in about 17 parts water. It enters readily into a number of reactions.

1. With water it is partly hydrolyzed. The hydrolysis is aided by the presence of a small amount of an inorganic acid and boiling.

2. With caustic alkalies, complete decomposition is readily effected with the production of alcohol and an acetate:

$$CH_3.CO.OC_2H_5 + NaOH = CH_3.CO.ONa + C_2H_5OH$$

This reaction, which can be carried out with all esters, is called "saponification" from the fact that soap is made in this way from fats, which are esters of glycerol (p. 160). The term is often extended to the decomposition by water, in which no salts are produced, and the saponification process is often termed *hydrolysis*.

The rate at which the hydrolysis proceeds depends on the temperature and concentration of the solution as well as on the nature of the hydrolyzing agent and of the ester.

3. Concentrated halogen acids when heated with ethyl acetate form acetic acid and ethyl halide:

$$CH_3.CO.OC_2H_5 + HCl = CH_3.CO.OH + C_2H_5Cl$$

The action is more rapid the higher the molecular weight of the acid; thus hydriodic acid acts most quickly and hydrofluoric acid the most slowly.

4. Ammonia converts ethyl acetate into acetamide (p. 138):

$$CH_3.CO.OC_2H_5 + NH_3 = \underset{\text{Acetamide}}{CH_3.CO.NH_2} + C_2H_5OH$$

Other esters of organic acids may be made by the methods used for ethyl acetate, and their reactions are of the same kind. Many organic esters are found in nature, and a considerable number are manufactured as artificial fruit essences. *Isoamyl acetate* has the odor of pears; *octyl acetate*, that of oranges; *ethyl butyrate*, that of pineapples; *isoamyl isovaleriate* that of apples, etc. The *natural fats*, as we have seen (p. 108), are esters of glycerol, and various *waxes* are composed chiefly of esters of the higher homologues of acetic acid and the higher alcohols. Spermaceti is mostly *cetyl palmitate;* beeswax contains *myricyl palmitate;* etc. (See also p. 160.)

Esters of both inorganic and organic acids are named as alkyl salts of the acids, and sometimes called ethereal salts. Most of their reactions are analogous to those of inorganic salts formed from weak bases and weak acids, and which are readily hydrolyzed. There is, however, this difference, that the hydrolysis of the salts takes place quickly, while that of the esters is slow. In other words, the esters are ionized very slightly, while the salts are usually more or less highly ionized.

The rate at which esters are formed from the alcohol and the acid, and the progress of their hydrolysis are both so slow that these processes have proved very valuable to theoretical chemistry. Their quantitative study has given information as to the influence of different conditions on the velocity of reactions: such as the effect of mass or molecular concentration, of temperature, and of ionic concentration (influence of acids and bases on hydrolysis).

In the esters of organic acids two carbon atoms are united by oxygen. We find a similar linkage in the ethers and in the acid anhydrides. In the ethers two alkyl groups are linked, in the anhydrides two acyl groups. In the esters the two groups held together by oxygen are an alkyl and an acyl group, and we find in comparing the reactions of these three classes of compounds that the esters are in some respects intermediate between the ethers and the anhydrides.

CHAPTER X

AMINES AND AMIDES. NITRO-COMPOUNDS

In several reactions which we have studied, ammonia has been represented as acting in such a way as to produce compounds containing the group NH_2. When this group is united to an alkyl radical, as in $CH_3.NH_2$, the compound is called an *amine;* when combined with an acyl radical, as in $CH_3.CO.NH_2$, an *amide.* The group NH_2 itself receives a correspondingly different name in the two classes of compounds, being termed the *amino group* in amines, and the *amido group* in amides. Both amines and the amides may be regarded as substituted ammonias, and their behavior, especially that of the amines, abundantly justifies this view.

There are, also, related compounds in which two or all three hydrogen atoms of the ammonia molecule are replaced by alkyl or acyl radicals; and the three classes of substituted ammonias are distinguished by the names of *primary*, *secondary*, and *tertiary*, according as one, two,or three hydrogen atoms have been replaced.

The Amines

The amines show their relationship to ammonia by combining directly and additively with acids to form salts which are like the ammonium salts, and from which the amines are liberated by alkalies, just as ammonia is from ammonium salts.

Formation.—1. By the action of ammonia in alcoholic solution on alkyl halides. This reaction does not take place readily, requiring a temperature which can be attained with these volatile substances only by heating them in sealed tubes. The product is a mixture of the three classes of amines together with *quaternary* compounds which are completely substituted ammonium halides. The reactions for the methyl compounds are:

$$NH_3 + CH_3I = CH_3NH_2.HI$$

$$CH_3NH_2.HI + CH_3I = (CH_3)_2NH.HI + HI$$

$$(CH_3)_2NH.HI + CH_3I = (CH_3)_3N.HI + HI$$

$$(CH_3)_3N.HI + CH_3I = (CH_3)_4N.I + HI$$

The formation of a single product cannot be assured by using definite proportions of ammonia and the alkyl halide, and the amounts of the four compounds which are produced depend on the nature of the alkyl group.

The alkyl ammonium salts, with the exception of the tetra-amine salt, are all decomposed by caustic alkalies, yielding ammonia-like amines; in the cases taken for illustration, $CH_3.NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$.

The mixture of amines, obtained by distillation of the salts with caustic alkali, is separated with some difficulty. Fractional distillation is not usually successful, and no entirely satisfactory general method can be given. When dealing with considerable quantities, the following procedure is often employed for the methyl and the ethyl amines: The greater part of the primary amine is obtained as chloride or oxalate by fractional crystallization of these salts. Then by the action of nitrous acid on the residue, the remaining amount of primary amine is decomposed into alcohol, water, and nitrogen, while the tertiary amine is unchanged; and the secondary amine is converted into a *nitroso-amine* (p. 131) which is an oil and readily separated from the unaltered tertiary amine. Finally from the nitroso-amine the secondary amine in the form of its chloride is obtained pure by treatment with concentrated hydrochloric acid.

Other Methods for Making the Amines.—Among the other methods by which primary amines can be formed, the following are the more important.

2. By treating an ester of isocyanic acid (p. 154) with potassium hydroxide:

$$C_2H_5.N{:}C{:}O + 2KOH = C_2H_5NH_2 + K_2CO_3.$$

This method is of especial interest as it is the one by which the first amine was discovered (Wurtz, 1848). The resulting gaseous amine was believed to be ammonia until, by chance, it was found to be inflammable.

3. From amides (p. 137), by treatment with bromine and sodium hydroxide (or sodium hypobromite); *Hofmann's reaction.*✓ The reaction, whose net result is the removal of CO from the acetamide, proceeds by the following steps:

$$CH_3.CO.NH_2 + Br_2 + NaOH = CH_3.CO.NHBr + NaBr + H_2O$$
$$CH_3.CO.NHBr + NaOH = CH_3.N{:}C{:}O + NaBr + H_2O$$
$$CH_3.N{:}C{:}O + 2NaOH = CH_3.NH_2 + Na_2CO_3.$$

The last step in this method is the Wurtz reaction given above (2).

This reaction furnishes a means of "building down" from higher to lower hydrocarbon derivatives. For instance, starting with propyl alcohol, ethyl alcohol may be made by the following steps:

$$CH_3.CH_2.CH_2.OH \rightarrow CH_3.CH_2.CO.OH \rightarrow CH_3.CH_2.CO.NH_2 \rightarrow CH_3.CH_2.NH_2 \rightarrow CH_3.CH_2.OH.$$

The last step is effected by decomposition of the amine nitrite (p. 131). (Compare this method of going from one compound to another with a less number of carbon atoms with the formation of hydrocarbons from the salts of the higher acids.)

4. By reduction of various nitrogen compounds—nitro-compounds, alkyl cyanides, oximes, and hydrazones. From the alkyl cyanide (nitrile), for example, by "nascent" hydrogen:

$$CH_3.CN + 4H = CH_3.CH_2.NH_2$$

This is best effected by the action of sodium in alcoholic solution.

Since the formation of an alkyl cyanide adds an atom of carbon to the original compound, its conversion into an amine may be employed as a means of passing from one alcohol to the next higher in the series. For instance, $CH_3OH \rightarrow CH_3I \rightarrow CH_3.CN \rightarrow CH_3.CH_2NH_2 \rightarrow CH_3.CH_2OH$. The last step is effected by the decomposition of the amine with nitrous acid.

5. From alkyl esters of inorganic acids by the action of ammonia. The reaction with the esters of the halogen acids (alkyl halides) has already been discussed. The nitric and sulphuric acid esters react in a similar manner. The action of ammonia on the esters of organic acids produces acid amides and alcohol.

In spite of the numerous methods for forming amines, there is no way by which the pure substances may be easily prepared in any quantity.

Properties.—The primary, secondary, and tertiary methyl amines, and primary ethyl amine are gases at ordinary temperatures. The amines of higher molecular weight are liquid and finally solid. The lower amines have odors unpleasantly resembling that of ammonia, and are freely soluble in water. The odor grows less and the solubility decreases with an increase in the number of the carbon atoms, and the highest amines are odorless and insoluble. They are all lighter than water. The solutions of the lower amines are strongly alkaline, and like that of ammonia probably contain the unstable hydroxides of the alkyl ammoniums. The ionization of these hydroxides is shown by their alkaline reaction, by the precipitation of hydroxides of metals from their salt solutions, and by the readiness with which they form ammonium-like salts. Their electrical conductivity indicates that the lower amine hydroxides are more highly dissociated than ammonium hydroxide, the bacisity being least in the tertiary, and greatest in the secondary amines (*cf.* p. 410).

The halide salts of amines are soluble in alcohol and may be thus separated from ammonium halides which are insoluble. Like ammonium chloride, however, the amine chlorides form double salts with platinum chloride, which are sparingly soluble in alcohol. Methyl and ethyl amines differ from ammonia most markedly by their inflammability; and their hydroxides, unlike solutions of ammonia, dissolve aluminium hydroxide.

Reactions.—1. On oxidation of the amines, the alkyl groups are split off and converted into the corresponding aldehydes or acids.

The other reactions of the amines differ with the number of alkyl groups they contain. The tertiary amines are rather indifferent to reagents, while the primary amines are more readily acted on than the secondary.

2. An important reaction which serves to distinguish the three classes is that with nitrous acid. A *primary amine* in acid solution, when warmed with sodium nitrite, decomposes with the production of nitrogen, alcohol, and water:

$$C_2H_5.NH_2 + HNO_2 = N_2 + C_2H_5OH + H_2O$$

We may suppose that the nitrite of the amine, $C_2H_5NH_2.HNO_2$, is first formed and then decomposes like ammonium nitrite, where, however, as no alkyl group is present, nitrogen and water, instead of alcohol and water, are formed:

$$NH_4NO_2 = N_2 + HOH + H_2O$$

On secondary amines, nitrous acid acts less vigorously, and gives insoluble *nitroso-amines*, compounds in which the hydrogen of the amine is replaced by the *nitroso-group*—NO:

$$(C_2H_5)_2{:}NH + HONO = (C_2H_5)_2{:}N.N{:}O + H_2O$$

When a nitroso-amine is treated with phenol and concentrated sulphuric acid, it gives a dark green solution which becomes red when diluted with water, and with an excess of alkali assumes an intense blue or green. This reaction (*Liebermann's*) serves for the detection of nitroso-amines and hence of secondary amines.

On *tertiary amines*, nitrous acid hardly acts at all, and if action occurs it is usually with the production of oxidation products and oxides of nitrogen.

Since the secondary amines can be recovered from their nitroso-compounds by means of concentrated hydrochloric acid, the reaction gives a means for obtaining them from mixtures with the other two:

$$(C_2H_5)_2{:}N.N{:}O + 2HCl = (C_2H_5)_2{:}NH.HCl + NOCl$$

3. Primary amines give a characteristic reaction with chloroform and caustic alkali. When warmed with chloroform and an alcoholic solution of potassium hydroxide, an isocyanide (formerly called carbylamine) is formed which is recognized by its characteristic and unendurable odor (*carbylamine reaction*):

$$C_2H_5.NH_2 + CHCl_3 + 3KOH = \underset{\text{Ethyl isocyanide}}{C_2H_5.NC} + 3KCl + 3H_2O.$$

4. With both primary and secondary amines, acetyl chloride reacts at once without warming, forming compounds by the withdrawal of hydrogen chloride. With tertiary amines no reaction occurs.

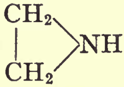
With alkyl halides, primary amines combine additively, forming the halide salt of the secondary amine. Secondary amines, in like manner, give the tertiary; and the tertiary, the quaternary amine salt.

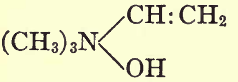
Some Individual Amines.—All three of the methyl amines occur in herring brine, the tertiary amine in the largest proportion. They are all gases. The primary amine has an odor very like that of ammonia, but with a fishy suggestion. In the secondary and tertiary amines the fishy character of the odor becomes very pronounced. *Monomethyl amine* also occurs in *Mercurialis perennis*, and is one of the products of the destructive distillation of wood, bones, and other natural substances. *Trimethyl amine* is found in a number of plants, and can be obtained from wine by distilling with caustic alkali. Commercial "trimethyl amine," obtained as a product of the dry distillation of residues left after making alcohol from beet-root molasses, is chiefly dimethyl amine (50 per cent.) with monomethyl and several higher amines, and only about 5 per cent. of the trimethyl amine. It is used as a source of methyl chloride and ammonia:

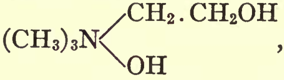
$$(CH_3)_3N + 4HCl = 3CH_3Cl + NH_4Cl$$

The best method for the laboratory preparation of trimethyl amine is by the distillation of tetramethyl amine hydroxide (p. 135). It is curious that trimethyl amine, which has a most offensive odor when diluted with other gases, is almost indistinguishable from ammonia when concentrated.

Hexamethylene tetramine, $C_6H_{12}N_4$, formed by the action of ammonia on formaldehyde (p. 84), is a weakly basic crystalline substance which under the name "urotropin," and in the form of the ethyl bromide, "bromalin," and of the salicylate, "salformin," has found some use in medicine. When heated with acids, it breaks up into formaldehyde and ammonia, some methyl amine being formed at the same time. Its constitution is unknown.

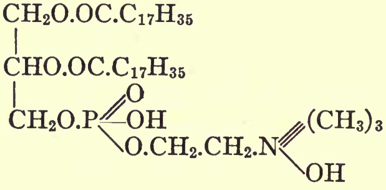
Vinyl amine, either $CH_2:CH.NH_2$ or  $\left.\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right\rangle NH$, is often cited as an unsaturated amine; but as it does not decolorize potassium permanganate as an unsaturated compound should, the second, cyclic formula, is the more probable one. The amine is known only in its strongly alkaline (hydroxide) aqueous solution and in its salts. It is made from bromethyl amine, $CH_2Br.CH_2NH_2$, by means of moist silver oxide or potassium hydroxide. It combines with sulphurous acid to form *taurine*, $CH_2(SO_3H).CH_2NH_2$, which in combination with cholic acid is the chief constituent of bile.

Neurine,  $(CH_3)_3N\begin{array}{l}\diagup CH:CH_2\\ \diagdown OH\end{array}$ is a mixed quaternary amine hydroxide which contains the vinyl radical. It has been synthesized, and is a substance of physiological importance, being formed in the putrefaction of meat and in other fermentative processes. It is very poisonous, belonging to the class of basic compounds formed in the decay of animal substances which are known as *ptomaines*, many of which are also poisonous. Neurine is a strong base and gives well-characterized salts.

Choline,  $(CH_3)_3N{<}^{CH_2.CH_2OH}_{OH}$, ethylol-trimethyl-ammonium hydroxide, is a mixed quaternary base in which hydroxyl has been substituted in the ethyl group.

The constitution of choline as represented in the formula has been established by its synthetical formation. It is obtained as one of the products of the hydrolysis of compounds called lecithins (λέκιθος, egg-yolk) which are found in all animal and vegetable tissues.

Lecithins are complex compounds which may be regarded as mixed glycerol esters of palmitic, stearic, or oleïc, and phosphoric acids, combined with choline. The formula for stearin-lecithin, which occurs in egg-yolk, is



When boiled with barium hydroxide, barium stearate, $(C_{17}H_{35}\text{-}CO.O)_2Ba$, is precipitated, choline is set free, and the barium salt of glycero-phosphoric acid, $CH_2OH.CHOH.CH_2.OPO(O_2Ba)$, is formed.

The importance of the lecithins in the functions of life is evident from their universal occurrence in the tissues and especially in the nervous tissue; and from the fact that they form a constant constituent of milk.

The lecithins are wax-like, hygroscopic substances, which swell up in water to gelatinous masses. They are soluble in alcohol, ether and chloroform, and crystallize with difficulty.

Cephalin, closely related to lecithin and probably as generally present in the tissues, is a derivative of amino ethyl alcohol as lecithin is of choline.

Tetraalkylammonium Hydroxides.—The quaternary halides are obtained by the direct union of a tertiary amine and the alkyl halide, and therefore appear in the mixture of amine salts formed by the reaction of ammonia on alkyl halides. It has been already stated that the tetraalkyl amines cannot be set free from their salts, like other amines, by caustic alkalies. When, however, solutions of the halide salts are digested with silver oxide, silver halide is formed and the solution becomes strongly alkaline. By evaporation in a vacuum, a white crystalline mass is obtained which is believed to be the hydroxide of the amine:

$$(CH_3)_4NI + AgOH = (CH_3)_4NOH + AgI$$

The tetraalkyl ammonium hydroxides are very strong bases, resembling the caustic alkalies in their behavior. For this reason the caustic alkalies do not react with their salts in aqueous solution; such a reaction would be like one between sodium hydroxide and potassium chloride with the formation of potassium hydroxide. The reaction with silver hydroxide is in consequence of the insolubility of silver iodide. Similarly, the hydroxides may be obtained from the chlorides by using potassium hydroxide in alcoholic solution, since potassium chloride is insoluble in alcohol.

These substituted ammonium hydroxides in solution absorb carbon dioxide from the air with the formation of carbonates, corrode the flesh, and saponify fats. When heated, they decompose with the formation of tertiary amines. Tetramethyl ammonium hydroxide, for example, gives trimethyl amine and alcohol:

$$(CH_3)_4NOH = (CH_3)_3N + CH_3OH$$

but the homologous compounds give an olefine and water:

$$(C_2H_5)_4NOH = (C_2H_5)_3N + C_2H_4 + H_2O$$

AMINES

	Primary		Secondary	Tertiary
	Melting Point	Boiling Point	Boiling Point	Boiling Point
Methyl	. . . . .	−6°	7°	3.5°
Ethyl	. . . . .	+16.2	56	90
Propyl	. . . . .	49	98	156
Propyl (iso)	. . . . .	32	84	
Butyl	. . . . .	76	160	215
Butyl (iso)	. . . . .	66	136	187
Butyl (sec.)	. . . . .	63		
Butyl (tert.)	. . . . .	46		
Amyl (iso)	. . . . .	95	187	235
Hexyl	. . . . .	129		260
Dodecyl	27°	248		
Tridecyl	27	265		
Heptadecyl	49	335–340		

Phosphines and Arsines

Alkyl derivatives of phosphine, PH_3, and of arsine, AsH_3, are known which are analogous to the amines. All of the classes of the amines are represented in the phosphines. The primary, secondary, and tertiary phosphines are weakly basic, but the alkylphosphonium hydroxides (*e.g.*, $(CH_3)_4POH$) are strong bases. Primary and secondary arsines in their chlorine and oxygen derivatives, such as CH_3AsCl_2, $(CH_3)_2AsCl$, and $(CH_3)_2As.O.As(CH_3)_2$ have been long known, and more recently the arsines themselves have been prepared and investigated. $(CH_3)AsH_2$ boils at 2°, $(CH_3)_2AsH$ boils at 36° and is spontaneously inflammable. The tertiary arsines such as $(CH_3)_3As$ have no basic properties, but the quaternary arsine hydroxide, $(CH_3)_4AsOH$, forms salts like the corresponding phosphorus and nitrogen compounds. We notice here a gradation in the behavior of amines, phosphines, and arsines which tallies with that which appears in comparing the other compounds of nitrogen, phosphorus, and arsenic.

Cacodyl Oxide, $(CH_3)_2As.O.As(CH_3)_2$, is a liquid of frightful odor, which is formed by distilling arsenious oxide with an acetate:

$$As_2O_3 + 4CH_3CO.OK = (CH_3)_2As.O.As(CH_3)_2 + 2K_2CO_3 + 2CO_2$$

This substance reacts with hydrochloric acid to form cacodyl chloride, $(CH_3)_2AsCl$; and from this, by the action of zinc, free *cacodyl*, $(CH_3)_2As.As(CH_3)_2$, is produced, as a spontaneously inflammable liquid.

The cacodyl radical, $(CH_3)_2As$, enters into many combinations, and is readily transferred by simple reactions from one compound to another. Cacodyl and its compounds are of great historical interest in the theory of organic radicals through their investigation by Bunsen (1837–1843). The compounds of cacodyl have very repulsive odors and are poisonous.

The Amides

The amides may be defined as ammonias in which hydrogen is replaced by acyl groups, or as acids whose hydroxyl is replaced by the NH_2 group.

As in the case of amines, we have primary, secondary, and tertiary amides, but quaternary amides, or compounds of them, are not known.

Formation.—*Primary amides can be made:* 1. From the ammonium salts of the acids by the removal of the elements of water through heating:

$$CH_3.CO.ONH_4 \rightleftarrows \underset{\text{Acetamide}}{CH_3.CO.NH_2} + H_2O$$

But since the ammonium salts of the fatty acids dissociate to a considerable degree into the acids and ammonia, when heated under ordinary pressure, this reaction is usually carried out at a high temperature (200°–250°) in sealed tubes. It is a reversible reaction and hence only a partial conversion into amide occurs—

under the above conditions some 75 per cent. of the theoretical amount is obtained.

A more convenient way which has been used for making acetamide, in which the use of sealed tubes is avoided, is by boiling dry ammonium acetate with rather more than its weight of glacial acetic acid for several hours with a reflux condenser. The water is thus removed, and the acetic acid on the principal of mass action inhibits the dissociation of the salt into acid and ammonia.

2. From esters, by the action of ammonia:

$$CH_3.CO.OC_2H_5 + NH_3 = CH_3.CO.NH_2 + C_2H_5OH$$

With esters which are quite soluble in water this reaction goes easily. The alcohol and water are readily removed by distillation.

3. From acid chlorides or anhydrides:

$$CH_3.CO.Cl + 2NH_3 = CH_3.CO.NH_2 + NH_4Cl$$
$$(CH_3.CO)_2O + 2NH_3 = 2CH_3.CO.NH_2 + H_2O$$

The reaction with acid chlorides is analogous to that for making amines from alkyl chlorides, but takes place much more easily—in the case of acetyl chloride, at room temperature. The difference is due to the presence of an acid group (acyl) instead of a basic group (alkyl). For the same reason, the reaction of ammonia with acid anhydrides is readily effected, while the analogous reaction for the formation of an amine from ether and ammonia does not take place at all.

4. From nitriles (alkyl cyanides) by partial hydrolysis. This is accomplished by dissolving the nitrile in concentrated sulphuric acid or by treatment with concentrated hydrochloric acid; also by means of hydrogen peroxide in alkaline solution:

$$CH_3CN + H_2O = CH_3CO.NH_2$$
$$C_5H_{11}CN + 2H_2O_2 = C_5H_{11}CO.NH_2 + O_2 + H_2O$$

Secondary amides are formed by reaction between primary amides and acid anhydrides, the acid being formed at the same time:

$$CH_3.CO.NH_2 + (CH_3.CO)_2O = (CH_3CO)_2NH + CH_3.CO.OH$$

or by heating nitriles with organic acids:

$$CH_3.CN + CH_3.CO.OH = (CH_3.CO)_2NH$$

Tertiary amides can be made by heating nitriles with acid anhydrides:

$$CH_3.CN + (CH_3.CO)_2O = (CH_3.CO)_3N$$

Neither of these classes of amides is of special importance.

Properties.—Formamide, $HCO.NH_2$ is a liquid. The other amides are crystalline solids. The amides of the lower acids are deliquescent and very soluble in water. They distil without decomposition at temperatures which are higher than the boiling points of the corresponding acids; formamide, however, suffering partial decomposition into ammonia and carbon monoxide. It may be noted that the boiling points of the amines are much lower than those of the hydroxyl compounds (alcohols) to which they bear the same relation as that of the amides to the acids. The amides usually have a disagreeable odor, which, however, is in most instances due to certain impurities. Acetamide, for example, when carefully purified, is odorless. Amides of highest molecular weight are almost insoluble in water, but they all dissolve in alcohol or ether.

Reactions.—Certain differences between amides and amines have been noted in respect to the reactions for their formation; and similar differences, also due to the presence of an acyl group instead of an alkyl group, are observed in the various reactions into which they enter. In the amides the basic and acidic properties are balanced so that they are neutral substances, while the amines are strong bases.

1. With strong acids amides form rather unstable salts, such as $CH_3.CO.NH_2HCl$.

2. On the other hand, the hydrogen atoms of the NH_2 group can be replaced by some metals. With mercuric oxide, for instance, the compound, $(CH_3.CO.NH)_2Hg$, is formed, whose alcoholic solution yields colorless crystals, melting at 195°.

3. The most characteristic reaction of the amides, and that in which their difference from the amines is most striking, is their ready hydrolysis, by which the bond between the nitrogen and carbon is broken, with the formation of ammonia and the corresponding acid (or the ammonium salt):

$$CH_3.CO.NH_2 + H_2O = CH_3.CO.OH + NH_3$$

This hydrolysis is a reversal of the first reaction given for their formation (p. 137), and occurs when they are heated with water alone, but more rapidly when an inorganic acid or alkali is present (*cf.* hydrolysis of esters, p. 124). Amines do not enter into an analogous reaction with water with the formation of ammonia and an alcohol; but at high temperatures amides act on alcohols, giving either an ester and ammonia, or the acid and a primary amine:

$$CH_3.CO.NH_2 + CH_3.OH = CH_3.CO.OCH_3 + NH_3$$
$$CH_3.CO.NH_2 + CH_3.OH = CH_3.CO.OH + CH_3NH_2$$

4. By the action of phosphorus pentoxide, the elements of water are withdrawn from amides, with the production of nitriles, thus reversing the reaction by which they are formed from these compounds.

5. Like the primary amines, the amides are changed into the corresponding hydroxyl compounds (acids) by the action of nitrous acid:

$$CH_3.CO.NH_2 + HNO_2 = CH_3.CO.OH + N_2 + H_2O$$

6. The reaction of amides with bromine and caustic alkalies has already been given (p. 129).

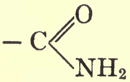
7. Amides are decomposed by concentrated nitric acid with evolution of nitrous oxide:

$$CH_3.CO.NH_2 + HNO_3 = CH_3.CO.OH + H_2O + N_2O.$$

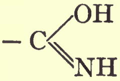
In this reaction the nitrate of the amide, $CH_3.CO.NH_2HNO_3$, is first formed and its decomposition is like that of ammonium nitrate:

$$NH_4NO_3 = N_2O + 2H_2O.$$

Structure of Amides.—We have assumed, in discussing the amides, that the structure of their characteristic group is



The only other arrangement possible would be



The facility with which an amide is formed from an ammonium salt, and the easy exchange of the amido-group for the hydroxyl are in favor of the first formula. The second formula with its hydroxyl group calls for an alcoholic character which is not indicated by most of the behavior of the amide. In the compound which acetamide forms with mercury, however, there is reason for believing that the metal is linked to carbon by oxygen, so that this substance is probably derived from a compound with the second formula. Unfortunately this question cannot be settled, as in other cases, by studying chlorine replacement products formed by the action of phosphorus pentachloride, because these products, if formed at all, are very unstable, breaking down almost at once into nitriles. Since the first formula agrees with most of the facts, it is taken as representing the ordinary structure of amides.

AMIDES

		Melting Point	Boiling Point
Formamide	$HCO.NH_2$	−1°	200–212°
Acetamide	$CH_3.CO.NH_2$	83	222
Propionamide	$C_2H_5.CO.NH_2$	79	213
Butyramide	$C_3H_7.CO.NH_2$	115	216
Butyramide (iso)	$C_3H_7.CO.NH_2$	128–129	216–220
Valeramide	$C_4H_9.CO.NH_2$	114–116(?)	
Capronamide	$C_5H_{11}.CO.NH_2$	100	255
Heptylamide	$C_6H_{13}.CO.NH_2$	95	250–258
Caprylamide	$C_7H_{15}CO.NH_2$	105–106	
Pelargonamide	$C_8H_{17}.CO.NH_2$	99	
Capramide	$C_9H_{19}.CO.NH_2$	98	
Palmitamide	$C_{15}H_{31}.CO.NH_2$	106–107	
Stearamide	$C_{17}H_{35}.CO.NH_2$	109	

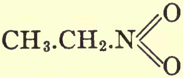
Nitro-paraffins

Hydrocarbons in which one or more hydrogen atoms have been replaced by the $-NO_2$ group, with a direct linkage of nitrogen to carbon, are called *nitro-compounds*. In the benzene series of hydrocarbons, these compounds are of great importance, and are readily made by the action of nitric acid upon the hydrocarbons; but the nitro-paraffins are seldom formed, and then in small amount, when nitric acid is forced to act on the indifferent hydrocarbons. They are relatively unimportant and were not known until 1872. They are briefly described here because of their relation to the amines.

Formation.—The most important method for making the nitro-paraffins is by adding an alkyl iodide gradually to solid silver nitrite:

$$CH_3.CH_2I + AgNO_2 = CH_3.CH_2.NO_2 + AgI$$

Except in the case of the methyl compound, the distillate from this reaction contains two substances which are readily separated by redistillation, as their boiling points are widely different. Both of the ethyl derivatives have the percentage composition and the molecular weight indicated by the formula given above. The one with the lower boiling point is readily hydrolyzed with the formation of alcohol and nitrous acid; and by nascent hydrogen it is reduced to alcohol and ammonia or hydroxylamine (*cf.* p. 122). It is evidently ethyl nitrite or nitrous ester, with the formula $CH_3.CH_2O.N:O$. The isomeric, higher boiling compound, is not hydrolyzed, and on reduction gives an amine, $CH_3.CH_2.NH_2$. We conclude from these facts that this is a true nitro-compound with the nitrogen directly united to carbon; while in the ester it is linked to carbon by oxygen. The structure of the nitro-compound is, therefore,



$$CH_3.CH_2.N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$$

Nitro-compounds are not produced from alkyl halides by the action of other nitrites, such as $NaNO_2$ or KNO_2. Silver nitrite appears therefore to have a different constitution from other nitrites and to be $Ag.NO_2$ with some $Ag.O.NO$.

Properties.—The nitro-paraffins are liquids of pleasant odor, which distil without decomposition, and are almost insoluble in water. The lower ones are heavier than water, but the specific gravity grows less as the number of carbon atoms increases, that of nitrobutane being already lighter than water. The lower nitro-paraffins have acid characteristics, due to the strongly negative nature of the NO_2 group. They dissolve in aqueous solutions of alkalies, and are precipitated from these solutions by acids. From an alcoholic solution of sodium hydroxide a sodium salt, $CH_3.CHNa.NO_2$ is precipitated. These salts decompose explosively when heated. The most important reaction of the nitroparaffins is that of their reduction to amines by "nascent" hydrogen.

The introduction of more than one nitro group cannot usually be effected directly, and only a few of the more highly nitrated paraffins have been made. Dinitromethane, $CH_2(NO_2)_2$, and trinitromethane, $CH(NO_2)_3$, "nitroform," are unstable oils, the latter exploding violently when heated. Tetranitromethane, $C(NO_2)_4$, however, is a stable liquid that can be distilled without decomposition.

CHAPTER XI

CYANOGEN AND CYANOGEN COMPOUNDS

The student has already learned, in inorganic chemistry, something about cyanogen, and has become acquainted with certain cyanogen compounds, particularly with potassium cyanide, and potassium ferro and ferricyanides, which are used as reagents in analysis. In the first chapter of this book the formation of sodium cyanide, on heating a nitrogen-containing organic substance with sodium, was given as a means for the detection of nitrogen. Nearly all nitrogenous organic substances react in this way with sodium or potassium, and on digestion of the soluble cyanide with a ferrous salt, the ferrocyanide of sodium or potassium is formed.

The chief sources of the cyanogen compounds are:

1. Potassium ferrocyanide, which is made commercially by heating a mixture of crude potash (K_2CO_3), scrap iron, and refuse animal substances, such as clippings of leather or horn, or dried blood, and treating the mass, after cooling, with water. Yellow crystals of the ferrocyanide are obtained from this solution. From the ferrocyanide, potassium cyanide, KCN, is obtained by heating it alone or with potassium carbonate.

2. Sodium cyanide, NaCN, is made in large quantities by passing ammonia over sodium at 300°–400°, and decomposing the sodium amide, $NaNH_2$, thus formed, by carbon at a red heat:

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

$$NaNH_2 + C = NaCN + H_2$$

Sodium cyanide may also be successfully manufactured by a method recently described by J. E. Bucher[1] in which nitrogen reacts with a mixture of sodium carbonate and powdered coke at a red heat in the presence of finely divided iron as a catalyst:

$$Na_2CO_3 + 4C + N_2 \ (+ Fe) - 2NaCN + 3CO \ (+ Fe)$$

Producer gas may be used to furnish the nitrogen, and in this case the carbon monoxide of the gas, under the catalyzing effect of the iron, yields a continuous supply of finely divided carbon:

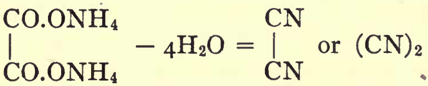
$$CO + C \rightleftarrows CO_2 + 38{,}080 \text{ calories}$$

Compounds containing cyanogen are also obtained by heating the carbides of calcium or barium in nitrogen. The calcium compound, CN.NCa, calcium cyanamide, "nitrolime," is manufactured on a large scale from calcium carbide and nitrogen from liquid air. It slowly decomposes in the soil, producing ammonia: $CN.NCa + 3H_2O = 2NH_3 + CaCO_3$ and is used, on this account, as a fertilizer, thus making atmospheric nitrogen available for plant life. With superheated steam all the nitrogen of cyanamide is converted into ammonia which is now prepared commercially in this way. Cyanamide on fusion with salts of alkalies and carbon yields the alkali cyanide:

$$CN.NCa + C + 2NaCl = NaCN + CaCl_2$$

Cyanogen $(CN)_2$.—The cyanogen radical, CN, can be transferred from one compound to another like the halogen atoms; and like them it is incapable of independent existence, but when forced from combination unites with itself forming molecules of $(CN)_2$, similar to the diatomic molecules of chlorine, etc. The evidence for this is its molecular weight as found from its density.

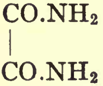
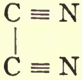
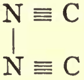
Cyanogen is formed when ammonium oxalate is strongly heated with phosphorus pentoxide:



$$\begin{array}{l} CO.ONH_4 \\ | \\ CO.ONH_4 \end{array} - 4H_2O = \begin{array}{l} CN \\ | \\ CN \end{array} \text{ or } (CN)_2$$

---

[1] Journal of Industrial and Engineering Chemistry, IX, 233 (1917).

This reaction, and the fact that an intermediate product, oxamide,  $\begin{array}{l}CO.NH_2\\ |\\ CO.NH_2\end{array}$, can be made both from ammonium oxalate and from cyanogen, are evidence that cyanogen is the nitrile of oxalic acid, and from the known structure of oxalic acid (p. 178) we conclude that that of cyanogen is  $\begin{array}{l}C \equiv N\\ |\\ C \equiv N\end{array}$ and not  $\begin{array}{l}N \equiv C\\ |\\ N \equiv C\end{array}$, which would be the other possible arrangement with tetrad carbon.

Preparation.—Cyanogen is prepared by heating mercuric cyanide:

$$Hg(CN)_2 = (CN)_2 + Hg$$

or more conveniently by slowly adding a solution of copper sulphate to a warm solution of potassium cyanide. The cupric cyanide first formed decomposes readily into cuprous cyanide, CuCN, and cyanogen. Cyanogen is also a product of the electrolysis of sodium cyanide.

Properties.—Cyanogen is a poisonous gas of characteristic pungent odor. It burns with a purple-fringed flame. It is somewhat soluble in water, but the solution is unstable. A brown solid separates, and the solution contains oxalate and carbonate of ammonia, hydrocyanic acid, and urea. A polymeric form of cyanogen of unknown molecular weight is produced in the form of a brown solid as a by-product in making cyanogen from mercuric cyanide; and in the electrolysis of potassiun cyanide all of the cyanogen is converted into this modification, which is called *paracyanogen*. At 860° this changes to cyanogen.

Cyanogen is readily converted into oxamide (p. 180) when led into hydrochloric acid containing 44 per cent. of hydrogen chloride. On heating the oxamide with the concentrated acid, the hydrolysis to oxalic acid is quickly completed (Bucher). When led into solutions of potassium hydroxide, cyanogen forms compounds analogous to those given by chlorine or bromine, namely, potassium cyanide, KCN, and cyanate, KOCN.

Hydrocyanic acid, HCN, commonly known as *prussic acid,* occurs in all parts of a tree, *Pangium edule,* which is native in Java. The seed-kernels of this tree are a deadly poison, but by soaking in flowing water the hydrocyanic acid is removed, and they are then used by the Malays as food. A substance called *amygdalin* which occurs in the leaves of laurel and cherry, and in the kernels of peach-stones, in bitter almonds, and other substances, when softened by water, usually undergoes a fermentation, one of whose products is prussic acid.

Hydrocyanic acid is readily made by distilling potassium cyanide or potassium ferrocyanide with dilute sulphuric acid:

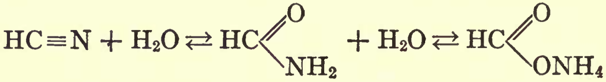
$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + 3K_2SO_4 + \underset{\text{Ferrous potassium ferro-cyanide}}{FeK_2Fe(CN)_6}$$

(Concentrated sulphuric acid with the ferrocyanide yields no hydrocyanic acid, but carbon monoxide.) The distillate is a dilute solution of hydrocyanic acid. The anhydrous acid is obtained by drying the vapors from this reaction by means of calcium chloride and condensing them by a freezing mixture.

Properties.—The anhydrous acid is a volatile liquid, boiling at 26°. It has the odor of bitter almonds, and burns with a violet flame. When unmixed with water the acid can be kept without change, but its solutions are unstable, depositing a brown substance with the production of ammonium formate and other compounds. This decomposition is retarded by the presence of a very small amount of an inorganic acid. Hydrocyanic acid is a very weak acid, hardly reddening litmus paper. It does not decompose carbonates, but, on the contrary, is set free from its salts by carbonic acid; and, in consequence, potassium cyanide always smells of prussic acid when exposed to the air. Hydrocyanic acid and the cyanides which contain the ion CN are very powerful and rapidly acting poisons. Complex ions containing cyanogen, like $Fe(CN)_6$, in solutions of potassium ferro- and ferricyanides, are not poisonous.

Structure.—Two structural formulas for hydrocyanic acid can be written: $H-C\equiv N$, and $H-N\equiv C$, or $H-N=C$.[1]

From the structure agreed on for cyanogen, $N\equiv C-C\equiv N$, the first of these, $H-C\equiv N$, is indicated. Some reactions are better explained by this formula, some by the second, and some are equally well explained by either. The first formula is that of a nitrile of formic acid, and hydrocyanic acid can be hydrolyzed to formamide and to formate of ammonium, and the reverse reactions can also be carried out:



$$HC\equiv N + H_2O \rightleftarrows HC\begin{matrix}\diagup O \\ \diagdown NH_2\end{matrix} + H_2O \rightleftarrows HC\begin{matrix}\diagup O \\ \diagdown ONH_4\end{matrix}$$

By nascent hydrogen hydrocyanic acid is converted into methyl amine:

$$H-C\equiv N + 4H = CH_3.NH_2$$

As nitrogen readily changes its valence from three to five and from five to three, these reactions might be written with the second formula.

When potassium cyanide acts on an alkyl halide, a nitrile is formed in which the carbon of the cyanogen group is certainly united to the CH_3 group:

$$CH_3I + KCN = CH_3CN + KI$$

But this again could be explained, through change of valence, by the other formula. Silver cyanide, however, with an alkyl halide, gives an isomeric compound whose structure has been proved to be $CH_3.N\equiv C$, or $CH_3.N=C$. The cyanogen group appears, therefore, in both arrangements, $-C\equiv N$ and $-N\equiv C$ or $-N=C$. The former is that usually adopted as that of *hydrocyanic acid*, whose formula is therefore written, $H-C\equiv N$; while the isomeric form, $H-N\equiv C$ or $H-N=C$, is called *isohydrocyanic acid;* the group $-N\equiv C$ or $-N=C$ being

---

[1] In this formula, and others which will be discussed, carbon is represented as divalent or unsaturated, as it is in CO.

called the *isocyanogen group*. Both of the possible forms may be present together. The great difficulty in deciding this question is the absence of an alkyl group. When such a group, instead of hydrogen, is combined with cyanogen, the decision is easily made by finding whether, in reactions by which the molecule is broken up, the carbon or the nitrogen atom of the CN group remains attached to the alkyl.

For the properties and uses of the salts of hydrocyanic acid, and of the ferro and ferricyanides of the metals the student is referred to his text-book on inorganic chemistry.

Cyanogen chloride, $CN.Cl$, is a very poisonous compound which is formed when chlorine is brought into a solution of hydrocyanic acid. It boils at 15.5°, and is somewhat soluble in water. On keeping, it partly polymerizes to *cyanuric chloride*, $C_3N_3Cl_3$. With ammonia it gives *cyanamide*, $CN.NH_2$. With potassium hydroxide, *potassium cyanate*, $CN.OK$, is formed:

$$CN.Cl + 2KOH = CN.OK + KCl + H_2O$$

Cyanamide, $CN.NH_2$, is a colorless, crystalline solid, melting at 40°. It is readily soluble in water, alcohol, and ether. The hydrogen of its amido-group is replaceable by metals. *Silver cyanamide*, $CN.NAg_2$, which, unlike most silver salts, is almost insoluble in ammonia, is precipitated from an ammoniacal solution of silver nitrate by cyanamide. The industrial manufacture of *calcium cyanamide*, $CN.NCa$, has already been referred to (p. 145).

Cyanuric acid, $(CNOH)_3$, is formed when cyanuric chloride is boiled with water, and is also one of the products obtained when urea, $CO(NH)_2$, is heated:

$$3CO(NH_2)_2 = (CNOH)_3 + 3NH_3$$

It crystallizes from water, in which it is sparingly soluble, with two molecules of water of crystallization, and forms well characterized salts.

Cyanic acid, $(H-O-C\equiv N$, is made by heating anhydrous cyanuric acid in a current of carbon dioxide, and condensing the gas which is formed in a receiver surrounded by a freezing mixture. It is a very volatile liquid, and unstable, polymerizing rapidly at 0° to *cymelide*, $(HOCN)_x$, a solid of unknown molecular weight, which regenerates cyanic acid on heating. In aqueous solution, cyanic acid decomposes at temperatures above 0° into carbon dioxide and ammonia:

$$HOCN + H_2O = CO_2 + NH_3$$

Potassium cyanate, $K-O-C\equiv N$, is formed by the reaction of cyanogen chloride and potassium hydroxide (p. 149); but is usually prepared by the oxidation of potassium cyanide through heating it with lead oxide, or by heating a mixture of potassium ferrocyanide and dichromate. The readiness with which potassium cyanide is oxidized to the cyanate explains its use as a reducing agent in inorganic chemistry. The cyanate is extracted from the resulting mass by boiling with 80 per cent. alcohol, and is obtained on evaporation of the solvent as a white crystalline powder. It is very soluble in water, and is slowly hydrolyzed in solution into ammonium and potassium carbonates.

When hydrochloric acid is added to its solution, the cyanic acid set free decomposes at once into carbon dioxide and ammonia. From the potassium cyanate other cyanates can be formed by double decomposition. The *ammonium salt* NH_4OCN is of especial interest because of its ready transformation into urea (p. 231).

Ammonium Cyanate may be prepared from sodium cyanide by leading carbon dioxide and ammonia into its solution; the reaction being exactly similar to that of the ammonia-soda process, the radical $-CNO$ taking the place of chlorine in the sodium chloride (Bucher):

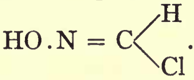
$$NaOCN + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4OCN$$

Esters of cyanic acid have not been isolated, the reactions which should give them yielding the polymeric cyanuric esters.

These exist in two isomeric forms, in one of which the alkyl group is linked to the CN group by oxygen, and in the other is directly united to the nitrogen of the group. These relations are proved by the products of hydrolysis: one form of ester giving cyanuric acid and an alcohol, and the other producing primary amines and carbon dioxide:

$$(CH_3.OCN)_3 + 3H_2O = 3CH_3OH + (HOCN)_3$$
$$(CH_3.NCO)_3 + 3H_2O = 3CH_3NH_2 + 3CO_2$$

There thus appear to be at least two isomeric cyanuric acids—one containing a hydroxyl group, called cyanuric acid; and another in which there is no hydroxyl group and where the hydrogen is united directly with nitrogen—the isocyanuric acid. Two cyanic acids: normal, $HOC\equiv N$ and iso, $HN=C=O$, correspond to these. Both forms may be present together in some of the compounds.

Fulminic Acid and Fulminates.—When ethyl alcohol is added to a mixture of mercuric nitrate and nitric acid a rather violent reaction occurs, with danger of explosion unless precautions are taken. After the reaction is finished, and as the solution cools, white crystals are precipitated which have the composition $Hg(CNO)_2$. A corresponding silver salt is formed under similar conditions. These salts, when dry, explode with great violence when heated or struck; and the mercury compound is the substance used in percussion and fulminating caps for firing gunpowder, dynamite and smokeless powders. The composition of these fulminates shows them to be salts of *fulminic acid*, which is a third isomer of cyanic acid. When sodium fulminate (formed by the action of sodium amalgam on the mercury salt) is treated with hydrochloric acid at 0°, an unstable crystalline compound is produced whose structure has been shown to be  $HO.N = C\begin{matrix}\diagup H \\ \diagdown Cl\end{matrix}$. This substance is regarded as an addition product of fulminic and hydrochloric acids, and the formula of fulminic acid is inferred to be $H—O—N = C$, in which the carbon atom acts as a dyad.

Fulminic acid is too unstable to be isolated, though it probably can exist in vapor and in solution. When fulminates are treated with hydrochloric acid, a prussic acid odor is perceived, which is evidently due to traces of fulminic acid. The fulminates are nearly if not quite as poisonous as hydrocyanides.

A special historical interest attaches to the fulminates, because of Liebig's demonstration in 1823 that the two different compounds, silver cyanate and silver fulminate had the same composition. This was the first case discovered of two different substances with the same composition; and it was to designate this phenomenon that Berzelius proposed the name *isomerism.*

It is seen that it is not a simple matter to determine the structure of the cyanogen compounds, and the task is complicated by an apparent mobility in the arrangement of the atoms, so that in some cases, at least, we must assume two forms to be present in the same compound, or to shift easily in the course of the reactions.

The possible arrangements of HCNO are four:
1. $H—O—C{\equiv}N$; 2. $H—O—N{=}C$ (or $H—O—N{\equiv}C$); 3. $H—C{\equiv}N{=}O$; 4. $H—N{=}C{=}O$. The generally accepted view is that the first represents cyanic acid, the fourth, isocyanic acid, and the second fulminic acid.

Thiocyanic Acid and Thiocyanates.—Sulphur combines directly with cyanides of the metals forming thiocyanates. For instance, when a solution of potassium cyanide is boiled with sulphur, the salt, $K—S—C{\equiv}N$, is produced. The acid, $H—S—C{\equiv}N$, is obtained in dilute solution by distilling this or the barium salt with sulphuric acid. The anhydrous acid is a very volatile liquid of sharp odor, which, like the cyanic acid, polymerizes very readily. In dilute solutions the acid is stable, but in strong solutions it decomposes into hydrocyanic acid and persulphocyanic acid, $H_2C_2N_2S_3$. The strength of thiocyanic acid approaches that of the halogen acids. Thiocyanates are converted into cyanides by melting them with zinc.

The salts of thiocyanic acid are obtained as a by-product in the coal gas industry, and are used as mordants. With the exception of the copper, mercury, and silver salts, the thiocyanates are soluble in water. Potassium and ammonium thiocyanates solutions are well-known reagents for ferric salts, giving a blood-red color even in very dilute solutions. Mercury thiocyanate, when heated, decomposes with the production of an extraordinarily voluminous ash, and is used in making the "Pharaoh's serpents." The ammonium salt, when melted, is partly transformed into thio-urea, $CS(NH_2)_2$.

Esters of thiocyanic acid are obtained by the action of alkyl iodides on the thiocyanates:

$$K-S-C\equiv N + CH_3I = CH_3-S-C\equiv N + KI$$

These alkyl thiocyanates are converted into isothiocyanates, such as $CH_3-N=C=S$, by heating. Thus, distillation of allyl thiocyanate, $CH_2{:}CH.CH_2-S-C\equiv N$, causes the change into $CH_2{:}CH.CH_2-N=C=S$. This compound, allyl isothiocyanate, was first obtained as an oil from mustard seeds where it is present as a glucoside, and the name of *mustard oils* is given to the group of isothiocyanic acid esters on this account.

ALKYL CYANIDES AND ISOCYANIDES

In the discussion of the structure of hydrocyanic acid it was stated that the action of silver cyanide on an alkyl halide gave a different compound from that obtained when potassium cyanide was used. The two compounds are isomeric, that produced by potassium cyanide probably having the structure of the cyanide or nitrile, $CH_3C\equiv N$, while the other is an isocyanide with the formula, $CH_3.N\equiv C$ or $CH_3.N=C$.

Alkyl Cyanides or Nitriles.—These compounds are esters of hydrocyanic acid, as the first name indicates, but their ready hydrolysis into ammonium salts or acids is their most interesting characteristic, and hence they are more often designated as nitriles. Thus, $CH_3.CN$ is methyl cyanide or *acetonitrile*. They are formed 1. by the withdrawal of the elements of water from the ammonium salts of acids, the acid amide being an intermediate product (p. 100); 2. By the action of potassium cyanide on alkyl halides (p. 35); or by distilling the potassium salt of an alkyl sulphuric acid with potassium cyanide:

$$C_2H_5.KSO_4 + KCN = C_2H_5.CN + K_2SO_4$$

In these reactions small amounts of the isocyanide (or *isonitrile*) are formed. There are also other less important methods by which nitriles can be formed.

The nitriles show the gradation in physical properties which is familiar in all homologous series of compounds. The lower members are liquids of not unpleasant odor, and are soluble in water.

The hydrolysis of the nitriles into acid amides and ammonium salts, and their conversion into primary amines by nascent hydrogen, have already been sufficiently discussed.

Alkyl isocyanides or isonitriles are formed, as has been stated, by treatment of an alkly halide with silver cyanide. Some nitrile is produced at the same time. Another reaction for making the isocyanides is carried out by heating a primary amine with an alcoholic solution of chloroform and potassium hydroxide:

$$C_2H_5.NH_2 + CHCl_3 + 3KOH = C_2H_5.NC + 3KCl + 3H_2O$$

Since in this reaction, a carbon atom replaces the two hydrogen atoms of the amino-group, the compounds are often given a third name, *carbylamines*, which indicates this relation. This reaction is employed as a test for primary amines (p. 132).

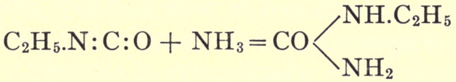
The isonitriles are volatile liquids of an almost unbearable odor, lighter than water and soluble in it. They are readily decomposed by water in the presence of inorganic acids into amines and formic acid:

$$C_2H_5.NC + 2H_2O = C_2H_5.NH_2 + H.CO.OH$$

Both the formation of these compounds and the mode of their hydrolysis justify the name of carbylamine, and are evidence for the structure which is assigned to them:

$$C_2H_5.N \equiv C \text{ or } C_2H_5.N = C$$

Alkyl Isocyanates such as C_2H_5NCO, are volatile liquids of penetrating and very disagreeable odor. They are formed by the action of silver cyanate on alkyl halides, and by oxidation of isonitriles with mercuric oxide. When heated with alkalies, they give primary amines and alkali carbonate (p. 129). With ammonia or amines they produce alkyl-substituted ureas:



$$C_2H_5.N:C:O + NH_3 = CO\begin{cases} NH.C_2H_5 \\ NH_2 \end{cases}$$

Hence, when boiled with water, they yield symmetrical dialkyl ureas, the amine formed at first reacting with excess of ester:

$$C_2H_5.NCO + H_2O = CO_2 + C_2H_5.NH_2$$

and

$$C_2H_5.NCO + C_2H_5.NH_2 = CO(NH.C_2H_5)_2$$

CHAPTER XII

ALCOHOLS WITH MORE THAN ONE HYDROXYL GROUP

Besides the alcohols with one hydroxyl group, which have been studied, there are many compounds known which are shown by their reactions to contain two or more hydroxyl groups. These polyhydroxyl compounds show the characteristic alcohol reactions and hence belong to the general group of alcohols.

The simplest formula which can be written for a dihydroxyl derivative of a paraffin is $CH_2(OH)_2$. Such a compound, however, cannot be made, nor can other similar compounds, such as $CH_3.CH(OH)_2$, be obtained. Methods which should give these compounds in which two hydroxyl groups are united to a single carbon atom, such as:

$$CH_3.CHI_2 + 2AgOH = CH_3.CH(OH)_2 + 2AgI$$

always result, as we have seen (p. 113a), in the formation of the aldehyde group $-C=O.H$, instead of the group $-CH.(OH)_2$.

The Glycols.—The simplest polyhydroxyl derivative is, therefore, $CH_2OH.CH_2OH$. This is called *glycol*, *ethylene glycol*, or *ethylene alcohol*. It is the first member of a series of "glycols" which have the general formula $C_nH_{2n}(OH)_2$. The isomeric higher glycols are distinguished as α, β, γ, δ, etc., glycols according as the hydroxyl groups are united to adjacent carbon atoms or to those farther apart. Thus, of the butylene glycols, $CH_3.CH_2.CHOH.CH_2OH$ is the α-compound, $CH_3.CHOH.CH_2.CH_2OH$, the β, and $CH_2OH.CH_2.CH_2.CH_2OH$, the γ glycol. (This notation is also employed to designate the positions of other substituting radicals or atoms in hydrocarbon derivatives.)

Since in the higher glycols derived from the normal hydrocarbons the alcohol groups may both be primary, both secondary, or one primary and one secondary, and in isomeric derivatives we may have both primary, both secondary, or both tertiary, or any combination of the three, the number of glycols which are theoretically possible is exceedingly great—far greater than the number of possible hydrocarbons. Very few of them, however, have been made.

Preparation.—1. The glycols may be made by replacing the halogen in paraffin dihalides with hydroxyl, as in the making of monohydroxyl alcohols; but the action of potassium hydroxide is usually so vigorous that unsaturated monohalide compounds or acetylene hydrocarbons are formed:

$$(CH_2Cl.CH_2Cl + 2KOH = CH_2OH.CH_2OH + 2KCl)$$
$$CH_2Cl.CH_2Cl + KOH = CHCl:CH_2 + KCl + H_2O, \text{ and}$$
$$CHCl:CH_2 + KOH = CH \vdots CH + KCl + H_2O$$

The reaction succeeds, however, when sodium carbonate is used, or when organic acid radicals are first substituted for the halogen, and these compounds are hydrolyzed. 2. Another method of formation is by first forming a compound containing one hydroxyl group and chlorine, a *chlorhydin*, through the union of an ethylene hydrocarbon and hypochlorous acid:

$$CH_2:CH_2 + HOCl = \underset{\text{Glycol chlorhydrin}}{CH_2Cl.CH_2OH}$$

and then replacing the chlorine with hydroxyl by means of moist silver oxide:

$$CH_2Cl.CH_2OH + AgOH = CH_2OH.CH_2OH + AgCl$$

3. The glycols are also formed by the oxidation of olefines by means of an alkaline solution of potassium permanganate or by hydrogen dioxide:

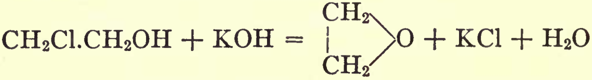
$$CH_2:CH_2 + O + H_2O = CH_2OH.CH_2OH$$

4. Diamines are converted into glycols by nitrous acid (cf. p. 131),

$$\begin{array}{l} CH_2.NH_2.HNO_2 \\ | \\ CH_2.NH_2.HNO_2 \end{array} = \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2N_2 + 2H_2O$$

Properties.—Ethylene glycol is typical of all the glycols, and will be alone described. It is an oily, sweetish liquid, which like most hydroxyl compounds is soluble in water and only slightly soluble in ether. It boils at 195°. Its chemical reactions are those of a double primary alcohol. Thus its hydroxyl hydrogen is replaceable by sodium, and its hydroxyl groups by halogens by means of phosphorus halides or halogen acids; it forms single and double esters with inorganic and organic acids, and its alcohol groups are oxidized to aldehyde and acid groups, with the final production of oxalic acid before breaking down into carbon dioxide and water. When the higher glycols contain secondary or tertiary alcohol groups, their behavior on oxidation is in part that of secondary or tertiary alcohols.

Alkylene Oxides.—Closely related to the glycols are the alkylene oxides, which may be regarded as glycols from which the elements of water have been subtracted. This cannot, however, be directly accomplished in most cases, but the compounds may be made by the action of potassium hydroxide on the corresponding chlorhydrines:



$$CH_2Cl.CH_2OH + KOH = \begin{array}{l} CH_2\diagdown \\ | \qquad\ \ O \\ CH_2\diagup \end{array} + KCl + H_2O$$

Alcohols with More than Two Hydroxyl Groups

Derivatives of the paraffins containing four, five, six, and seven hydroxyl groups are known. Certain hexahydroxyl alcohols occur in the sap of various trees; mannitol or manna, $CH_2OH(CHOH)_4CH_2OH$, being obtained from the mountain ash. As the number of hydroxyl groups increases, the compounds are sweeter and become more like sugars, to which they are closely related; and the tendency to decompose when heated, with the loss of the elements of water, becomes greater. Among the polyhydroxyl alcohols the only one of practical importance is that commonly known as glycerine or glycerol

Glycerol, $CH_2OH.CHOH.CH_2OH$, or "glycerine," is the simplest possible trihydroxyl alcohol. It may be formed by methods like those used for the formation of glycol; and is produced in large quantities from fats (which are glyceryl esters of certain of the higher paraffin or fatty acids) by replacement of the acid radicals with hydroxyl. This is effected by alkali hydroxides with the production of *soap* (p. 109) and glycerol, or by the action of superheated steam, when the products are glycerol and the fatty acids. The watery liquid containing the glycerine is purified by filtration through animal charcoal and the water removed by evaporation in a partial vacuum. The product, which is still impure, is refined for medical purposes and for making nitroglycerine, by distillation in a current of superheated steam, and treatment again with animal charcoal. It is finally concentrated in a vacuum. Glycerine is always formed in small amounts in the alcoholic fermentation of sugars, so that it is present in all undistilled alcoholic beverages.

Glycerol is a syrupy liquid, colorless and odorless, heavier than water (specific gravity 1.265 at 15°), miscible with water or alcohol in all proportions, but insoluble in ether and chloroform. It boils at 290° with very slight decomposition. It dissolves many inorganic and organic substances. It is very hygroscopic, and this property together with its non-volatility leads to an extensive use in non-drying inks, such as copying inks and those employed on typewriter ribbons and the pads for rubber stamps. Other uses are in pharmacy, in the preparation of tobacco, in confectionery, preserves, and cosmetics; but the largest amount is employed in making "nitroglycerine."

The formula given to glycerol is the only one that can explain the methods of its formation and the products which are obtained from it in various reactions. Its oxidation products show the presence of two primary and one secondary alcohol groups. On heating glycerol with dehydrating substances, (P_2O_5) acroleïn is formed (p. 86). Glycerol can undergo fermentation, and yields different products according to the nature of the ferment. One bacillus converts it chiefly into butyl alcohol, which is often prepared in this way.

Glycerol, like all alcohols, forms esters with acids, and since it contains three hydroxyl groups, it can form three different esters with a monobasic acid, according as one, two, or all three of the hydroxyls are replaced by acid radicals. The most important of its esters are those that occur in the natural fats and oils (p. 160) and nitroglycerine.

Nitroglycerine is the common name of the **trinitrate of glycerol,** $CH_2(O.NO_2).CH(O.NO_2).CH_2(O.NO_2)$, and is not a *nitro*-compound as the name implies. It is made by adding glycerine slowly to a well-cooled mixture of concentrated nitric and sulphuric acids, so long as it dissolves. On pouring the solution thus obtained into a large quantity of water, the nitroglycerine separates, as a heavy oil. It is thoroughly washed with a solution of sodium carbonate to remove all acid, and then with water, and finally dried by chloride of calcium. Pure nitroglycerine is colorless and odorless. Its specific gravity is 1.6 at 15°. It is almost insoluble in water but dissolves somewhat in alcohol and mixes in every proportion with ether, chloroform and benzene. A comparison of its solubility with that of glycerol is a good illustration of the influence of hydroxyl groups on this property. Nitroglycerine is poisonous, but is a valuable remedy in heart disease. It is saponified by caustic alkalies, but the reaction is accompanied by the production of some oxidation products of glycerol and reduction of the alkali nitrate to nitrite. Pure nitroglycerine keeps without change, but if impure, it slowly decomposes. Hence it is important to use pure glycerol in its manufacture, and to remove from it all traces of acid. Nitroglycerine is best known as a powerful explosive. It is used largely in the form of "dynamite," which is nitroglycerine absorbed in infusorial earth or some other substances. By this device it is brought into solid form which can be conveniently used. The most powerful dynamite contains 75 per cent. of nitroglycerine. It is also converted into a jelly-like solid by dissolving in it a small quantity (7–8 per cent.) of gun-cotton (p. 223), and in this form is known as "explosive gelatine." Small amounts of nitroglycerine may be kindled without exploding, and considerable quantities of dynamite burn quietly. Dynamite is not very sensitive to shocks, and is transported with little danger, but nitroglycerin is readily exploded by shock. All forms are exploded by a detonating substance such as mercury fulminate (p. 151), which is usually "fired" by electricity.

Natural Oils and Fats.—Besides the petroleum oils, whose origin is still in question, and ozokerite or earth wax, there are many oils and fats and a few waxes that are obtained from plants and animals. Two classes of oils are recognized: the *fixed or fatty oils* and the *essential oils*. The essential oils are practically all of vegetable origin, and are characterized by strong and individual odors. They can usually be distilled without decomposition and evaporate from paper without leaving a permanent oily stain. Most of them are not sensibly soluble in water but impart to it their characteristic odors. Their composition is very varied, including hydrocarbons such as cymene, pinene (in turpentine oil), camphene, and limonene; alcohols—benzyl alcohol in balsam of Peru and menthol in peppermint oil; phenols—thymol in oil of thyme; esters of acetic, butyric, valeric, benzoic, salicylic, and and other acids; many aldehydes such as benzaldehyde in oil of bitter almonds, cinnamic aldehyde in cinnamon oil, and vanillin (p. 347) in vanilla; ketones such as camphor; and others.

The fixed oils and fats are insoluble in water, leave a permanent oily stain on paper, and decompose when heated, giving acrolein (p. 86) as one of the decomposition products. They are found in both plants and animals, and most commonly consist of triglyceryl esters of organic acids. The esters most frequently present are the glycerides of palmitic, stearic, and oleïc acids, known as palmitin, stearin, and oleïn. The first two of these esters are solids and oleïn a liquid; and when these three are the principal constituents—as is the case with many of the animal fats especially, their proportions determine the consistency of the fat. Thus, olive oil contains about 75 per cent. of oleïn; lard which melts at 35°–38°, about 60 per cent.; and tallow, melting at 47°–48°, about 25 per cent. Among the constituents of some of the fats and oils are also glyceryl esters of a number of other fatty acids, such as butyric, caproic, caprylic, lauric, and myristic of the saturated series; crotonic, physetoleïc, and ricilinoleïc (hydroxyoleïc) of the oleïc series; linolic, an acid with two double bonds; linolenic and isolinolenic (p. 112), acids with three double bonds.

Butter fat differs from all other fats and oils by containing about 7.7 per cent. of triglyceryl butyrate in addition to stearin, palmitin, oleïn, and traces of other glyceryl esters.

Oils like linseed oil, that consist chiefly of glycerides of the highly unsaturated acids, linolic, linolenic, and isolinolenic, are called "drying" oils because they absorb oxygen from the air and become dry and hard. Such oils, on this account, are extensively used in paints and varnishes. Linseed oil dries more rapidly if it has been "boiled," a process in which the oil is heated to about 150° with certain oxides or salts such as litharge or borate of manganese that are called "driers" and probably act as contact agents. Much heat is developed in the drying of these oils and occasions the danger of spontaneous combustion in the oily rags and waste used by painters.

Some oils, such as cotton seed oil, that contain small amounts of linolic acid ester are semi-drying, while many such as olive and rape oils are non-drying. These oils generally become rancid from exposure to air, apparently because of a partial hydrolysis occasioned by bacterial action followed by oxidation of the fatty acids that are set free.

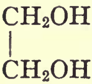
In the last few years the production of "hardened" oils has developed into an industry of considerable importance. The chemical change involved consists in "hydrogenation" or addition of hydrogen to the unsaturated esters in the oils, by which they are converted into saturated compounds. The reaction is effected by leading hydrogen into the moderately heated oil after the addition of a substance that acts as a catalyst. The most important of these catalysts is finely divided nickel (Sabatier and Senderens), though palladium, platinum, and other metals are also employed. A large variety of oils can be thus hardened—vegetable, animal, train, fish, and whale oils—and the resulting fats are of great commercial importance, being largely used in soap and candle making, and also providing edible fats from oils. One of the latter products is "crisco," a substitute for lard.

A method of saponifying fats for soap-making has recently been introduced into the industry by Twitchell, in which an aromatic sulphonic acid acts as a catalyzer. The exact nature of the compound is not disclosed, but it is prepared by the action of sulphuric acid on a solution of oleïc acid in an aromatic hydrocarbon: and 1–2 per cent. of it is effective in producing saponification.

CHAPTER XIII

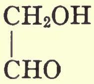
OXIDATION DERIVATIVES OF POLYHYDROXYL ALCOHOLS

A large number of compounds may be regarded as oxidation derivatives of the alcohols discussed in the last chapter. The compounds may contain unchanged alcohol groups—primary, secondary, and tertiary—with aldehyde groups, ketone groups, or carboxyl groups, in every possible combination. From glycol, for example, the derivatives are:



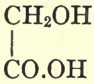
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol



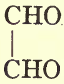
$$\begin{array}{l} CH_2OH \\ | \\ CHO \end{array}$$

Glycollic aldehyde



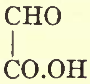
$$\begin{array}{l} CH_2OH \\ | \\ CO.OH \end{array}$$

Glycollic acid



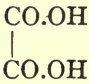
$$\begin{array}{l} CHO \\ | \\ CHO \end{array}$$

Glyoxal



$$\begin{array}{l} CHO \\ | \\ CO.OH \end{array}$$

Glyoxylic acid



$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Oxalic acid

From glycerol and the higher polyhydroxyl alcohols ketone derivatives may also be obtained such as dihydroxy-acetone, $CH_2OH.CO.CH_2OH$.

But while many of these substances are formed by the actual oxidation of the corresponding glycols, etc., this method is not often used for their preparation, because of the difficulty of controlling the reaction so as to obtain a good yield of the individual products. Glyceric acid is, however, usually made by oxidizing glycerol with nitric acid, but, in general, the compounds which form the subject of this chapter are prepared by indirect methods.

The student will recall that the most important general methods for the introduction of the hydroxyl groups are: By replacement of a halogen atom through the action of water, alkali hydroxide, or silver hydroxide; by saponification of an ester; for a primary alcohol group, the reaction of nitrous acid on a primary amine group, and for a secondary alcohol group, the reduction of a carbonyl group. For the general methods of introducing the aldehyde, ketone, (CO), and carboxyl groups, reference should be made to the methods of forming aldehydes, ketones and acids.

Aldehyde-alcohols and Ketone-alcohols

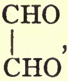
The simpler compounds of these classes are of interest chiefly because of the fact that some of the sugars are aldehyde or ketone-alcohols, while other so-called carbohydrates are converted into aldehyde or ketone-alcohols by hydrolysis. The carbohydrates themselves form the subject of a separate chapter. Only a few of the simpler aldehyde-alcohols and ketone-alcohols have been made, and these are of no especial practical importance.

Glycollic aldehyde, $CH_2(OH).CHO$, or *hydroxy-acetaldehyde,* is formed in the oxidation of glycol. It can be prepared from acetal, $CH_3.CH(OC_2H_5)_2$, by appropriate reactions. Chlorine is substituted in the CH_3 group, and replaced by hydroxyl, making $CH_2OH.CH(OC_2H_5)_2$; and then by the action of a dilute acid, this glycolacetal is hydrolyzed into glycollic aldehyde and alcohol (*cf.* p. 79). It is known only in solution. Its aldehyde character is marked. It reduces Fehling's solution at room temperature, is colored yellow when heated with alkalies, and is oxidized by bromine water to glycollic acid. On standing at 0° with dilute alkali it suffers "condensation" like that of acetaldehyde, with the formation of a tetrose, $CH_2(OH).CH(OH).CH(OH).CHO$.

Aldol or *β-hydroxybutyric aldehyde,* $CH_3.CH(OH).CH_2.CHO$, is formed by the polymerization of acetaldehyde (p. 82), and was the first known case of this characteristic aldehyde reaction ("aldol condensation").

Ketoles.—A number of compounds with a ketone group and a hydroxyl group are known, such as *hydroxyl acetone* or *acetocarbinol,* $CH_3.CO.CH_2(OH)$, and *acetobutyl alcohol,* $CH_3.CO.(CH_2)_3.CH_2(OH)$.

Dialdehydes and Diketones

Glyoxal,  $\begin{array}{l}CHO\\ |\\ CHO\end{array}$, is one of the several products formed by the oxidation of glycol or ethyl alcohol or aldehyde with nitric acid. A solution of it may be prepared in this way from aldehyde or paraldehyde, and on evaporation the glyoxal is obtained as an amorphous, hard mass, not entirely free from water. Its aldehyde character is shown by the formation of a silver mirror with ammoniacal silver nitrate, and the presence of two aldehyde groups by the composition of the crystalline addition products with acid sodium sulphite. By dilute alkalies it is converted into a glycollic acid salt, $CH_2(OH).CO.ONa$, one aldehyde group being reduced, and the other oxidized.

Acetonylacetone, $CH_3.CO.CH_2.CH_2.CO.CH_3$, is an example of a diketone, which may be regarded as an oxidation product of a γ-hexylene glycol. It is made, however, in an indirect way. It is a liquid of pleasant odor, which boils at 194°.

Aldehyde-ketones

The simplest representative of this class is the **methylglyoxal,** $CH_3.CO.CHO$, and may be looked on as a derivative of propylene glycol.

Alcohol-acids

Carbonic acid, $HO.CO.OH$, may be considered as hydroxyformic acid. It and its derivatives will be discussed later.

Glycollic acid, $CH_2OH.CO.OH$, or *hydroxyacetic acid,* is (with the exception of carbonic acid) the simplest of these compounds. Its structure is shown by its formation from monochloracetic acid, when this is boiled with water:

$$CH_2Cl.CO.OH + HOH \rightarrow CH_2OH.CO.OH$$

It occurs in unripe grapes. It is formed by the oxidation of glycol or of ethyl alcohol with nitric acid, by reduction of oxalic acid, and by the action of dilute alkalies on glyoxal (p. 163.) Glycollic acid is a crystalline substance, which melts at 80° and dissolves readily in water. Nitric acid converts it into oxalic acid.

Hydroxypropionic Acids.—There are two chemically different acids of this name whose formulas are, $CH_3.CHOH.CO.OH$, and $CH_2OH.CH_2.CO.OH$. They may be made from other compounds such as iodo- or amino-propionic acids by the usual methods of hydroxyl substitution. That they are monobasic acids is proved by the composition of their salts; and that they contain one hydroxyl in addition to that of the carboxyl, is shown by the fact that sodium acts on them with the formation of compounds in which it takes the place of two hydrogen atoms—those of the hydroxyl and carboxyl group. Both acids form thick, sour syrups. Their diversity is shown by a great difference in the solubility of their zinc salts, and by the following reactions which serve to decide which of the two formulas represents the structure of each. One of them when oxidized with potassium permanganate is converted into a ketone acid, acetylformic acid, $CH_3.CO.CO.OH$. This result is evidence of the presence of a secondary alcohol group in the acid, the reaction being:

$$CH_3.CHOH.CO.OH + O = CH_3.CO.CO.OH + H_2O$$

The formula given the acid in this equation is also indicated by the fact that when heated with dilute sulphuric acid, it breaks up into aldehyde and formic acid, a reaction which is characteristic of many α-hydroxy acids:

$$CH_3.CHOH.CO.OH = CH_3.CHO + HCO.OH$$

and that its nitrile may be made by direct combination of aldehyde and hydrocyanic acid:

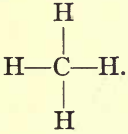
$$CH_3.CHO + HCN = CH_3.CHOH.CN$$

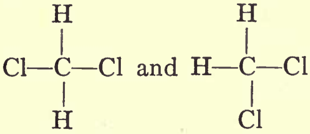
This acid is, therefore, *α-hydroxypropionic acid.*

The other must, then, be β-hydroxypropionic acid, $CH_2OH.CH_2.CO.OH$; and this formula is confirmed by its oxidation into the corresponding dibasic malonic acid, $CO.OH.CH_2.CO.OH$, showing the presence of a primary alcohol group; and also by its breaking up when heated into the unsaturated acrylic acid, $CH_2{:}CH.CO.OH$ (p. 110).

α-Hydroxypropionic acid, $CH_3.CHOH.CO.OH$, is the acid of sour milk, being formed by the action of certain bacteria on the milk sugar. Hence it is known as *lactic acid.* (Tablets containing pure cultures of lactic acid bacteria are sold under the name of "lactone" or "butter-milk tablets.") Lactic acid is also the product of special fermentations of other sugars, and is found in "sauerkraut" and in the gastric juice, and is present in "beef-extract." But the lactic acid obtained from the last source differs from that from most other sources and from the synthetic lactic acid, by being "optically active;" that is, its solutions rotate the plane of polarized light. On fermentation of cane-sugar by means of a special culture of bacteria, an active lactic acid is formed which also rotates the plane of polarized light, but in the opposite direction from that which is made from beef-extract. The latter turns the plane to the right, the former to the left. The salts of these two acids give optically active solutions which rotate the plane in a sense opposite to the rotation by the respective acids. The ordinary salts of both these acids have the same solubility, but the strychnine salt of the levo-rotatory acid is less soluble than that of the dextro-rotatory, and from a solution of the strychnine salt of the ordinary lactic acid, which is "inactive," two lots of crystals can be obtained by fractional crystallization, and from these the two optically active acids may be set free. The dextro-acid may be also made from the ammonium salt of the inactive acid by means of a mould, *penicillium glaucum,* which destroys the levo form. Special ferments determine the formation from sugars of one or the other of the active acids. When the zinc salts of the two active acids in solution are mixed in equal proportions, the less soluble salt of the inactive acid crystallizes out. It appears, therefore, that the inactive acid is a mixture in equal parts of the two oppositely active acids. The three acids differ in no chemical way, and this "physical isomerism" which is found cannot be represented by such structural formulas as we have thus far employed. A satisfactory explanation is, however, found in formulas which give arrangements of atoms and groups in space of three dimensions, instead of the representations in a single plane such as have served in our discussions up to this point.

Stereochemistry

In methane we saw that each of the four hydrogen atoms bore the same relation to the other three and to the carbon atom; at least, it has not proved possible to make different monosubstitution products of methane. This symmetry of the methane molecule is satisfactorily indicated by the usual plane graphic formula,  $\mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}$. If chlorine replaces any one of the hydrogen atoms, we have formulas which may be considered identical. But when two atoms of hydrogen are replaced there are two formulas possible which are not strictly identical in this mode of representation; for in one the hydrogen and chlorine atoms alternate as we go round the carbon atom, and in the other the two chlorine atoms are next each other:

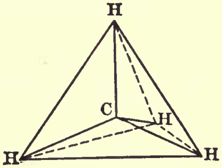


$$\mathrm{Cl}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{Cl} \quad \text{and} \quad \mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{C}}}-\mathrm{Cl}$$

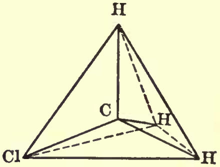
And yet only one dichlormethane has ever been obtained.

Such differences in arrangement have been hitherto disregarded in our discussions. The phenomena of optical activity or physical isomerism, however, has led to the development of spatial representations, which account for the existence of but one dichlormethane and other similar failures of the plane formula; and also gives a good explanation of the facts of optical activity. There is, of course, every reason to believe that the molecular arrangement is never confined to bi-dimensional space, but that the atoms and groups form tri-dimensional structures; and the graphic formulas have been regarded as giving merely a plan or diagram with no attempt to represent the actual relative positions.

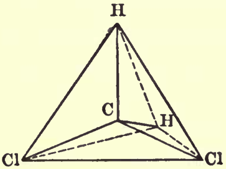
The tetrahedron, the simplest regular solid, is the only form that can give full expression to the symmetry of methane, and this was taken by Van't Hoff and Le Bel as the basis for their formulation of spatial relations. The carbon atom is placed at the center of the tetrahedron, its four valencies being directed to the four solid angles.



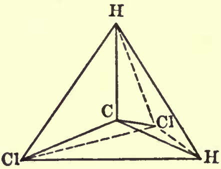
1. Methane



2. Monochlormethane



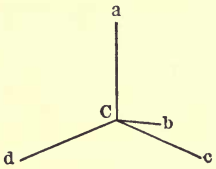
3. Dichlormethane

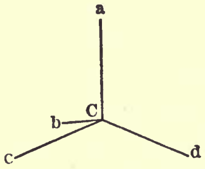


4. Dichlormethane

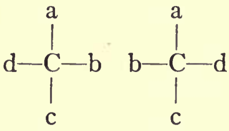
The diagrams show the tetrahedral formulas for methane, monochlormethane, and dichlormethane. They are all symmetrical, and formulas 3 and 4 are identical; for 3 may readily be turned so that the chlorine and hydrogen atoms coincide, or, in other words, the two figures are superposable.

This symmetry holds good for all compounds in which a carbon atom is combined with four elements or groups of the same kind, or any combination of elements or groups except that of four different ones. In this case there are possible two arrangements which are unsymmetric or *asymmetric* and which cannot be turned into coincidence or superposed. On this account, a carbon atom united to four different atoms or groups is called an *asymmetric carbon atom*. The two asymmetric arrangements bear the relation to each other of an object and its image in a plane mirror, as may be seen by study of the diagrams, or better by tetrahedral forms.





The relations shown in the tetrahedral formulas may also and more conveniently be indicated by formulas like those below, which are projections of the tri-dimensional arrangements on the plane of the paper:



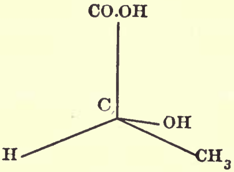
$$\begin{array}{ccc} & a & \\ & | & \\ d- & C & -b \\ & | & \\ & c & \end{array} \qquad \begin{array}{ccc} & a & \\ & | & \\ b- & C & -d \\ & | & \\ & c & \end{array}$$

It will be noticed that the configurations cannot be made to coincide by turning one of them in the plane of the paper. This will be found true of all such projections of asymmetrical tetrahedral formulas, and we shall make use of this mode of representation in future instances of physical isomerism.

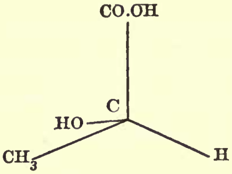
By these formulas, we have a means of recording the physical difference which we are discussing, while the chemical identity is still preserved.

A large number of optically active organic substances is known. When the plane of polarized light is rotated on passing through a solid substance, it can be assumed that the effect is due to the arrangement of the molecules, as in the various crystal forms; but in the case of the lactic acids and other so-called optically active chemical compounds, the activity is shown in solution, where free motion of the molecules is probable, and where they certainly do not assume any fixed relations to each other; and camphor and certain terpenes retain their optical activity unimpaired in the state of vapor. In all the optically active compounds, we find on examining their ordinary structural formulas that there is an asymmetric carbon atom.

In lactic acid, $CH_3.\mathbf{C}H(OH).CO.OH$, the four different groups CH_3, H, OH, and CO.OH are in combination with the carbon atom which is printed in blacker type. The formulas of the two optically active lactic acids are:

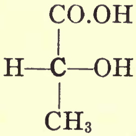


d-Lactic acid

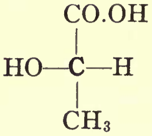


l-Lactic acid

or



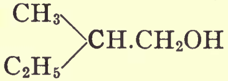
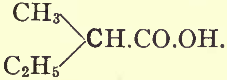
$$\begin{array}{c} CO.OH \\ | \\ H—\mathbf{C}—OH \\ | \\ CH_3 \end{array}$$



$$\begin{array}{c} CO.OH \\ | \\ HO—\mathbf{C}—H \\ | \\ CH_3 \end{array}$$

The choice of one formula rather than the other to represent the dextro- or levo-compound is arbitrary.

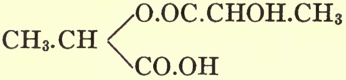
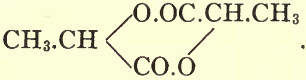
When a compound contains an asymmetric carbon atom, and is optically inactive, the explanation is that equal amounts of the two oppositely active substances are probably present: and this, as we have seen, agrees with the facts which have been stated as to the separation and the mixing of the two active lactic acids. In case of compounds with two asymmetric carbon atoms, as in mesotartaric acid (p. 193), the optical inactivity may be due to a different cause.

Optically active compounds which have been previously mentioned are: active amyl alcohol,  $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right>CH.CH_2OH$ (p. 67), and one of the four valeric acids (p. 108) which has the formula,  $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right>CH.CO.OH$. Each formula contains an asymmetrical carbon atom. The active alcohol from fermentation is levo-rotatory; on oxidation it yields dextro-rotatory valeric acid. An inactive modification of the acid has been synthesized, and resolved by its brucine salts into dextro and levo components.

It is of great interest to note that this theory of the relation of optical activity to the asymmetric tetravalent carbon atom has been found to explain in a similar manner the phenomena of optical activity recently discovered in compounds of other tetravalent elements. These are compounds of tetravalent tin, silicon, sulphur, and selenium, in all of which four different groups or atoms are directly united to these elements, and can be represented as tetrahedral arrangements.

Lactic acid is made commercially by fermentation of sugar, and is used in dyeing and calico printing as a substitute for tartaric and citric acids, and its antimony salt is used in place of tartar emetic as a mordant.

The lactic-acid fermentation is often induced in making grain alcohol, as a 1 per cent. solution of the acid inhibits the action of other bacterial ferments, while having little effect on yeast.

When distilled, lactic acid is decomposed into aldehyde, water, carbon monoxide and other products. Since lactic acid is both an alcohol and an acid, two molecules of it may react to form an ester,  $CH_3.CH\left\langle\begin{array}{l}O.OC.CHOH.CH_3\\ CO.OH\end{array}\right.$, and this by a second reaction of the same kind may give a compound called *lactide* and having the constitution . The lactide is formed when the acid is heated to 150° in a current of dry air. Lactide is an indifferent substance, and in contact with water slowly changes back to lactic acid.

β-Hydroxypropionic acid, $CH_2OH.CH_2.CO.OH$, is also called *hydracrylic acid*, on account of its relation to acrylic acid. To the evidence for its structure already given, may be added the fact of its synthesis from ethylene through ethylene chlorhydrin. Ethylene unites directly with hypochlorous acid, when led into its dilute solution, giving ethylene or glycol chlorhydrin:

$$CH_2:CH_2 + HOCl = CH_2OH.CH_2Cl,$$

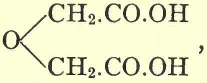
and the chlorhydrin, which is a liquid, boiling at 128°, reacts with potassium cyanide forming hydracrylic nitrile, from which the acid is readily obtained by hydrolysis:

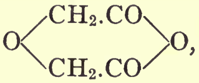
$$CH_2OH.CH_2Cl + KCN = CH_2OH.CH_2CN + KCl$$
$$CH_2OH.CH_2.CN + 2H_2O = CH_2OH.CH_2.CO.OH + NH_3$$

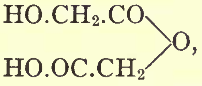
It will be noticed that hydracrylic acid contains no asymmetric carbon atom.

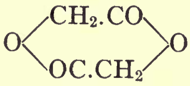
Dehydration of Hydroxy-acids.—By this is meant the removal of the elements of water from the acids. This is readily effected, and the nature of the compounds which result depends on the relative positions of the hydroxyl and carboxyl groups.

a-Hydroxy-acids form various complex compounds by the loss of the elements of water from hydroxyl and carboxyl groups, and the union of two molecular residues, as in the case of lactic acid (p. 171). From glycollic acid, for example, the following compounds have been obtained:









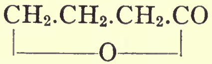
The last is *glycollide*, corresponding to lactide. Compounds of this constitution have received the general name of *lactides*.

When heated with dilute sulphuric acid, α-hydroxy acids often split off formic acid (or its equivalent, CO and H_2O), as in the case of lactic acid.

β-Hydroxy acids when heated give unsaturated acids, as in the case of hydracrylic acid which produces acrylic acid:

$$CH_2OH.CH_2.CO.OH = CH_2 : CH.\,CO.OH$$

δ- and γ-hydroxy-acids lose the elements of water very easily from the hydroxyl and carboxyl groups of a single molecule, forming *lactones:*



$$CH_2OH.CH_2.CH_2.CO.OH = CH_2.CH_2.CH_2.CO \quad (—O—)$$

The tendency of the γ-acids to form lactones is so great, that when the acids are in solution it occurs in most cases slowly at ordinary temperature, and immediately on boiling. The γ-lactones are neutral compounds which distil without decomposition. On boiling with water the acid is reproduced to a small extent.

Glyceric acid, $CH_2OH.CHOH.CO.OH$, is an example of a dihydroxy-acid. It may be made by careful oxidation of glycerol, preferably with nitric acid. Its constitution as a dihydroxy-propionic acid is determined by its formation from chlorlactic acid, $CH_2Cl.CHOH.CO.OH$, by reaction with silver hydroxide. Glyceric acid is a thick syrup which mixes in all proportions with water and alcohol, but is insoluble in ether (alcohol-hydroxyl groups). It is seen that this acid contains an asymmetric carbon atom. As usually prepared its solutions have no effect on polarized light; but a special bacillus produces a dextro-rotatory acid from it, and by the action of *penicillium glaucum* on the solutions of the ammonium salt of the inactive acid, a levo-rotatory acid may be obtained.

Aldehyde and Ketone Acids

Glyoxylic acid, CHO.CO.OH, is the simplest aldehyde acid. It is a product of the oxidation of alcohol, glycol, or glycollic acid with nitric acid, and can be prepared from dichlor or dibromacetic acid by heating with water. It shows itself to be an aldehyde by its reducing power (being itself oxidized to oxalic acid), its reduction to glycollic acid, and its reactions with acid sodium sulphite and hydroxylamine. It forms a syrup from which crystals separate on long standing. These crystals, however, do not have the composition of the acid, but contain an additional molecule of water which cannot be driven off without decomposition of the acid. Its salts also, except the ammonium salt, contain water and cannot be obtained in the anhydrous condition. Consequently its composition is sometimes considered to be $CH(OH)_2.CO.OH$, analogous to that of chloral hydrate (p. 92). But its reactions are best explained by the formula CHO.CO.OH.

Pyroracemic acid, *pyruvic acid*, or *acetyl formic acid*, $CH_3.CO.CO.OH$, is a ketone acid, which owes its first name to its formation by heating racemic (tartaric) acid. This is the usual way for preparing it. The yield is increased by distilling the acid with acid potassium sulphate. The structure of pyroracemic acid is evident from its formation by oxidizing lactic acid:

$$CH_3.CHOH.CO.OH + O \rightarrow CH_3.CO.CO.OH,$$

and also from its production by the following methods: from a dibrompropionic acid, $CH_3.CBr_2.CO.OH$, by the action of silver oxide; and from acetyl chloride by means of potassium cyanide, and subsequent hydrolysis:

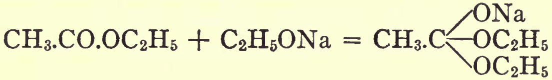
$$CH_3.CO.Cl + KCN = CH_3.CO.CN + KCl$$
$$CH_3.CO.CN + 2H_2O = CH_3.CO.COONH_4$$

Pyroracemic acid gives the characteristic reactions of a ketone and of an acid. It is a liquid, boiling with little decomposition at about 165°, and when frozen at a low temperature, melts at 9°.

Acetoacetic acid, $CH_3.CO.CH_2.CO.OH$, is not known in the anhydrous condition. It may be obtained by the evaporation of its solutions as a syrup, but decomposes when warmed to somewhat below 100° into acetone and carbon dioxide.

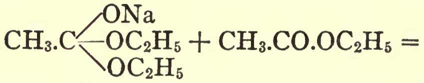
Acetoacetic acid is formed by the oxidation of butyric acid with hydrogen peroxide, and is also a product of the oxidation of fats and proteins in the body. By the splitting off of carbon dioxide it is converted into acetone: $CH_3.CO.CH_2.CO.OH = CH_3.CO.CH_3 + CO_2$; and in the enol form, $CH_3.COH{:}CH.CO.OH$, β-hydroxycrotonic acid, is reduced to β-hydroxybutyric acid, $CH_3.CHOH.CH_2.CO.OH$. These three substances, acetoacetic acid, β-hydroxybutyric acid, and acetone are present in considerable quantities in the urine in severe cases of diabetes mellitus.

Acetoacetic ethyl ester is a more stable compound, and, as it readily reacts with many substances, is an important aid in various organic syntheses. It is prepared by the action of sodium on ethyl acetate. The reaction is believed to proceed in the following way: Sodium acts first on traces of alcohol, which are present in the acetate, forming sodium ethoxide, and then this forms an addition product with the acetate:



$$CH_3.CO.OC_2H_5 + C_2H_5ONa = CH_3.C\begin{cases} ONa \\ OC_2H_5 \\ OC_2H_5 \end{cases}$$

This immediately reacts with another molecule of the acetate, forming a sodium compound of acetoacetic ester, and alcohol:



$$CH_3.C\begin{cases}ONa \\ OC_2H_5 \\ OC_2H_5\end{cases} + CH_3.CO.OC_2H_5 =$$

$$CH_3.C(ONa):CH.CO.OC_2H_5 + 2C_2H_5OH$$

Finally on adding acetic acid to the sodium compound thus formed, the ester, $CH_3.COH:CH.CO.OC_2H_5$ or $CH_3.CO.CH_2CO.OC_2H_5$, is set free.

It will be noticed that two alternate formulas have just been given for the ester. The first is the formula of an unsaturated hydroxy ester, the second of a saturated ketone ester. The explanation of its formation leads most naturally to the first formula and some of its reactions accord with this view; but, on the other hand, many of its reactions are those of a ketone compound. It is probable that it exists in both forms, and that they are both present in varying proportions in it and in its substitution products, and change readily into each other. We have noticed before in the acid amides a similar case, where the compound probably exists in two forms which are structurally different. This double behavior is found in a number of compounds and is called *tautomerism*, tautomeric compounds being such as possess a double function though usually represented as a single substance. In this way they differ from the usual cases of isomerism in which, when the structure is once determined by the reactions of formation, the arrangement is a stable one. The hydroxy form is known as the *enol* modification, and the other the *keto* form.

Acetoacetic ester is a liquid of pleasant strawberry-like odor, which boils at 181°. It is only slightly soluble in water, and is colored violet by a solution of ferric chloride. This color reaction is common to compounds having an unsaturated alcohol group, and is evidence of the presence of some, at least, of the ester represented by the first formula. Treated with cold, dilute alkali, the ester is saponified into the alkali salt of acetoacetic acid and alcohol. Heated with stronger solutions of alkalies, it is partly converted into alkali acetate and alcohol:

$$CH_3.CO.CH_2.CO.OC_2H_5 + 2KOH = 2CH_3.CO.OK + C_2H_5OH$$

and partly hydrolyzed into acetone, alcohol and carbon dioxide:

$$CH_3.CO.CH_2.CO.OC_2H_5+H_2O = CH_3.CO.CH_3+C_2H_5OH+CO_2.$$

This latter reaction occurs completely when it is heated with dilute acids. There are, therefore, two distinct varieties of hydrolysis possible which may be distinguished as *ketone hydrolysis* and *acid hydrolysis*.

The most notable property of acetoacetic ester is that of forming compounds with metals, which are either of the type, $CH_3.CONa{:}CH.CO.OC_2H_5$, or $CH_3.CO.CHNa.CO.OC_2H_5$.

By treating the sodium compound with alkyl halides, alkyl groups are introduced in place of the metals, and since the substituted esters undergo decompositions of the same character as the ester itself, many substitution derivatives of acetone and acetic acid may be prepared in this way.

In general the ester shows the characteristic ketone reactions: By nascent hydrogen it is converted into β-hydroxybutyric acid, $CH_3.CHOH.CH_2CO.OH$; it forms a crystalline addition product with acid sodium sulphite, etc. Further, acetyl substitution products are not formed by acetic acid, or its chloride or anhydride, substances which always react with hydroxyl groups.

Reactions of acetoacetic ester that are characteristic of ketones are: the formation of β-hydroxybutyric acid on reduction; the production of additive compounds with hydrogen cyanide and with acid sodium sulphite; and the hydrolysis of the ester and of its alkyl derivatives by alkalies and acids into acetone and its homologues. Further, with acetic anhydride the ester yields so little of an acetyl derivative that the presence of an hydroxyl group seems very improbable, and acetyl chloride acting on the sodium compound gives mainly diacetoacetic ester:

$$CH_3.CO.CHNa.CO.OC_2H_5 + CH_3.CO.Cl = (CH_3.CO)_2CH.CO.OC_2H_5 + NaCl$$

On the other hand, the acidic character of the ester indicates the hydroxyl form, and ammonia and amines yield amino and alkyl-amino crotonic esters of the general formula: $CH_3.C(NR_2):$-$CH.CO.OC_2H_5$.

It is now generally agreed that the free acetoacetic ester consists chiefly of the ketonic form, while the solid sodium compound must be represented by the isomeric formula as a derivative of β-hydroxycrotonic acid.

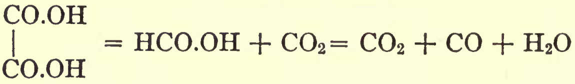
CHAPTER XIV

POLYBASIC ACIDS AND ALCOHOL-ACIDS

SOME DIBASIC ACIDS

Name	Formula	Melting Point
Oxalic	CO.OH.CO.OH	189° (Anhydrous)
Malonic	$CO.OH.CH_2.CO.OH$	132
Succinic	$CO.OH.(CH_2)_2.CO.OH$	184
Glutaric	$CO.OH.(CH_2)_3.CO.OH$	98
Adipic	$CO.OH.(CH_2)_4.CO.OH$	153
Pimelic	$CO.OH.(CH_2)_5.CO.OH$	105.5
Suberic	$CO.OH.(CH_2)_6.CO.OH$	141
Azelaic	$CO.OH.(CH_2)_7.CO.OH$	108
Sebacic	$CO.OH.(CH_2)_8.CO.OH$	134.5

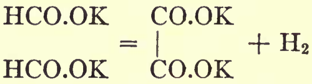
Oxalic acid, $(CO.OH)_2$, one of the well-known organic acids, is one of the products formed when ethyl alcohol or glycol is oxidized by nitric acid, and also results from the oxidation of many more complex organic substances. When sugar, for instance, is warmed with concentrated nitric acid, a strong reaction occurs, and oxalic acid crystallizes from the resulting solution as it cools. It is prepared commercially from saw-dust by mixing it with a strong solution of potassium hydroxide and heating to about 250°; or, more usually now, by heating an alkali formate (see p. 106, and below). The potassium oxalate produced is extracted with water, changed into the insoluble calcium oxalate by milk of lime, and the acid set free by sulphuric acid. The white crystalline solid which is obtained from solutions of oxalic acid contains two molecules of water of crystallization. It begins to lose water at 30° and becomes anhydrous at 100°. On further careful heating, the anhydrous acid sublimes, and this fact is employed for its purification, as it is thus readily freed from the small amount of its salts which crystallize with it The acid is moderately soluble in water, more readily soluble in alcohol, and nearly insoluble in ether. When strongly heated, it breaks down into carbon dioxide, carbon monoxide, and water, with the production of some formic acid as an intermediate step:



$$\begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{CO.OH}\end{array} = \mathrm{HCO.OH} + \mathrm{CO_2} = \mathrm{CO_2} + \mathrm{CO} + \mathrm{H_2O}$$

Heated with concentrated sulphuric acid, it gives the end products of water and the oxides of carbon at once.

The relation of oxalic acid to formic acid is of interest. As stated, some formic acid is produced when oxalic acid is heated, and the usual method for the preparation of formic acid is by heating oxalic acid with glycerol (p. 104); on the other hand, when an alkali formate is sharply heated (400°) with exclusion of air, the alkali oxalate is produced:



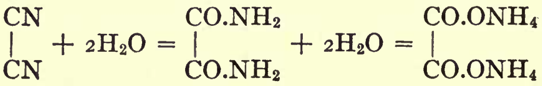
$$\begin{array}{l}\mathrm{HCO.OK}\\ \\ \mathrm{HCO.OK}\end{array} = \begin{array}{l}\mathrm{CO.OK}\\ |\\ \mathrm{CO.OK}\end{array} + \mathrm{H_2}$$

From two molecules of formate one molecule of oxalate is formed, with hydrogen as a by-product; and one molecule of oxalic acid yields one molecule of formic acid with carbon dioxide as a by-product; the two by-products being equivalent to the one molecule of formic acid which is lost in completing the cycle.

Besides this formation of oxalic acid from formic acid, two other methods of theoretical interest may be given: An alkali oxalate is obtained when carbon dioxide is led over sodium or potassium heated to 360°:

$$2\mathrm{Na} + 2\mathrm{CO_2} = (\mathrm{CO.ONa})_2$$

By hydrolysis of cyanogen, the acid or its salts are formed, cyanogen thus showing itself to be the nitrile of oxalic acid:



$$\begin{array}{l}\mathrm{CN}\\ |\\ \mathrm{CN}\end{array} + 2\mathrm{H_2O} = \begin{array}{l}\mathrm{CO.NH_2}\\ |\\ \mathrm{CO.NH_2}\end{array} + 2\mathrm{H_2O} = \begin{array}{l}\mathrm{CO.ONH_4}\\ |\\ \mathrm{CO.ONH_4}\end{array}$$

Oxalic acid resists the oxidizing action of nitric acid, as is evident from its preparation by means of this acid; but it is readily oxidized in sulphuric acid solutions by potassium permanganate, and is used in volumetric analysis to standardize permanganate solutions. The reaction is, at first, slow, but soon becomes instantaneous, being accelerated by the catalytic effect of the manganous sulphate which is formed. When manganous sulphate is added before the titration begins, the permanganate is instantly decolorized.

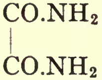
Salts and Esters of Oxalic Acid.—Oxalic acid is a strong dibasic acid, being highly ionized in its solutions. Its salts, chiefly the acid potassium oxalate and calcium oxalate, are found in many plants, such as sorrel and rhubarb, and crystals of calcium oxalate are found generally in the cell-walls of plants. *Ammonium oxalate* is a well-known laboratory reagent.

Besides the acid and normal potassium salts, another salt called *potassium tetroxalate*, $(CO.O)_2HK.(CO.OH)_2.2H_2O$, is readily obtained pure. It is sometimes used as a standard substance in volumetric analysis and is sold as "salt of sorrel" for removing rust and ink stains (of iron inks). The insolubility of calcium oxalate in acetic acid serves as a test for calcium and for oxalic acid. Many double oxalates are known. *Potassium-ferrous oxalate*, $K_2Fe(C_2O_4)_2$, made by mixing solutions of ferrous sulphate and potassium oxalate, is a powerful reducing agent, and used as a developer in photography. The corresponding ferric salt, $K_3Fe(C_2O_4)_3$, is reduced to the ferrous compound by light, and this reaction is the basis for making platinum prints. The paper coated with the double salt is exposed under a negative and then treated with a solution of platinum salt. The platinum is reduced and deposited in proportion to the change which the light has produced. Oxalic acid and some of its salts are used as mordants.

Of the esters of oxalic acid, the *dimethyl ester*, $C_2O_4(CH_3)_2$, is used for preparing pure methyl alcohol. It is prepared by dissolving anhydrous oxalic acid in the alcohol and heating.

Methyl oxalate is a solid which melts at 54°. Ethyl oxalate, made in a similar manner, is a pleasant smelling liquid, boiling at 186°.

Other Derivatives.—The *acid chloride*, $Cl.CO.CO.Cl$, cannot be made. Phosphorus pentachloride acts as a dehydrating agent in this case, and gives carbon dioxide, carbon monoxide, phosphorus oxychloride, and hydrogen chloride.

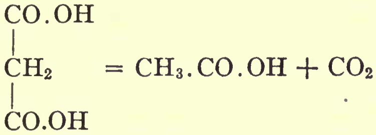
Oxalic acid amide or oxamide,  $\begin{matrix} CO.NH_2 \\ | \\ CO.NH_2 \end{matrix}$, is formed when ammonium oxalate is heated; when a neutral oxalic ester is shaken with aqueous ammonia; or from cyanogen by the action of water in the presence of a trace of aldehyde. It is a white crystalline substance, almost insoluble in water, alcohol or ether. When heated it partly sublimes unchanged and partly decomposes into cyanogen and water. When heated to 200° with water it is converted into ammonium oxalate.

When acid ammonium oxalate is heated, the first product is *oxamic acid*, $NH_2.CO.CO.OH$. The anhydride of oxalic acid does not exist.

Malonic acid, $CO.OH.CH_2.CO.OH$, may be looked at as acetic acid in which carboxyl has been substituted for one hydrogen atom in the CH_3 group. It is, in fact, made from acetic acid by such substitution. Monochloracetic acid, $CH_2Cl.CO.OH$, is first made, and after conversion into the potassium salt, is changed into the cyanacetate, $CH_2.CN.CO.OK$, by means of potassium cyanide. This is the nitrile of malonic acid, and from it the acid (or its salt) is obtained in the usual way by hydrolysis. This method of formation is satisfactory evidence of the constitution of the acid.

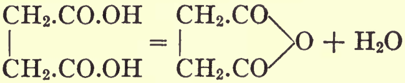
Malonic acid was first observed as an oxidation product of malic acid (p. 185), and its name was given it on account of this origin. It is a solid, melting at 133°–134°, and very soluble in water and in alcohol.

Heated a little above its melting point, malonic acid breaks up quantitatively into carbon dioxide and acetic acid:

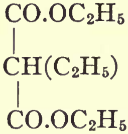
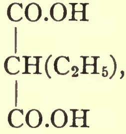
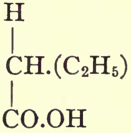


$$\begin{array}{l} \mathrm{CO.OH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OH} \end{array} = \mathrm{CH_3.CO.OH} + \mathrm{CO_2}$$

This is a typical general reaction which takes place on heating compounds containing two carboxyl groups united to the same carbon atom. We have here an unstable arrangement, which is like that already noticed in the case of hydroxyl groups; but while, in general, the dihydroxyl combination is unstable under all conditions, the dicarboxyl compounds decompose only when heated to their melting point or above. When a compound contains two carboxyl groups which are not immediately united to the same carbon atom, it decomposes on heating with the loss of the elements of water and formation of an anhydride. Thus in the case of succinic acid (p. 184):



Ethyl malonate, $CH_2(CO.OC_2H_5)_2$, has a special interest because of the fact that one or both of the hydrogen atoms of the CH_2 group can be replaced by sodium. The ester itself may be made by the reaction of malonic acid with alcohol, but is usually prepared by treating a mixture of cyanacetate of potassium (made as above) and alcohol with hydrogen chloride. It is a liquid, boiling at 198°. When sodium is added to it, hydrogen is evolved and $CHNa(CO.OC_2H_5)_2$ or $CNa_2(CO.OC_2H_5)_2$ is formed according to the proportion of sodium used. These sodium compounds are also formed by the action of sodium ethoxide on the ester. In this case intermediate addition products are probably formed as in the case of acetoacetic ester

(p. 174). The structure of the resulting sodium compounds, as in that case, is in doubt. Most of the reactions, however, are in agreement with the formulas given above. These sodium compounds react readily with alkyl halides and with acetyl chloride, giving replacements of the sodium by alkyl groups or by the acetyl group. By hydrolysis of these substituted esters the substituted dibasic acids are obtained; and from these, on heating, carbon dioxide is split out as in the decomposition of malonic acid by heat and the corresponding substituted monobasic acid is made. For instance, the sodium compound, $CHNa(CO.OC_2H_5)_2$ with C_2H_5I gives  $\begin{array}{l} CO.OC_2H_5 \\ | \\ CH(C_2H_5) \\ | \\ CO.OC_2H_5 \end{array}$, and this on hydrolysis yields  $\begin{array}{l} CO.OH \\ | \\ CH(C_2H_5) \\ | \\ CO.OH \end{array}$, which on heating =  $\begin{array}{l} H \\ | \\ CH.(C_2H_5) \\ | \\ CO.OH \end{array}$ or $CH_3.CH_2.CH_2.CO.OH$, ethyl acetic acid or normal butyric acid. This method of *malonic acid synthesis* is, therefore, a very useful means for making a great variety of compounds, and is especially employed for the synthesis of isomonobasic acids. A step-by-step replacement makes it possible to substitute two different alkyl groups for the two hydrogen atoms in the CH_2 group of malonic acid.

Other Derivatives of Malonic Acid

Among other derivatives the hydroxyl substitution products have the most interest.

Tartronic acid, $CO.OH.CHOH.CO.OH$, or *monohydroxymalonic acid,* can be made by the usual method for replacing hydrogen by hydroxyl: formation of brommalonic acid by direct action of bromine, and treatment of this with silver hydroxide. The name of this acid is derived from tartaric acid, from which it was first prepared by oxidation. It is a solid, melting at 187°.

Dihydroxymalonic acid, $CO.OH.C(OH)_2.CO.OH$, can be made from dibrommalonic acid by boiling it with barium hydroxide. Although this acid can be melted without loss of water, and forms salts which correspond to the formula given for the acid, it deports itself in reactions like a ketone-acid, *mesoxalic acid*, $CO.OH.CO.CO.OH$. Esters of both forms are known.

Dihydroxymalonic acid is interesting as one of the very small number of compounds which appear to contain two hydroxyl groups united to a single carbon atom (*cf.* p. 113). It is evident, however, from the ketone reactions it gives, that the combination is rather unstable.

The acid melts at 115°, and at higher temperatures decomposes into carbon dioxide, water, and glyoxylic acid:

$$CO.OH.C(OH)_2.CO.OH = CHO.CO.OH + CO_2 + H_2O$$

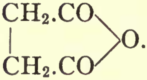
and on evaporation of its aqueous solution it breaks up into carbon monoxide, oxalic acid, and water:

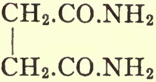
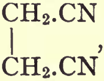
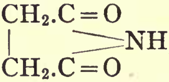
$$CO.OH.C(OH)_2.CO.OH = (CO.OH)_2 + CO + H_2O$$

The appearance of carbon monoxide in this reaction causes it to reduce ammoniacal silver nitrate with evolution of carbon dioxide. By sodium amalgam it is reduced to tartronic acid, and it unites with acid sodium sulphite like a ketone.

Succinic acid, $CO.OH.CH_2.CH_2.CO.OH$, occurs in many plants, in fossil wood, and derives its name from the fact that it is a product of the distillation of amber (*succinum*). It is prepared for medicinal purposes from amber, but may also be made by the fermentation of calcium malate or ammonium tartrate; or synthetically from propionic acid, or from ethylene by the usual method of forming the corresponding cyanogen compounds (nitriles). It is produced in small amounts in the alcoholic fermentation of sugar, and is frequently one of the products of the oxidation of fatty acids, etc., of higher molecular weight, by nitric acid. The structure of succinic acid is clear from the methods of its synthetic formation.

It melts at 182°, and boils at 235°, decomposing in great part into its anhydride. Dehydrating agents also produce the anhydride,



Succinamide.—The amide of succinic acid,  $\begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CO.NH_2\end{array}$, can be prepared, like other acid amides, by the reaction of an ester of succinic acid with ammonia. It behaves, in general, like other acid amides, but when strongly heated does not give the corresponding nitrile,  $\begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array}$, with loss of the elements of water, but loses one molecule of ammonia with conversion into a compound whose structure appears to be,  *succinimide* (NH being the *imido group*). This compound is also formed by distilling ammonium succinate, and by heating succinic anhydride in a current of ammonia.

Succinic anhydride and the imide both have formulas in which there is a closed ring of atoms instead of the open single or branched chains which represent the structure of most of the aliphatic compounds. The tendency to form such closed rings, or *cyclic compounds*, is most pronounced where the ring contains five or six connected atoms; others with a smaller or larger number are formed, but are less stable (*cf.* p. 257).

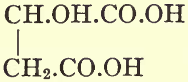
Succinamide melts at 242–243° and is somewhat soluble in water. Succinimide melts at 126°, boils at 287–288° and is readily soluble in water. Its reaction is neutral, but the hydrogen of the imido group is replaced by metals more readily than that of the amido group in acid amides.

Isosuccinic acid, $CH_3.CH(CO.OH)_2$, is a methyl derivative of malonic acid, and decomposes like this, when heated, giving propionic acid and carbon dioxide:

$$CH_3.CH(CO.OH)_2 = CH_3.CH_2.CO.OH + CO_2$$

Hydroxyl Derivatives of Succinic Acid

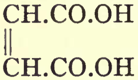
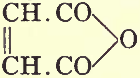
Malic acid,



$$\begin{array}{l} CH.OH.CO.OH \\ | \\ CH_2.CO.OH \end{array}$$

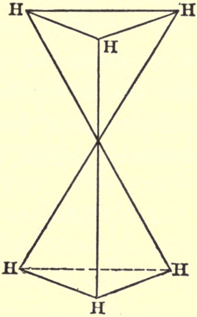
, is *monohydroxy-succinic acid.* It was first obtained from unripe apples (*malum*) and owes its name to that fact. It occurs very generally in acid fruits, such as gooseberries and currants, and is found in the roots, leaves and seeds of many plants and vegetables. It is readily prepared from the berries of the mountain ash. The juice of the berries is neutralized with calcium hydroxide, and the acid obtained from the difficultly soluble calcium salts by means of sulphuric acid. Another good source of malic acid is the so-called "maple sugar sand" formed in the making of maple sugar. The acid may also be made by the usual synthetic methods. It melts at 100°, and at a somewhat higher temperature begins to decompose. Instead of forming an anhydride by loss of water from the carboxyl groups, however, the decomposition is similar to that of the β-hydroxy-monocarboxylic acids with the production of an unsaturated acid (p. 172). At 140°–150° the chief product is fumaric acid. When heated rapidly to 180°, maleïc anhydride is a considerable product which is readily converted into maleïc acid by water.

The malic acid obtained from fruits is optically active, but its solutions show a somewhat unusual behavior in that the rotatory power changes with their concentration, so that dilute solutions are levo-rotatory, while concentrated solutions are dextro-rotatory. From the synthetic malic acid, which is inactive, two oppositely active acids can be obtained by means of the cinchonine salts. It will be noticed that the formula of the acid contains an asymmetric carbon atom.

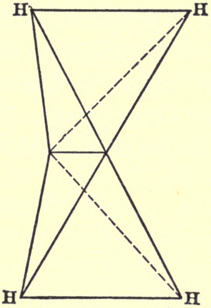
Fumaric and **maleïc acids,** which are formed by heating malic acid and can be made in other ways, present an interesting case of physical isomerism. The simple formula which stands for either is  $\begin{array}{l}\text{CH.CO.OH}\\ \|\\ \text{CH.CO.OH}\end{array}$. There is no asymmetric carbon atom and no optical activity, but the two acids differ widely in their solubility, their crystalline form, and their behavior when heated. Fumaric acid which occurs in many plants, in Iceland moss, and in some fungi, is the more stable of the two isomers. It is very sparingly soluble, and volatilizes at 200°, without melting. When heated higher it decomposes into water and maleïc anhydride,  $\left.\begin{array}{l}\text{CH.CO}\\ \|\\ \text{CH.CO}\end{array}\right\rangle\text{O}$ with partial charring. Maleïc acid is exceedingly soluble, melts at 130°, and at 160° boils and decomposes into water and its anhydride. It is converted into fumaric acid when heated with water at 130°, and under several other conditions. Maleïc acid solutions are precipitated by barium hydroxide, fumaric acid solutions are not. Other instances of similar isomeric pairs are known among unsaturated compounds.

Stereo-isomerism of Unsaturated Compounds.—Fumaric and maleïc acids present a case of isomerism like that of crotonic and isocrotonic acids (p. 111), in which decided differences in physical behavior are to be accounted for. An explanation given by stereochemistry is, in brief, as follows:

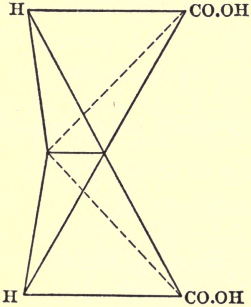
When a compound contains two carbon atoms united by a single bond, the tetrahedral formula is that shown in 1. When each of the carbon atoms is joined to four different atoms or groups (is asymmetrical), we may have such optical isomerism as is shown by lactic or tartaric acid (pp. 165 and 193). But in any other case the free rotation possible to the carbon atoms about their common axis is unattended by isomerism of any kind except that provided for by the usual structural formulas. If, however, the carbon atoms are united by a double bond, it is assumed that their rotation is no longer possible, and the condition is represented by 2, where the two tetrahedra are shown with one edge in common, indicating the double bond. Diagram 1 is the stereochemical formula of ethane, 2 that of ethylene. If two different atoms or groups are united to each of the carbon atoms joined by a double bond, two distinct arrangements can be made, as shown in 3 and 4, which give the stereochemical



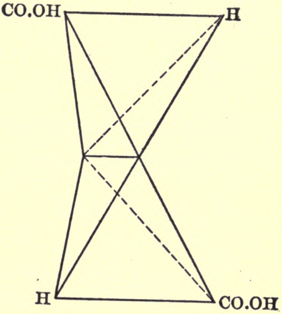
1. Ethane



2. Ethylene

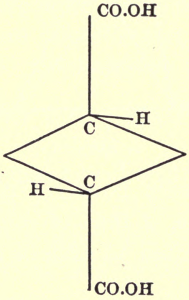


3. Maleïc acid

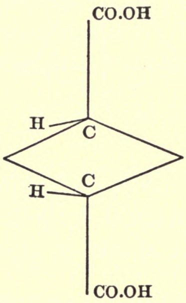


4. Fumaric acid

formulas of maleïc and fumaric acids. In these diagrams, as in those for the lactic acids and tartaric acids, the two forms cannot be superposed, but, unlike the cases of optical isomers, one is not the mirror image of the other. This type of isomerism which is shown by fumaric and maleïc acids, and by crotonic and isocrotonic acids, as well as by other unsaturated compounds, is called *geometric isomerism*, since the four atoms or groups united to the carbon atoms are represented as lying in the same plane. The two configurations may also be shown in diagrams which present the tetrahedral axes, as follows:

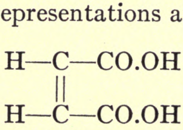


5. Fumaric acid



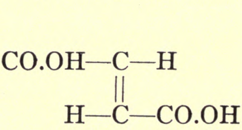
6. Maleïc acid

The corresponding projection formulas which are commonly used for these representations are:



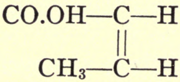
$$\begin{array}{rcccl} \mathrm{H} & - & \mathrm{C} & - & \mathrm{CO.OH} \\ & & \| & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{CO.OH} \end{array}$$

Maleïc acid



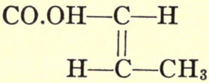
$$\begin{array}{rcccl} \mathrm{CO.OH} & - & \mathrm{C} & - & \mathrm{H} \\ & & \| & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{CO.OH} \end{array}$$

Fumaric acid



$$\begin{array}{rcccl} \mathrm{CO.OH} & - & \mathrm{C} & - & \mathrm{H} \\ & & \| & & \\ \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{H} \end{array}$$

Isocrotonic acid



$$\begin{array}{rcccl} \mathrm{CO.OH} & - & \mathrm{C} & - & \mathrm{H} \\ & & \| & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{CH_3} \end{array}$$

Crotonic acid

The assignment of the formulas to the maleïc and fumaric acids, as above, is based on the assumption that the positions of the carboxyl groups in the maleïc acid formula is the more favorable one for the formation of the anhydride which maleïc acid forms more readily than fumaric acid. This arrangement with like groups on the same side is called the *cis* or *maleïnoid form*, and the other, with opposed positions, the *trans* or *fumaroid form*. The latter is always given to the more stable isomer, as in the case of the crotonic acids (p. 111).

Tartaric acid, CO.OH.CHOH.CHOH.CO.OH, is dihydroxysuccinic acid. This well-known acid is widely distributed in nature both as free acid and in the form of potassium and calcium salts. Acid potassium tartrate, especially, is found in many fruits, and is present in considerable amount in the juice of grapes. As this salt is even less soluble in alcohol than in water, it is precipitated in wine casks as alcohol is formed by the fermentation of the grape-juice. Tannin and other substances are deposited with it, forming crystalline crusts which are known as *argol*, and from this the pure acid tartrate and the acid are prepared.

Preparation.—To obtain the pure salt, the crude argol is boiled with water and bone black, the solution filtered, and then evaporated to crystallization. For the preparation of the acid, the nearly insoluble calcium tartrate is precipitated from a solution of argol by chalk (or gypsum), and after filtration the acid is set free by sulphuric acid (with precipitation of calcium sulphate), and the tartaric acid is then crystallized from the clear solution.

Uses.—Tartaric acid and the acid potassium salt are used in medicine, in dyeing and calico printing, and for other purposes. Under the name of "cream of tartar" acid potassium tartrate is largely used as an ingredient of one class of baking powders. Potassium sodium tartrate, known as "Rochelle salt," has long been used in medicine, especially in Seidlitz powders which contain (1) this salt with sodium bicarbonate and (2) tartaric acid.

In the laboratory it is used in the preparation of Fehling's solution. Tartar emetic, potassium antimonyl tartrate, CO.OK.CHOH.CHOH.CO.O(SbO), is used as a mordant, and was formerly considered an important remedy.

Properties.—Tartaric acid crystallizes in long monoclinic prisms. It melts at 168°–170°, and when heated somewhat above its melting point, loses the elements of water with the formation of several substances which may be considered as anhydrides, since they are converted into tartaric acid again by boiling with water. At higher temperatures a more profound decomposition occurs; the acid becomes brown and chars, giving an odor like burnt sugar, and a distillate may be obtained which contains pyrotartaric (methyl succinic) and pyroracemic (p. 173) acids. When heated with concentrated sulphuric acid, tartaric acid chars, and carbon monoxide, dioxide, and sulphur dioxide are evolved. Tartaric acid is readily soluble in water and in alcohol, but insoluble in ether. When its solution is boiled alone or with addition of hydrochloric acid, tartaric acid is partly converted into the isomeric racemic acid. Tartaric acid is readily oxidized in solution. Ammoniacal silver nitrate solutions are reduced by it, and it is used in making silver mirrors. Solutions of the acid and of its salts are subject to change through the action of moulds and bacteria, and consequently do not keep well when exposed to the air. Succinic acid may be prepared from ammonium tartrate by bacterial fermentation. Calcium tartrate, on the other hand, yields no succinic acid, but gives volatile fatty acids, acetic, propionic, and butyric. Solutions of tartaric acid and its salts are optically active, being dextro-rotatory.

Tartaric acid is readily proved to be a dibasic acid, and its constitutional formula, which represents it as dihydroxy succinic acid, is established by its reduction (by HI) to malic and then to succinic acid. Other evidence to the formula is found in the synthesis of racemic acid whose relation to tartaric acid will now be discussed.

Racemic acid is an acid of the same composition as tartaric acid, but which differs from the latter in several particulars. It crystallizes in a different form (triclinic) and with one molecule of water of crystallization which is lost at 110°, and the acid melts with decomposition at 205–206°. It is much less soluble in water than tartaric acid, and the solutions are optically inactive. Its salts, the racemates, often differ from the tartrates of the same metals both in their crystalline form and in their water of crystallization and solubility. The calcium racemate is still less soluble in water than the calcium tartrate, while the acid potassium racemate is more soluble. These differences led to its recognition and separation in the preparation of tartaric acid from argol. Racemic acid is formed in tartaric acid solutions under certain conditions, and this probably accounts for its appearance as a by-product in the working up of argol, though it or its salts may be a natural product. Berzelius proved the identity of its composition with that of tartaric acid in 1830, and it is of interest to note that this fact together with the earlier discovery, that the fulminate and cyanate of silver had the same composition (Liebig, 1823), and some other similiar instances, led to the introduction of the word and idea of isomerism into chemistry.

Formation.—Racemic acid is formed from tartaric acid by boiling it for some time with water or with solutions of hydrochloric acid or sodium hydroxide. The conversion is, however, under these conditions, only partial; but when tartaric acid is heated with about one-ninth its weight of water to 125° (in a sealed tube) for some 30 hours, the change is almost complete. Racemic acid, together with mesotartaric acid, can be made from dibromsuccinic acid by substitution of hydroxyl for bromine:

$$\begin{aligned}&\mathrm{CO.OH.CHBr.CHBr.CO.OH} + 2\mathrm{AgOH}\\&\qquad = \mathrm{CO.OH.CHOH.CHOH.CO.OH} + 2\mathrm{AgBr}\end{aligned}$$

This reaction, which gives evidence for the structural formula of racemic acid, may be made the final step for its synthesis from the elements, as follows:

$$2C + 2H_2 \rightarrow CH_2:CH_2 \rightarrow CN.CH_2CH_2CN \rightarrow CO.OH.CH_2.CH_2.CO.OH, \text{ etc.}$$

Resolution of Racemic Acid into Optically Active Tartaric Acids.—In 1848, Pasteur found that the sodium ammonium salt of racemic acid gave two sets of crystals differing slightly in the disposition of their faces, and in such a way that one form corresponded to the mirror image of the other. On separating the two kinds, he found that the solution of one kind turned the plane of polarized light to the right, while that of the other was levo-rotatory. When the acids were set free from these salts, one proved to be the ordinary dextro-rotatory tartaric acid, and the other an isomeric, levo-rotatory acid. On mixing solutions containing equal weights of the two acids, and crystallizing, racemic acid is obtained. Pasteur also resolved racemic acid into the two active tartaric acids by taking advantage of the different solubilities of compounds which the two acids, mixed in racemic acid, form with certain optically active bases, such as cinchonine. By a third method, consisting in the action of certain organisms, one modification may be destroyed, leaving the other. Thus *penicillium glaucum* in a solution of ammonium racemate causes the dextro-tartrate to disappear, and ammonium levo-tartrate remains alone in solution.

Racemic acid, like ordinary lactic acid, is, therefore, a combination of two optically active isomeric acids whose power on polarized light is equal, but opposite.

The work of Pasteur by which these facts were brought out is of great historical interest, as it gave the first explanation of the relation of tartaric and racemic acids, and was the first time that an inactive substance was resolved into optically active compounds.[1] *Racemic* is now used as a general term to designate an

---

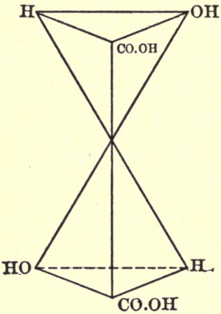
[1] See Pasteur's "Researches on The Molecular Asymmetry of Natural Organic Products," in Alembic Club Reprints, No. 14.

inactive substance which consists of a mixture of dextro and levo forms.

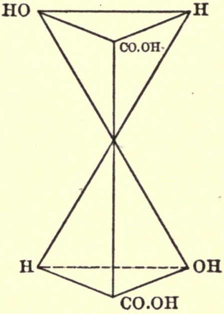
Mesotartaric acid, also has the same composition as tartaric acid, and is formed together with racemic acid when ordinary tartaric acid is heated with water or sodium hydroxide; but its formation takes place more slowly than that of racemic acid, so that the yield is increased by prolonging the heating. It is also formed with racemic acid by the synthesis from dibromsuccinic acid. It is separated from ordinary tartaric and racemic acids by taking advantage of the much greater solubility of its acid potassium salt. It crystallizes with one molecule of water of crystallization in a form differing from those of the other acids, and the anhydrous acid melts at 140°. Its solubility is about the same as that of tartaric acid, but its solutions are optically inactive, and it is not possible to resolve the acid into active components. It can, however, be partly converted into racemic acid by heating, and thus indirectly into the active tartaric acids. Its structural formula is the same as that of racemic acid and tartaric acid, as is shown by its formation from dibromsuccinic acid.

We have, therefore, *four dihydroxysuccinic acids:* two of these are optically active, turning the plane of polarized light to an equal degree in opposite directions, and differing in no other respect except in the modifications of their crystalline forms, in the solubility of the compounds they form with optically active organic bases, and in their behavior toward certain organisms. The other two inactive acids differ from the active acids and from each other in crystalline form, in their melting points, the solubility of their salts, etc., as well as by the fact that one of them can be resolved into active components, while the other cannot.

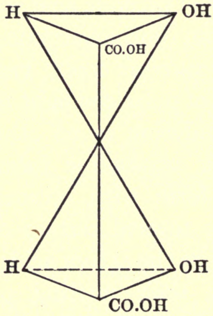
Stereochemistry of the Tartaric Acids.—The student has noticed that the structural formula for these acids contains two asymmetric carbon atoms. One such atom accounts for the existence of two oppositely active and one inactive compound, as we have seen in a former discussion (p. 169). When there are two or more asymmetric carbon atoms in the molecule the principles of stereochemistry admit the possibility of a larger number of physical isomers. With two as in this case, and two which are each combined with the same groups, there is but one additional arrangement. The formulas for the tartaric acids are:



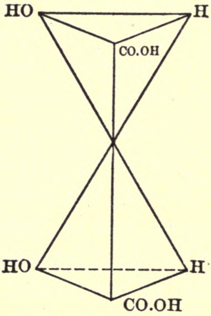
1. d-Tartaric acid.



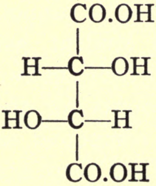
2. l-Tartaric acid.



3. Mesotartaric acid.

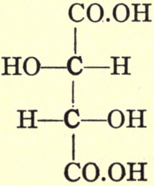


4. Mesotartaric acid.



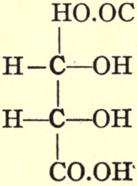
$$\begin{array}{rcl} & \mathrm{CO.OH} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ \mathrm{HO}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{CO.OH} & \end{array}$$

1



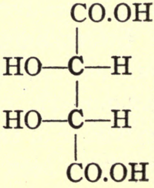
$$\begin{array}{rcl} & \mathrm{CO.OH} & \\ & | & \\ \mathrm{HO}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ & \mathrm{CO.OH} & \end{array}$$

2



$$\begin{array}{rcl} & \mathrm{HO.OC} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ & \mathrm{CO.OH} & \end{array}$$

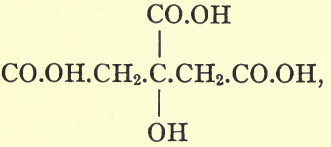
3



$$\begin{array}{rcl} & \mathrm{CO.OH} & \\ & | & \\ \mathrm{HO}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ \mathrm{HO}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{CO.OH} & \end{array}$$

4

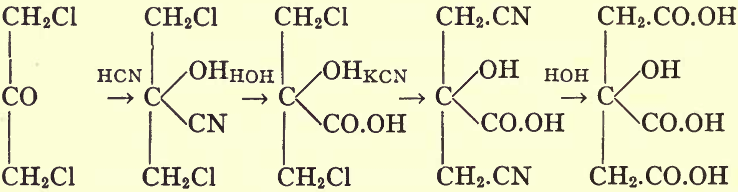
The lower and upper halves of formula 1 or 2 can be exactly superposed, and we may suppose that each half therefore supplements the optical activity of the other. One molecule will then be wholly dextro-rotatory, the other wholly levo-rotatory. A mixture of the two in equal amounts will be inactive through external or *intermolecular compensation.* This accounts for the two active tartaric acids and for racemic acid. But in the arrangements 3 or 4 the lower and upper halves of the figure cannot be superposed; one half of each formula is identical with one of the two halves of 1, and the other with one of the two halves of 2, so that both levo and dextro arrangements are present in the same molecule, and there is, therefore, optical inactivity through internal or *intramolecular compensation.* This is the representation of mesotartaric acid. Formula 4 differs in no essential feature from formula 3.



Citric acid, $CO.OH.CH_2.\overset{\displaystyle CO.OH}{\underset{\displaystyle OH}{C}}.CH_2.CO.OH$, occurs in many acid fruits often together with malic and tartaric acids. The juice of unripe lemons contains 6–7 per cent. of citric acid, and the acid is prepared commercially from this source. It is first precipitated as the calcium salt from the hot clarified juice by adding powdered chalk until no more carbon dioxide is evolved, and then milk of lime. The calcium citrate, after thorough washing with hot water, is decomposed by the calculated amount of sulphuric acid which precipitates the calcium as calcium sulphate. The acid is finally purified by recrystallization. It is readily soluble in water and in alcohol. It ordinarily crystallizes with one molecule of water, which is lost at about 130.° The anhydrous acid melts at 153°, and recrystallizes from cold water without water of crystallization. When the solid acid is heated, it chars and gives irritating vapors, but no odor of burnt sugar as in the case of tartaric acid. It differs from tartaric acid also by charring much less readily when heated with concentrated sulphuric acid, and by the fact that its calcium salt is more soluble in cold than in hot water. Like tartaric acid and some other organic acids, it prevents the precipitation of certain hydroxides of metals from solutions of their salts.

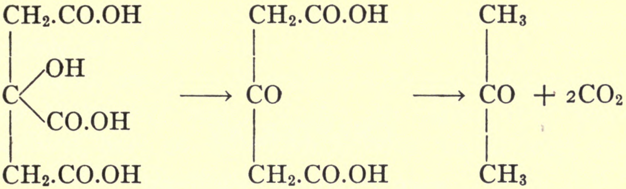
The acid is used for making lemonade, and is employed in medicine and in dyeing and calico printing. Magnesium citrate, $(C_6H_5O_7)_2Mg_3,14H_2O$, is a readily soluble salt which is used in medicine and, mixed with acid sodium carbonate and sugar, forms the well-known "effervescing citrate of magnesia" or "fruit salts." Ferric ammonium citrate is used in making "blue-print" paper.

Structure of Citric Acid.—The acid is readily proved to be a tribasic acid and to contain one hydroxyl group by the usual methods. The positions of the hydroxyl and carboxyl groups is demonstrated by the synthesis of the acid from symmetrical dichloracetone by the following steps:

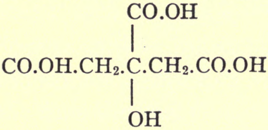


Dichloracetone   Citric acid

Also, when carefully heated with concentrated sulphuric acid the first reaction is the general one for the α-hydroxy-acids—the splitting off of formic acid (p. 171)—with the formation of acetone-dicarboxylic acid, followed by the decomposition of this acid into acetone and carbon dioxide:



HYDROXY-ACIDS

		Melting Point
Glycollic	$CH_2(OH).CO.OH$	79–80°
Lactic	$CH_3.CH(OH).CO.OH$	(Syrup)
Hydracrylic	$CH_2(OH).CH_2.CO.OH$	(Syrup)
Glyceric	$CH_2(OH).CH(OH).CO.OH$	(Syrup)
α-Hydroxybutyric	$CH_3.CH_2.CH(OH)CO.OH$	42–44
β-Hydroxybutyric	$CH_3.CH(OH).CH_2.CO.OH$	(Syrup)
γ-Hydroxybutyric	$CH_2(OH).CH_2.CH_2.CO.OH$	(Unstable)
Trihydroxy-isobutyric	$(CH_2OH)_2.C(OH).CO.OH$	116
Malic	$CO.OH.CH_2.CH(OH).CO.OH$	c.100°
Tartaric	$CO.OH.CH(OH).CH(OH).CO.OH$	168–170
Racemic	$CO.OH.CH(OH).CH(OH).CO.OH$	205–206
Mesotartaric	$CO.OH.CH(OH).CH(OH).CO.OH$	140
Citric	 $CO.OH.CH_2.\overset{\overset{CO.OH}{\vert}}{\underset{\underset{OH}{\vert}}{C}}.CH_2.CO.OH$	153

CHAPTER XV

THE CARBOHYDRATES

The compounds which are produced most abundantly, by growing plants, and which are the most important products of vegetation, are substances which contain hydrogen and oxygen, in the proportion in which they form water, combined with carbon. For this reason they were called *carbohydrates*. They do not contain water as such, and they are in no sense hydrates of carbon, as the name implies. Other compounds of carbon, hydrogen, and oxygen, in which the hydrogen and oxygen atoms are in the proportion of two to one, such as formaldehyde, acetic acid, or dihydroxyl acetone, might with equal reason be called carbohydrates. But, as in other cases, the old name has been retained, in spite of its erroneous suggestion, as a convenient designation of a group of substances which are definitely related to each other.

The study of the structure of the carbohydrates has shown that the simpler ones are aldehyde-alcohols or ketone-alcohols, and the more complex are converted into such compounds by hydrolysis. The most important and best known members of the group are the *sugars*, *starches*, and *celluloses*. Our knowledge of the structure of the sugars has been greatly extended in the last twenty-five years, especially by the investigations of Emil Fischer, who has succeeded in adding a considerable number of new synthetic sugars to those found in nature. The starches and celluloses are much more complex substances than the sugars and we have no definite knowledge of their structure except through the fact that they all yield simple sugars on hydrolysis. This indicates that they, as well as the more complex sugars, may be regarded as anhydride-like derivatives of the simple sugars. Their molecular weights cannot be determined with any certainty, but they appear to be very large. Unlike the sugars, they cannot be crystallized, have no characteristic taste, and in some cases are entirely insoluble in water.

The sugars, and the other carbohydrates from which sugars are derived by hydrolysis, are called *saccharoses* and are divided into two classes: the *monosaccharoses*, which do not undergo hydrolysis; and the *polysaccharoses*, which can be converted by hydrolysis into monosaccharoses.

The Monosaccharoses

These sugars have names that end in *ose*. Those which are aldehyde-alcohols are known as *aldoses*, and those that are ketone-alcohols are called *ketoses*. They are further distinguished according to the number of carbon atoms they contain as *dioses*, *trioses*, etc. Except in one instance, the rhamnose, the molecules contain no unsubstituted alkyl groups, but only primary or secondary alcohol groups with one aldehyde or ketone group. Further, their carbon atoms are united in open, unbranched chains, so that they are all derivatives of normal hydrocarbons. When the aldehyde group is present it is a terminal group, and the ketone group is always next to a terminal alcohol group. Compounds of this structure have been met with in glycollic aldehyde (p. 162), glyceryl aldehyde, and dihydroxyl acetone, (p. 161). These represent the classes of dioses and trioses and may properly be included in the group of sugars. The student will recall that glycollic aldehyde is "condensed" by the action of dilute alkali into a tetrose (p. 162).

All of the aldoses and ketoses, with the exception of glycollic aldehyde, and dihydroxyl acetone, contain one or more asymmetric carbon atoms. Hence stereochemical isomerism is possible, with an increase in the number of groupings as the number of the asymmetric carbon atoms is greater. The rule for the number of isomers is given by the formula 2^n, n being the number of asymmetric carbon atoms. The aldohexoses contain four such atoms, and hence there are sixteen stereo-isomers; the ketohexoses have three asymmetric carbon atoms and hence their possible number is eight. We find that the sugars are all optically active when they are not in the "racemic" form.

The structure of these compounds is determined by the methods with which we have become familiar in the study of simpler substances. The presence of hydroxyl groups and their number is found by examination of the acetyl substitution products which are obtained when the sugar is treated with acetic anhydride in the presence of zinc chloride; and the presence of the aldehyde or ketone group is determined by the products of careful oxidation and by their reactions. An aldehyde group, being monovalent, must always be at the end of the chain of carbon atoms, and the position of the divalent ketone group is inferred from the numbers of carbon atoms in the first oxidation products (*cf.* p. 90).

The monosaccharoses are all colorless and odorless substances. They dissolve readily in water, with difficulty in absolute alcohol, and are insoluble in ether. Their solutions are sweet, and are neutral to litmus. Those which contain five or more carbon atoms are mostly solids which usually crystallize well from pure solutions, but the crystallization is often very slow, and is retarded or prevented by the presence of other substances. When heated above their melting point, they are decomposed, turning brown, and finally charring. Glycerose (glyceryl aldehyde) and the natural hexoses are fermented by yeast with the production of alcohol. The pentoses do not enter into alcoholic fermentation, and the property of such fermentation appears to be restricted to sugars which contain three, or a multiple of three, carbon atoms.

Monosaccharoses with Less than Six Carbon Atoms.— *Glycollic aldehyde*, $CH_2OH.CHO$, is the simplest possible aldose;

glyceryl aldehyde, $CH_2OHCHOH.CHO$, is the next aldose, and *dihydroxylacetone*, $CH_2OH.CO.CH_2OH$, is the simplest of the ketones. *Erythrose*, $C_4H_8O_4$, or $CH_2OH.CHOH.CHOH.CHO$, is the first product of the oxidation of erythritol, the normal tetrahydroxyl alcohol, and is probably identical with the *tetrose* which is formed by the aldol condensation of glycollic aldehyde. Tetroses are also formed by oxidation of pentonic acid (tetrahydroxy valeric acid, $CH_2OH(CHOH)_3.(CO.OH)$ in the form of its calcium salt.

Pentoses.—*Arabinose* and *Xylose* are both aldoses with five carbon atoms and have the formula $CH_2.OH(CHOH)_3.CHO$. They are obtained by the hydrolysis of natural polysaccharoses —arabinose from gum-arabic or cherry gum, and xylose (wood sugar) from wood gum, by boiling beech-wood, jute, etc., with dilute acids. *Rhamnose* is a methyl substituted pentose, $CH_3.(CHOH)_4.CHO$, which is a product of the hydrolysis of certain glucosides.

These three pentoses are all dextro-rotatory. They are oxidized by bromine to corresponding monocarboxylic acids, and by nitric acid to trioxyglutaric acid, $CO.OH(CHOH)_3.CO.OH$. They can all be reduced by sodium amalgam to the corresponding pentahydroxyl alcohols.

Hexoses

Two natural sugars, glucose and fructose, are hexoses. They are widely distributed in the vegetable kingdom, occurring together in the juices of many sweet fruits, in the roots, leaves, and flowers of plants, and in honey. These two sugars are formed in equal amounts by the hydrolysis of cane sugar, and isomers, identical in every respect except in the matter of optical activity, have been made synthetically from formaldehyde and from glycerol. They crystallize less readily than cane sugar. In solution both undergo alcoholic fermentation with yeast but the rate of the fermentation is usually not the same, and depends on the yeast that is used. Both reduce Fehling's solution to the same extent, the fructose here acting more rapidly than the glucose; both give silver mirrors with ammoniacal silver nitrate; and neither when pure is discolored by cold concentrated sulphuric acid. Their solutions are both optically active, glucose being dextro-rotatory, and fructose (levulose) levo-rotatory. The action of fructose on polarized light is more powerful than that of glucose; and hence a solution containing equal amounts of the two sugars (invert sugar) is levo-rotatory. (See table of Specific Rotations p. 408). Both sugars form compounds with calcium and barium when treated with the hydroxides of these metals.

d-Glucose, $C_6H_{12}O_6$, is also known as *dextrose* and *grape-sugar*. The name of dextrose was given this sugar because it is dextro-rotatory; but with the discovery of other dextro-rotatory hexoses, and of a levo-rotatory glucose, the name is no longer distinctive, and is little used. Glucose is present in considerable quantities in ripe grapes, and forms the brownish nodules which are seen in raisins. Certain natural substances known as *glucosides* are esters of glucose, and yield this sugar as one of the products of hydrolysis. Among these are: *amygdalin* (p. 147), *æsculin* (in horse-chestnut bark), and the *tannins* (p. 367). Glucose appears in diabetic urine, sometimes to the amount of 8–10 per cent.

Formation and Preparation.—Glucose is a product of the hydrolysis of a number of polysaccharoses, which occurs when they are heated with water with the addition of a little inorganic acid. Starch, dextrin, and maltose can in this way be completely converted into glucose. Cellulose is soluble in concentrated sulphuric acid, and when the solution is largely diluted with water and boiled, soluble carbohydrates are formed, the final product of the hydrolysis being glucose. It is thus possible to make wood and other vegetable fibers into a sugar, and through this into alcohol.

Certain other carbohydrates on hydrolysis yield glucose with some other hexose. Cane sugar gives equal amounts of dextrose and levulose (invert sugar), milk sugar is converted into dextrose and galactose, and raffinose into glucose, fructose, and galactose.

Glucose may be prepared in the laboratory by hydrolysis of cane sugar in alcoholic solution by means of hydrochloric acid. Since glucose is less soluble in alcohol than the fructose which is simultaneously formed, a considerable part of it will crystallize from the solution.

Commercial glucose or "grape-sugar" is made from starch by heating it with very dilute acid. In Europe the starch of potatoes, rice and sago is used and sulphuric acid is employed as the hydrolytic agent. In this country corn starch is the source of "dextrose" and the syrup known as "glucose." The starch is heated with a 1 to 3 per cent. solution of hydrochloric acid, usually under pressure. For the production of "glucose," the heating is stopped when iodine no longer gives a blue color (starch) with the solution. The solution is then nearly neutralized with sodium carbonate, clarified by bone-black and evaporated in vacuum pans to a specific gravity of 1.375–1.43. This "glucose" contains d-glucose with maltose, and considerable amounts of dextrin which is an intermediate product. In the manufacture of grape-sugar, the heating is prolonged a little beyond the point at which alcohol fails to produce a precipitate in a sample of the solution (absence of starch and dextrin). The solution is then neutralized, clarified, and evaporated so far that it solidifies on cooling. Grape-sugar forms a mass of waxy texture, and contains a small amount of dextrin. Glucose is also obtained when cellulose (wood fiber) is heated with dilute acids under pressure of six or eight atmospheres. In a recent process for making alcohol from wood waste such as saw-dust, sulphurous acid is used under pressure to cause the conversion into glucose.

Uses of "Glucose."—Glucose is largely used as a table syrup, in making confectionery, jellies, and preserves; as an addition to wine and beer wort before fermentation in order to increase the amount of alcohol; as an adulterant for thick liquids, such as extracts of logwood, etc.; and as a reducing agent in indigo dyeing.

Properties of Glucose.—Glucose crystallizes from water at ordinary temperatures with one molecule of water, but from alcohol or concentrated aqueous solutions at 30°–35°, anhydrous crystals are formed which melt at 146°. It is much less sweet than fructose or cane sugar. It is not charred by concentrated sulphuric acid, as cane sugar is, but like cane sugar is oxidized to oxalic acid by nitric acid. Heated with alkalies it turns brown.

Structure.—By the acetyl reaction glucose is shown to contain five hydroxyl groups. Reduction by sodium amalgam in aqueous solution converts it into *sorbitol*, a normal hexahydroxyl alcohol, which shows that the carbon atoms in glucose are linked in an unbranched chain. By careful oxidation it forms *gluconic acid*, $C_6H_{12}O_7$ or $CH_2OH(CHOH)_4.CO.OH$, by the addition of one oxygen atom, which indicates that glucose contains an aldehyde group. Gluconic acid cannot be crystallized, as on concentrating its solution it is dehydrated and forms gluconic lactone (*cf.* p. 172), a crystalline substance that is reconverted into glucose on reduction with sodium amalgam in slightly acid solution. This is a reaction of great synthetical importance (p. 207). Further oxidation of glucose gives *saccharic acid*, $C_6H_{10}O_8$, $HO.OC(CHOH)_4.CO.OH$. This is a dibasic acid and a comparison of its formula with that of gluconic acid shows that both gluconic acid and glucose contain a primary alcohol group. We arrive thus at the following constitutional formula for glucose as an aldose:

$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO$$

d-Fructose, $C_6H_{12}O_6$, also known as *fruit sugar*, and *levulose*. We have seen that fructose frequently occurs in nature with glucose, and is formed with it in the hydrolysis of certain polysaccharoses. Honey contains about 80 per cent. of invert sugar, and cane sugar is completely hydrolyzed into this mixture of glucose and fructose. From such mixtures fructose can be separated in the form of an insoluble calcium compound which yields fructose when treated with carbon dioxide; but it is best prepared by the hydrolysis of *inulin*, a polysaccharose which occurs in the tubers of the dahlia and some other plants, and yields only fructose.

Properties.—Fructose is somewhat less soluble in water than glucose, but crystallizes with greater difficulty. Anhydrous crystals are obtained from its alcoholic solution which melt at 95°. It is sweeter than glucose.

Structure.—As in the case of glucose, five hydroxyl groups may be proved to be present; but on oxidation it gives two acids, one with four carbon atoms, and one with two, instead of a single acid with six carbon atoms. When boiled with mercuric oxide it gives a mixture of trihydroxy-butyric acid and glycollic acid; carefully oxidized with nitric acid, it yields tartaric and glycollic acids:

$$C_6H_{12}O_6 + 2O = \underset{\text{Trihydroxy-butyric acid}}{CH_2OH.(CHOH)_2.CO.OH} + \underset{\text{Glycollic acid}}{CH_2OH.CO.OH}$$

$$C_6H_{12}O_6 + 4O \rightarrow \underset{\text{Tartaric acid}}{CO.OH.(CHOH)_2.CO.OH} + \underset{\text{Glycollic acid}}{CH_2OH.CO.OH}$$

These reactions are those of a compound with a ketone structure (p. 90) and show that fructose is a ketose with the formula, $CH_2OH.CHOH.CHOH.CHOH.CO.CH_2OH$.

d-Galactose, $C_6H_{12}O_6$, is a sugar which is formed together with glucose by the hydrolysis of milk sugar. A number of other carbohydrates, such as certain gums, also yield galactose as one of the products of their hydrolysis; and it is formed by the careful oxidation of *dulcitol*, a hexahydroxyl alcohol which occurs in certain plants. It is less soluble in water than either glucose or levulose, and its solutions are fermented by yeast, though more slowly than those of these sugars. It is strongly dextro-rotatory and forms minute hexagonal crystals which melt at 168°.

d-Mannose, $C_6H_{12}O_6$, is produced together with fructose by the careful oxidation of the natural hexahydroxyl alcohol, *mannitol*, and is also formed by the hydrolysis of certain carbohydrates, especially from one contained in vegetable ivory. It is a hard amorphous substance which is hygroscopic and very soluble in water, but difficultly soluble in alcohol, even when hot. It is dextro-rotatory and readily fermented by yeast.

Both galactose and mannose are aldoses with the same structural formulas as glucose, as is shown by their conversion by careful oxidation into galactonic and mannonic acids which are physical isomers of gluconic acid, and then into mucic and mannosaccharic acids, which stand in similar relation to saccharic acid.

Sorbose, $C_6H_{12}O_6$, is found in the juice of mountain ash berries after standing, being apparently formed by bacterial oxidation of the hexahydroxyl alcohol, sorbitol, which is present in the berries. It is a ketose, a stereo-isomer of fructose.

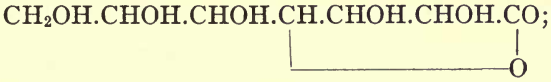
Formation and Synthesis of the Monosaccharoses.—Besides the method of formation which consists in the hydrolysis of polysaccharoses, and which is applicable to both pentoses and hexoses, the members of this group can be made in other ways, of which the following are the most important:

1. Oxidation of the corresponding polyhydroxyl alcohols. The products obtained by ordinary oxidizing agents (nitric acid) are aldoses, while the sorbose bacteria (*bacterium xylinum*) cause the formation of ketoses not only from sorbitol, but also from glycerol and other polyhydric alcohols.

2. Through the addition product which hydrocyanic acid forms with aldehydes, one aldose may be converted into another with one more atom of carbon in the molecule. For example, an aldohexose forms with hydrocyanic acid a *cyanhydrin*,

$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CH\Big\langle\begin{matrix}OH\\CN\end{matrix}.$$

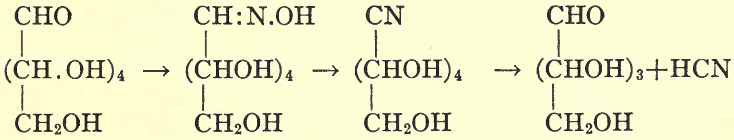
This is converted on hydrolysis into a seven-carbon-atom monobasic acid, $CH_2OH.CHOH.CHOH.CHOH.CHOH.CHOH.CO.OH$, which readily loses the elements of water with the production of a γ-lactone (*cf.* p. 172).



$$CH_2OH.CHOH.CHOH.\underbrace{CH.CHOH.CHOH.CO}_{O};$$

and finally, the lactone in aqueous solution is reduced by sodium amalgam to the corresponding aldehyde, which is an *aldoheptose*, $CH_2OH(CHOH)_5CHO$. By this method heptoses, octoses and nonoses have been prepared.

3. One of the methods for descending from one sugar to another with one less carbon atom is the following: the oxime (p. 79) is made, and this on heating with concentrated sodium hydroxide gives the nitrile, which on further heating loses hydrocyanic acid and gives the lower sugar. The transformations in the groups affected are:



$$\begin{array}{ccccccc} CHO & & CH{:}N.OH & & CN & & CHO \\ | & & | & & | & & | \\ (CH.OH)_4 & \rightarrow & (CHOH)_4 & \rightarrow & (CHOH)_4 & \rightarrow & (CHOH)_3 + HCN \\ | & & | & & | & & | \\ CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH \\ \text{Glucose} & & \text{Oxime} & & \text{Nitrile} & & \text{Arabinose} \end{array}$$

Glucose Oxime Nitrile Arabinose

4. The formation of a tetrose from glycollic aldehyde and of a hexose from formaldehyde and from glyceric aldehyde by aldol condensation have already been referred to, as has also the significance of the synthesis of a sugar from formaldehyde with its suggestion of the mode by which the natural carbohydrates may be built up in plants from the carbon dioxide and water (p. 86).

5. Aldoses can be converted into the isomeric ketoses by means of the osazones which can be made from them (see below).

6. Ketoses can be changed into the corresponding aldoses by the following steps: the ketone is reduced by sodium amalgam to the polyhydroxyl alcohol; this may be converted into the aldose by careful oxidation (method 1); or is oxidized into a monobasic

acid which is then changed to the aldose by the lactone reaction (method 2).

Inactive fructose is of especial historic interest as it is the first sugar which was produced from substances which are themselves capable of synthetic formation. It results from the polymerization of formaldehyde by bases (p. 85); from glyceric aldehyde by aldol condensation; from glycerose (formed by oxidation of glycerol) by the action of dilute alkalies. It was originally called *acrose.* It has all the properties of natural fructose, except optical activity. It ferments with yeast, but the fermentation is partial, destroying the levo-rotatory component and leaving a dextro-rotatory fructose.

By a series of reactions, mostly of the kind which have been discussed, the synthetic inactive fructose can be converted into the natural sugars mannose, glucose and fructose.

Another interesting fact is that glucose, fructose and mannose are each partially converted into both of the others under the influence of dilute alkalies, an equilibrium being established which may be thus represented;

$$\text{Glucose} \rightleftarrows \text{Fructose} \rightleftarrows \text{Mannose}$$

The study of the sugars has been greatly facilitated by the fact that they form compounds called *osazones* which, unlike the monosaccharoses themselves, are sparingly soluble in water, are readily obtained in the pure state by crystallization, and have characteristic melting points. Through these properties of the osazones, the sugars, which by themselves are separated with great difficulty, may be distinguished and identified.

We have seen (p. 80) that hydrazine and its derivatives react with the aldehydes and ketones to form hydrazones. By reaction with phenyl (C_6H_5) hydrazine, $C_6H_5NH{:}NH_2$, both the aldoses and the ketoses form hydrazones, which, when an excess of the phenyl hydrazine is present, react with it with the final production of double hydrazones called osazones. The steps in the case of an aldose are:

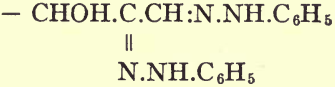
$$\underset{\text{Aldose}}{-\mathrm{CHOH.CHOH.CHO}} + \mathrm{C_6H_5.NH.NH_2} \rightarrow$$

$$\underset{\text{Hydrazone}}{-\mathrm{CHOH.CHOH.CH{:}N.NH.C_6H_5}}$$

$$\underset{\text{Hydrazone}}{-\mathrm{CHOH.CHOH.CH{:}N.NH.C_6H_5}} + \mathrm{C_6H_5NH.NH_2} \rightarrow$$

$$\mathrm{NH_3} + \mathrm{C_6H_5.NH_2} + \underset{\text{Carbonyl compound}}{-\mathrm{CHOH.CO.CH{:}N.NH.C_6H_5}},$$

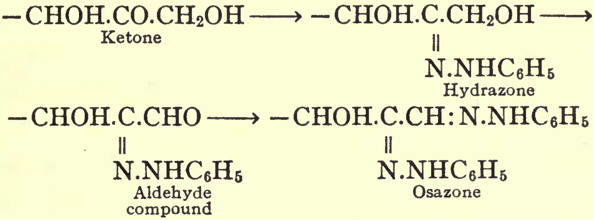
and this + $\mathrm{C_6H_5.NH.NH_2} \rightarrow$



$$-\mathrm{CHOH.}\underset{\substack{\| \\ \mathrm{N.NH.C_6H_5}}}{\mathrm{C}}\mathrm{.CH{:}N.NH.C_6H_5}$$

Osazone

With a ketose the steps are:



$$\underset{\text{Ketone}}{-\mathrm{CHOH.CO.CH_2OH}} \longrightarrow -\mathrm{CHOH.}\underset{\substack{\| \\ \mathrm{N.NHC_6H_5} \\ \text{Hydrazone}}}{\mathrm{C}}\mathrm{.CH_2OH} \longrightarrow$$

$$-\mathrm{CHOH.}\underset{\substack{\| \\ \mathrm{N.NHC_6H_5} \\ \text{Aldehyde} \\ \text{compound}}}{\mathrm{C}}\mathrm{.CHO} \longrightarrow -\mathrm{CHOH.}\underset{\substack{\| \\ \mathrm{N.NHC_6H_5} \\ \text{Osazone}}}{\mathrm{C}}\mathrm{.CH{:}N.NHC_6H_5}$$

The osazones of the aldoses and of corresponding ketoses are identical. On treatment of an osazone with strong hydrochloric acid it is decomposed with the formation of a ketone-aldehyde, $-\mathrm{CO.CHO}$, called an osone, and this is reduced by nascent hydrogen into a ketose. Thus it is possible to convert an aldose into its isomeric ketose, as for instance, glucose into fructose.

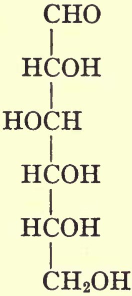
By the reactions which have just been discussed, many synthetical sugars have been made and definitely distinguished. All of the sixteen possible aldolhexoses are known and five of the eight ketohexoses, including the natural sugars. The synthetical sugars which have been made are stereo-isomers of the natural sugars, having a different optical activity or being inactive.[1]

---

[1] For further discussion of the methods of sugar synthesis and for the stereochemistry of the sugars, see: "The Simple Carbohydrates and the Glucosides" by E. Frankland Armstrong, and "Modern Organic Chemistry" by C. A. Keane.

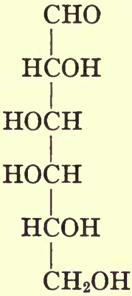
Stereochemistry of the Hexoses.—The configurations, or stereo-formulas of all of the possible sixteen aldo-hexoses have been determined by Fischer, as well as those of many of the related alcohols and acids; and the following projection formulas of the three aldo-hexoses which we have considered, and of the two fructoses (ketohexoses) are given here as illustrations:

d-Glucose



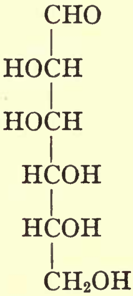
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Galactose



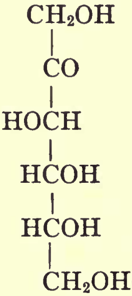
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Mannose



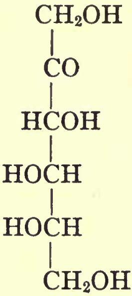
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Fructose



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

l-Fructose



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

In the systematic nomenclature of sugars which the synthetic additions to the group have made necessary, all monosaccharoses derived from a dextro-, levo-, or inactive hexose are designated by the letter *d*, *l*, or *i*, without reference to the rotatory power they may actually possess. Thus ordinary fructose which is levo-rotatory is called d-fructose because it can be obtained from "d-glucose." The same method of classification is adopted for the hexahydroxyl alcohols and other derivatives of the hexoses. This has not been emphasized in the brief discussion of the sugars in this book, but is necessary in any extended study of the literature of the subject.

The Polysaccharoses

We may divide this group into the *disaccharoses*, of which cane sugar is the most important member, the *trisaccharoses*, and the carbohydrates of unknown molecular weight—the *starches* and the *celluloses*—to which the name of polysaccharoses is often restricted.

Disaccharoses

These sugars have the molecular formula, $C_{12}H_{22}O_{11}$, equal to a double hexose less a molecule of water; and they are readily converted into hexoses by hydrolysis:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

From the ease with which this conversion occurs, it is inferred that the hexose residues in the disaccharoses are not united by the linkage of carbon atoms, but by oxygen; so that the disaccharoses are, in a sense, *anhydrides* of the hexoses. They cannot, however, be obtained from the hexoses by means of water-withdrawing agents, as many anhydrides are made; but by indirect methods in which acetyl substitution products of the hexoses play a part, artificial disaccharoses have been made.

Saccharose, sucrose, or **cane sugar,** $C_{12}H_{22}O_{11}$, is our common sugar and commercially much the most important of all the sugars. It is widely distributed in nature, occurring in the juice of the sugar cane, sorghum and many other species of grass, in beets and many other roots, in the sap of the sugar maple and other trees, and in many fruits, and in seeds such as walnuts, almonds, and coffee, and in the nectar of flowers. Nearly all of the world's supply is obtained from the sugar cane and the sugar beet. In the growing cane the only sugar present is dextrose, but this disappears as the plant matures and the ripe cane contains only a trace of it with about 18 per cent. of saccharose. The sweet juice is usually expressed from the cane by crushing it between heavy rolls. Beets contain from 12 to 15 per cent. of sugar. They are cut into thin slices or rasped to a pulp, and digested with warm water, into which the crystallizable sugar passes by diffusion, leaving the colloids—albuminoids, gums etc., for the most part in the root cells. This diffusion process, consequently, gives a purer juice than can be obtained by other means. The subsequent processes are much the same in both the sugar cane and the beet industries. The juice is boiled with milk of lime with the result that calcium salts of the acids which are present, together with coagulated albuminous substances and gum, are separated as a scum. The clarified juice is finally concentrated by evaporation, usually in vacuum pans, allowed to crystallize, and separated from the mother-liquor or "molasses" by draining from hogsheads with perforated bottoms, or more commonly by centrifugal machines. The product is a raw sugar of a more or less brownish color, containing a number of impurities. White granulated sugar is obtained from it by a refining process which consists essentially in dissolving the sugar in water, decolorizing by bone black and recrystallizing.

The molasses contains 40 to 50 per cent. of sugar. This is diluted, clarified and boiled down for a "second sugar." The "second molasses" from this sugar, when obtained from the sugar cane, still contains about 40 per cent. of sugar which it does not pay to recover. It is sometimes fermented for making rum or alcohol, and sometimes used as fuel. It is not suitable for table use or cooking, but a little of the first molasses from cane sugar is used in this way. Beet sugar molasses is unfitted for table use, by its very unpleasant odor and taste from the presence of certain nitrogenous substances. Much of the sugar remaining in the second molasses from beet sugar is recovered by changing it into an insoluble calcium or strontium sucrate by treatment with lime or strontium hydroxide. After separation and washing, the sucrate is mixed with water and decomposed into sugar and insoluble calcium or strontium carbonate by carbon dioxide. The final molasses from beet sugar contains a large amount of organic salts of potassium together with the nitrogenous substances which have been mentioned. This molasses is usually fermented and the alcohol distilled, leaving these substances in the residue, which is called *vinasse.* If this is evaporated and calcined, the ash contains about 35 per cent. of potassium carbonate. If the residue from evaporation is destructively distilled, methyl alcohol, ammonia and "trimethyl amine" (p. 132) are obtained as valuable products, and the potassium products are recovered from the cinder left in the retort.

Properties.—Cane sugar is soluble in about half its weight of cold water. It crystallizes well from concentrated solutions (syrups) in large, transparent crystals known as "rock-candy." It melts at 160° and solidifies, on cooling, to an amorphous, glass-like mass, which after a time becomes crystalline. On stronger heating, it turns brown, being converted into "caramel," an amorphous substance, much used as a flavoring and coloring material. At a high temperature it is completely decomposed, with the evolution of gases and vapors, leaving a residue of nearly pure, porous charcoal (sugar charcoal). Among the products of its destructive distillation are the oxides of carbon, hydrocarbon gases, aldehyde, acetic acid, etc. When moistened and treated with concentrated sulphuric acid it turns brown and finally chars.

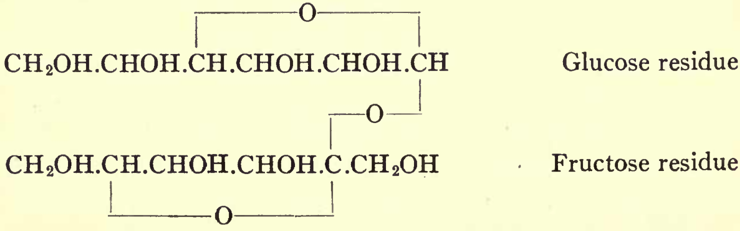
Sugar is oxidized easily by such agents as chromic acid, potassium chlorate, or nitric acid. With the first two the reaction is explosive; with concentrated nitric acid, a considerable product is oxalic acid (*cf.* p. 177). Caustic alkalies do not turn cane-sugar solutions brown as they do solutions of dextrose.

Cane-sugar solutions are strongly dextro-rotatory. In the presence of acids, the sugar is hydrolyzed into a mixture of equal amounts of glucose and fructose (invert sugar), which is levorotatory because of the stronger optical effect of fructose. The hydrolysis takes place slowly in cold solutions and more rapidly when they are heated. Even carbonic acid effects the conversion.

Cane sugar is not fermented by zymase, the enzyme of yeast, which produces alcoholic fermentation in glucose and fructose; but ordinary yeast causes alcoholic fermentation, though not as quickly as with the hexoses, because it contains another enzyme, called invertase, which first converts the saccharose into invert sugar. Strong syrups, however, do not ferment, and sugar is used in the preserving of fruit and in jellies.

Sugar combines with various oxides and hydroxides of metals, which are resolved into sugar and the metal carbonate by carbon dioxide. The calcium and strontium sucrates, as has been noted, play a part in the recovery of sugar from molasses.

Structure of Saccharose.—Saccharose is shown by its acetyl substitution products to contain eight hydroxyl groups, and its reactions indicate the absence of aldehyde and ketone groups. In the natural synthesis of cane sugar, which appears to be effected from the hexoses, these groups must be involved in the change. We have seen in the case of the polyhydroxy-acids that lactones are readily formed by the loss of the elements of water from the carboxyl and γ-hydroxyl group; and while the structure of saccharose has not been definitely established, it is probable for this and other reasons that it is represented by the following formula:

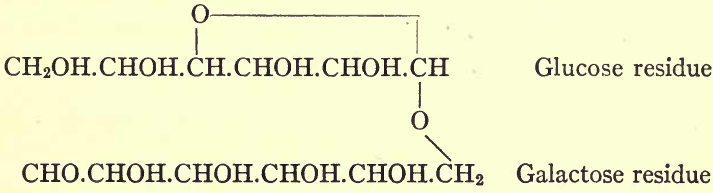


$$\begin{array}{ll} CH_2OH.CHOH.CH.CHOH.CHOH.CH & \text{Glucose residue} \\ CH_2OH.CH.CHOH.CHOH.C.CH_2OH & \text{Fructose residue} \end{array}$$

Lactose, milk sugar, $C_{12}H_{22}O_{11}$ is present to the amount of 3 to 5 per cent. in the milk of mammals. When the fats (cream) have been removed from milk and the casein (curds) has been precipitated, as by rennet in cheese-making, the whey or watery solution contains most of the milk sugar, which is readily obtained by evaporation, and purified by recrystallization. It crystallizes with one molecule of water, $C_{12}H_{22}O_{11}, H_2O$. It is much less soluble, and much less sweet than cane sugar. Lactose is not affected by cold concentrated sulphuric acid.

Solutions of lactose are dextro-rotatory. It differs from cane sugar and resembles dextrose by turning brown when heated with solutions of caustic alkalies, by reducing Fehling's solution and ammoniacal silver nitrate, by forming a phenyl osazone, and in being reduced to polyhydroxyl alcohols by sodium amalgam. It differs from both cane sugar and the hexoses by not fermenting with yeast. It is converted into lactic acid by the lactic acid ferment, and is hydrolyzed by dilute acids into a mixture of glucose and galactose, both of which are aldoses.

Structure.—The reactions of lactose indicate the presence of an aldehyde group, and reasons similar to those given for the constitution of saccharose point to the following as the probable formula for lactose:



$$\begin{array}{ll}
\text{CH}_2\text{OH.CHOH.}\overset{\text{O}\text{———————}}{\text{CH}}\text{.CHOH.CHOH.CH} & \text{Glucose residue}\\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | & \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{O} & \\
\text{CHO.CHOH.CHOH.CHOH.CHOH.CH}_2 & \text{Galactose residue}
\end{array}$$

Maltose $C_{12}H_{22}O_{11}$, is produced from starch by the action of diastase, an enzyme present in malt, by an enzyme contained in saliva, and by other ferments, and is an intermediate product in the hydrolytic conversion of starch and dextrin into dextrose. Its formation from starch is a important factor in the manufacture of beers and other alcoholic beverages, and of alcohol.

Maltose is very readily soluble in water and its solutions are more strongly dextro-rotatory than those of any other sugar. It reduces Fehling's solution, and is readily and completely fermented by yeast into alcohol and carbon dioxide. It forms a phenyl osazone. From dextrose, which it so greatly resembles in its behavior, it is distinguished by its stronger rotatory power, by being less soluble in water and in alcohol, and by not reducing a weak acetic acid solution of copper acetate. Its reduction of Fehling's solution, too, is slower and less in amount than that of glucose. Maltose yields only glucose when hydrolyzed.

As the anhydride from two molecules of an aldose, glucose, it is given the same *structural* formula as lactose.

Trisaccharoses

Raffinose, $C_{18}H_{32}O_{16}$, is the only one of this group which has any importance. It occurs in small amounts in the sugar beet and is obtained from the molasses. It is also found in cotton seed and in barley. It is much less soluble in water than cane sugar and crystallizes with five molecules of water. The crystals lose their water at 100°, and the sugar melts at 118°–119°. The solutions are strongly dextro-rotatory. It is indifferent toward alkalies and Fehling's solution, but is completely fermented by yeast. On hydrolysis it yields first fructose and melebiose (melebiose being a disaccharose) which breaks down into glucose and galactose.

Two or three crystallizable carbohydrates obtained from various roots seem to belong between the well-characterized sugars and the amorphous carbohydrates of much higher molecular weight. Their molecular weights are not known with certainty but are possibly expressed in the formula $C_{36}H_{62}O_{31}$. They are readily soluble in water, are dextro-rotatory and give mixtures of sugars on hydrolysis.

Carbohydrates of Unknown Molecular Weight

Polysaccharoses

Most of these carbohydrates are amorphous substances and have no distinctive taste. The most important members of the group —the starches and celluloses—are insoluble in water, and those which appear to dissolve form "colloidal solutions." Like other amorphous and colloidal substances they have no definite melting points. Their composition is represented by the formula $C_6H_{10}O_5$, but their molecular weights are unknown though there is evidence that they must be very large. The formula usually given them is, therefore $(C_6H_{10}O_5)$.

Since these carbohydrates give simple sugars on hydrolysis, we may infer that they are built up of monosaccharose residues united, as in the disaccharoses, by linking oxygen atoms. If this is the case their relation to the simple sugars would be represented by

$$xC_6H_{12}O_6 - (x-1)H_2O = C_{6x}H_{10x+2}O_{5x+1}$$

It would be practically impossible to determine by analysis the differences between the composition represented by this last formula and that shown by $(C_6H_{10}O_5)_x$, if x is very large. For instance, if x = 100, the percentages of carbon, hydrogen, and oxygen corresponding to the two formulas would be:

	For $(C_6H_{10}O_5)_{100}$	For $C_{600}H_{1002}O_{501}$
C =	44.42	44.37
H =	6.22	6.23
O =	49.36	49.40
	100.00	100.00

Most of these carbohydrates are the products of plant life, and together with the natural sugars are built up from the carbon dioxide of the air and water, probably through the formation of formaldehyde and subsequent polymerizations. Cane sugar appears to be the first definite carbohydrate formed which can be isolated, though fructose, glucose, and maltose are also present in the green leaf. The more complex starches and celluloses are the final products of the plant synthesis.

Starch occurs in nearly all plants, and is utilized by the plant for the elaboration of other substances. It is stored in considerable quantities in the seeds, tubers, and many roots, where it forms an important reserve material for the nourishment of the future plant until it can become self-supporting from atmospheric supplies.

The chief industrial sources of starch are potatoes, wheat, corn, rice, arrowroot and certain palms. In this country corn and wheat are used; in Europe, potatoes, rice and wheat are mainly employed. The manufacture of starch is essentially a mechanical separation from the gluten, fats, etc., which accompany it in the original material. In making corn starch, for instance, one process is in outline as follows: Much of the oil is removed and the gluten softened by first steeping in warm water for some days. Next, the grain is ground, while a current of water carries the product to revolving sieves and then to bolting cloth strainers, through which the starch passes in suspension in the water. On standing, the crude starch is deposited, and after being washed with fresh water is stirred up in vats with a dilute solution of caustic soda. After several hours the suspended matters are allowed to settle, and the solution containing much of the impurity is drawn off. The sediment is again stirred up with water, and allowed to stand until the gluten is deposited, while the starch, still in suspension, is drawn off and deposited in other tanks. By several repetitions of this process the starch is mostly removed from the gluten and at the same time separated into several grades. Modifications of this process are also employed, and centrifugal machines are sometimes used to separate the starch from the wash water. Corn contains about 58 per cent.

of starch and about 50 per cent. is actually obtained, and, at the same time, over 20 per cent. of gluten suitable for cattle food.

Properties.—Starch is a white, glistening powder, consisting of microscopic granules which have a concentric structure and are doubly refracting. The form, size and markings of the granules vary with the source, so that this is readily determined by a microscopical examination.

Starch is very hygroscopic, and ordinary starch contains from 16–18 per cent. of water, which can be driven off by careful heating up to 110°. The granules are enveloped in a cellulose membrane which completely protects them from the action of cold water, but when heated with water the granules swell up and burst, forming starch paste, and on longer heating some of the starch goes into colloidal solution. If treated for some days with a cold dilute inorganic acid, "soluble starch" is produced which dissolves in hot water without forming a paste.

When heated to 200°–250° starch is changed into dextrin, and a similar change is effected at a lower temperature, when the starch has first been moistened with hydrochloric or nitric acid, dried at 50°, and then heated to 140°–170°. Starch is hydrolyzed to dextrin, maltose, and glucose, by dilute acids, and also by *diastase*, an enzyme contained in barley sprouts, and by *ptyalin*, the characteristic enzyme of saliva. It does not form an osazone, and its solutions do not reduce Fehling's solution or ferment with yeast.

Starch is readily detected by the intense blue color which it gives when brought in contact with free iodine. The nature of this "starch iodide," is not known. It usually contains 18 to 20 per cent. of iodine.

Uses.—Starch is a very important food, both in natural substances and when prepared from them, being first hydrolyzed and then supplying the chief fuel material for the maintenance of the temperature of the body. It is used in the preparation of glucose and dextrin, and is employed in laundry work, in finishing cotton cloth, in sizing paper, for making paste, etc. Different starches vary in their properties to some extent and are adapted to different purposes. Sago, tapioca, arrowroot, and some other starches are used chiefly for food. Wheat starch makes the best paste, rice starch is preferred for toilet powders, while potato and corn starch are most largely employed in the glucose and dextrin industries, and are also used for other purposes.

Inulin $(C_6H_{10}O_5)_x$, occurs in many *compositæ* and some other plants in a swollen or dissolved state. It differs from ordinary starches by being readily soluble in warm water, and giving solutions which are not colored by iodine, and do not form a jelly. The solutions are levo-rotatory, and the inulin is easily hydrolyzed by dilute acids with the formation of fructose as the sole product (*cf.* p. 204). Inulin is not affected by diastase. When dried, it forms a white powder, consisting of minute spherical granules.

Glycogen $(C_6H_{10}O_5)_x$, is a starch-like substance found in the animal organism, being especially abundant in the liver. It also occurs in mollusca, and in moulds and other fungi. It resembles starch in appearance, but dissolves in warm water to an opalescent solution from which it can be precipitated by alcohol. Its solutions are colored red by iodine. They are dextro-rotatory, and are hydrolyzed by acids, and by diastase and ptyalin, into the products similar to those given by starch.

Dextrin is produced, as already stated, when starch is heated alone, or after it has been moistened with acids. It is of a brownish color, which is lighter when the acid process is used; but in this case the dextrin contains some sugar and its adhesive power is less. It is also the first product of the hydrolysis of starch. Dextrin is readily soluble in water and is precipitated from its solutions by alcohol. The solutions reduce Fehling's solution, and give a red to violet color with iodine. They are dextro-rotatory and are hydrolyzed to maltose and glucose.

Dextrin is not directly fermentable by yeast. It is used for making mucilage, and is also employed in calico printing and tanning to thicken the colors and extracts, in brewing and in confectionery.

Gums.—This name is given to certain products of plants which sometimes occur as translucent amorphous masses, and in other cases are precipitated from alkaline extracts of plant substances by hydrochloric acid and alcohol. They go into colloidal solution in water, forming sticky liquids, and are precipitated from these solutions by alcohol. They appear to be mixtures, but contain certain carbohydrates, which, unlike any we have so far considered, often yield pentoses on hydrolysis. *Gum arabic*, and the gums which appear on cherry and peach trees, give *arabinose; xylan*, a gum frequently found in tree bark, and a gum obtained from grains, give *xylose*. Galactose is formed at the same time in most cases.

Cellulose forms the cell membrane in all plants, and is their chief solid constituent. It is, however, almost always incrusted with other substances (lignin, resins, etc.). These substances can be removed more or less completely by treatment with various reagents which act on them more readily than on the cellulose. Thus paper pulp is made from wood, and the textile fibers of linen, hemp, and jute are prepared by a bacterial fermentation in water ("retting") which softens and partly destroys the gummy and resinous matters. Cotton, linen, and various piths are almost pure cellulose, and the best "washed" filter paper is cellulose with only a trace of impurity.

Properties.—Cellulose is a stable substance, insoluble in all ordinary solvents; but it is dissolved by an ammoniacal solution of copper hydroxide ("Schweitzer's reagent" made by forcing a current of air through a solution of ammonia in which copper turnings are placed); and is precipitated from this solution by acids and salts. The precipitated cellulose, when washed with alcohol and dried, forms a white amorphous powder. A waterproof paper can be prepared by passing unsized paper through a strong solution of Schweitzer's reagent and then pressing several sheets together without washing.

Strong sulphuric acid (4:1) dissolves cellulose, and if the fresh solution is poured into water a colloidal substance is precipitated, which, so long as it is in contact with the acid, is colored blue by iodine, as starch (amylum) is, and is hence called *amyloid*. The blue color also appears when cellulose is moistened with a solution containing free iodine (iodine in potassium iodide) and then treated with concentrated sulphuric acid or zinc chloride solution (test for cellulose). "*Parchment paper*" is paper coated with amyloid by dipping unsized paper into sulphuric acid (4:1) and washing it immediately with water. A strong solution of zinc chloride acts in the same way as sulphuric acid.

If the colloidal solution of cellulose in sulphuric acid is allowed to stand for some time before diluting it, and is then boiled, soluble carbohydrates are formed, among which glucose is usually present in considerable quantity.

Dilute alkalies do not affect cellulose, but strong solutions form compounds which are decomposed when washed with water, leaving a hydrate of cellulose. When cotton cloth is treated in this way (under tension to prevent shrinking) the fibers acquire a silky luster, and the cloth is known as "mercerized" cotton.[1]

When the compound formed by the action of the alkali on cellulose is treated with carbon disulphide it produces a substance, cellulose xanthate (p. 243) which, when beaten with water, forms a thick solution known as "viscose." This is easily decomposed with the formation of a cellulose hydrate. By squirting viscose through fine tubes into a solution which causes this decomposition, lustrous threads of artificial silk are formed. Artificial silks are also made from nitrocellulose, and by treatment of cellulose with ammoniacal copper solutions. Viscose is also employed in making photographic films, in sizing paper, and for other purposes.

The presence of alcohol groups in cellulose can be proved by the

---

[1] Process discovered by John Mercer about 1850.

usual method. It can therefore form esters, and among the esters of cellulose is a *cellulose triacetate* which on evaporation of its chlor form or other solution leaves a tough water-proof film. Such films are non-inflammable and used in photography, for water-proofing, insulation of wires, etc. The esters which are formed by reaction with nitric acid are, however, the most important ones. The number of acid radicals introduced depends on the strength of the acid used, the temperature, and the time allowed the reaction. These esters are called "nitrocelluloses," just as the glyceryl nitrate is called "nitroglycerine." A mixture of the lower nitrates, in which two to five nitric acid radicals have replaced hydroxyl in $C_{12}H_{20}O_{10}$ is called "pyroxylin" and its solution in alcohol and ether is "collodion." "Celluloid" is an intimate mixture of pyroxylin with camphor. These substances burn with a quick flare, but are not definitely explosive. When cellulose is nitrated further by means of a mixture of concentrated nitric and sulphuric acids the explosive hexanitrate is produced $[C_{12}H_{14}O_4(NO_3)_6]_x$. This is used in making smokeless powder. "Gun-cotton" made by this treatment from cotton fiber resembles closely in appearance the cotton from which it is made. It is insoluble in alcohol and ether as well as in water. It burns rapidly but without explosion, when unconfined. When confined, it explodes violently on detonation.[1]

Storage of Energy in Plants.—In connection with this study of carbohydrates, the amount of energy stored by plants in the form of carbohydrates is of interest. In the building up of the amount of these substances which is represented by the gram-molecular weight of the simple composition formula of starch or cellulose (162 grams), about 670 large calories are required. Roughly indicated, the change is shown as follows:

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2 - 670 \text{ calories}$$

The necessary energy for this process comes from sunlight, which

---

[1] See J. B. Bernadou, "Smokeless Powder, Nitrocellulose, etc."

is the source of almost all of the energy at man's disposal, since that obtained from water power and wind is also the result of solar radiation. The storage of energy in the formation of carbohydrates, it should be noted, is not only through the synthesis of these substances, but also in the release of oxygen with its potential chemical energy. In the various processes of utilization of this energy, in the use of fuels, of food, etc., the potential energy of the organic materials and of oxygen is transformed into kinetic energy which largely appears as heat.

Fermentation and Enzymes[1]

The term fermentation originally signified the effervescent action which occurs when sugars are converted into alcohol by yeast. It has since come to include a great variety of changes in which more or less complex organic substances are resolved into simpler ones under the influence of certain living organisms or of substances contained in them. While it was long believed that the living yeast cells were essential to the process of alcoholic fermentation, other changes, like that of starch into glucose by means of malt, were found to be due to "unorganized ferments" or substances which, like the diastase in malt, are not living organisms, though formed by such organisms. Such unorganized or "unformed" ferments are known as *enzymes*. The inversion of cane sugar which is effected by yeast before alcoholic fermentation sets in is effected by such an enzyme known as *invertase*. In 1898 Buchner demonstrated that the living yeast was not necessary for alcoholic fermentation, but that this change can be brought about by means of a substance in the juice expressed from yeast and freed from all living organisms. This enzyme is called *zymase*.

The present view in regard to all the reactions which are classed as fermentations is that they are the result of the action of

---

[1] See W. M. Bayliss, "The Nature of Enzyme Action," and Cohnheim, "Enzymes."

enzymes which probably act as catalytic agents. Some of them cause the splitting of the complex substance into simpler ones, as in the breaking down of glucose into alcohol and carbon dioxide; others bring about hydrolysis, as in the conversion of starch into glucose by diastase, and the production of various hexoses from the disaccharoses; others, still, effect oxidations with the aid of the oxygen of the air, as in the fermentation processes by which acetic acid is formed from alcohol, and lactic and butyric acids from sugars. Certain reductions, also, are apparently the result of enzymic action.

The enzymes, like other catalyzers, show a very definite selective power in their action. We have had a number of instances showing this fact, and may recall as an illustration the destruction of one of the two optically active components in racemic acid by certain bacteria, while the other is untouched (p. 192). The enzymes are probably asymmetric substances, and we may imagine that that selective action is due to some relation between their (unknown) structure and that of the compound on which they act. As Emil Fischer suggests, the enzymes and the compounds may possess complementary configurations like those of a lock and its key.

None of the enzymes have been obtained in a state of complete purity. They are very complex substances of a protein character, and efforts to isolate them from the other proteins with which they are associated cause a loss of their activity. They occur chiefly in moulds, yeasts, bacteria, and living tissues, and these organisms are usually employed to bring about the fermentations without attempting to separate the enzymes from them. In a few instances, powders are prepared which contain the enzymes, such as diastase, pepsin, and rennin.

While some of the reactions which are effected by enzymes can also be brought about by inorganic catalyzers (notably those of hydrolysis of sugars, starch, and glucosides), and alcohol can readily be converted into acetic acid by ordinary oxidizing agents, many other transformations, such as the production of alcohol and of lactic acid from sugars, cannot be realized by the usual chemical means. Very many of the chemical changes which go on in living plants and animals are now known to be dependent on the presence of enzymes.

We have spoken of enzymes as catalytic agents. They at least resemble them, as appears from the facts that, like the inorganic catalysts, they are not used up in the processes which they conduct, they do not enter into the products of the reactions, and their amount in proportion to the quantity of substance transformed is often infinitesimally small. It is probable that no catalyst is capable of starting a reaction; but that it acts rather as an accelerator of actions which are already proceeding, though often with such slowness that we are quite unable to note their progress.

It is believed that enzymes, or substances of the nature of enzymes, are generated abundantly in the tissues of both plants and animals, and that the secretions which are so intimately associated with digestion and other functions of the body owe their special effectiveness to the presence of these substances.

CHAPTER XVI

DERIVATIVES OF CARBONIC ACID

Carbonic acid, $CO(OH)_2$, which is assumed to be present in solutions of carbon dioxide, carbon dioxide its anhydride, and the carbonates, are always treated in inorganic chemistry; but these compounds, as well as carbon monoxide, belong also to organic chemistry if we define it broadly as the chemistry of the compounds of carbon. As these compounds have been sufficiently presented in inorganic chemistry, it is only necessary for us here to recall the part which they play in the synthesis of some organic compounds and to call attention to the fact that carbonic acid may be regarded as hydroxyl formic acid, HO.CO.OH, and may indeed be reduced to formic acid (and carbonates to formates).

There are certain compounds, however, which may be regarded as derivatives of carbonic acid, in the sense in which this term has been employed, and which from their character are usually classed with the organic substances. Some of these compounds are briefly discussed in this chapter by themselves, because of the unusual character of carbonic acid as compared with other organic acids.

Carbonyl chloride, $COCl_2$, may be considered as the dichloride of carbonic acid. It is, in fact, formed, though in small amount, by the action of phosphorus pentachloride on sodium carbonate, just as chlorides of other organic acids are from their salts. It is also formed from carbon tetrachloride when this is heated with sulphur trioxide or phosphorus pentoxide; and when a mixture of carbon dioxide and carbon tetrachloride vapor is led over pumice heated to 350°:

$$CO_2 + CCl_4 = 2COCl_2$$

It is also one of the products of the oxidation of chloroform (*cf.* p. 39); and carbon monoxide and chlorine unite directly under the influence of sunlight to carbonyl chloride. The compound was first obtained in this way and was given the name of *phosgene*, as a product formed by the action of light.

Carbonyl chloride is prepared commercially by passing a mixture of chlorine and carbon monoxide over charcoal, which acts as a catalyzer.

Carbonyl chloride is a gas (boiling point 8.2°) which dissolves readily in benzene and toluene. It has a stifling odor, and is very irritating to the throat and lungs. It is sold in liquid form in cylinders and in solution in toluene, and is employed in synthetical work, both in laboratories and in the making of coal tar dyes.

Reactions.—Carbonyl chloride gives the reactions which are characteristic of acyl chlorides with water, alcohol, and ammonia (*cf.* p. 115); but in some respects is a more powerful agent than acetyl chloride, as is seen by the fact that it reacts with acetic acid at 120° with the production of acetyl chloride, and converts the sodium salts of the fatty acids into their acid anhydrides.

A monochloride of carbonic acid would be chloroformic acid, $ClCO.OH$; but this, like formyl chloride, $HCO.Cl$, has not been obtained. Both these compounds, if formed, must be very unstable, breaking down into hydrogen chloride and carbon dioxide or carbon monoxide.

Esters of Carbonic Acid.—By the action of alcohols on carbonyl chloride, esters are formed. The first product is an ester of chlorcarbonic (or chlorformic) acid:

$$ClCO.Cl + C_2H_5OH = ClCO.OC_2H_5 + HCl$$

By further action of alcohol or of alkali alkoxide on the chlorcarbonic ester, the neutral ester, $CO(OC_2H_5)_2$, is produced. In this way both simple esters, and mixed esters, such as $CH_3O.CO.OC_2H_5$, can be made.

The chlorcarbonic esters are liquids of tear-compelling odor. They are used in synthetic reactions for the purpose of introducing the carboxyl group. For instance, by reaction with the sodium compound of ethyl malonic ester (*cf.* p. 181), ethyl chlorcarbonate gives the ethyl ester of methane-tricarboxylic acid.

$$CHNa(CO.OC_2H_5)_2 + ClCO.OC_2H_5 = CH(CO.OC_2H_5)_3 + NaCl$$

In many reactions these esters split into carbon dioxide and the alkyl chloride; *e.g.*, with $ZnCl_2$:

$$ClCO.OC_2H_5 = CO_2 + C_2H_5Cl;$$

and by nascent hydrogen they are converted into esters of formic acid.

The neutral esters are liquids of ethereal odor, insoluble in water, and readily saponified. When heated with an alcohol which contains a higher alkyl group, this is substituted for the lower one in the ester:

$$CH_3O.CO.OC_3H_7 + C_3H_7OH = CO(OC_3H_7)_2 + CH_3OH$$

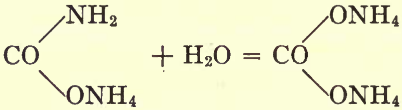
Acid esters of carbonic acid, such as $C_2H_5O.CO.OH$, are too unstable to exist, but their alkali salts, $C_2H_5O.CO.ONa$, are formed by leading carbon dioxide into an alcoholic solution of an alkoxide. These ester-salts are decomposed by water with the production of alcohol and alkali carbonate.

Amides of Carbonic Acid

As in the case of the carbonic acid chlorides, the diamide is a stable compound while the monamide cannot be isolated.

Carbamic acid, $NH_2.CO.OH$, the monamide of carbonic acid, exists only in its salts, esters, and chloride. *Ammonium car-*

bamate, the ammonium salt of the monamide, $NH_2CO.ONH_4$, is formed when carbon dioxide and ammonia gas are brought together. Commercial ammonium carbonate, which is prepared by sublimation from a mixture of ammonium sulphate and calcium carbonate, contains both ammonium carbamate and acid ammonium carbonate. The carbamate is precipitated when ammonia and carbon dioxide are led into cool, absolute alcohol, and may be prepared in this way. In solution in water it is partly converted into the carbonate:



$$\mathrm{CO}\begin{matrix}\diagup\mathrm{NH_2}\\ \diagdown\mathrm{ONH_4}\end{matrix} + \mathrm{H_2O} = \mathrm{CO}\begin{matrix}\diagup\mathrm{ONH_4}\\ \diagdown\mathrm{ONH_4}\end{matrix}$$

Acids decompose it into carbon dioxide and the ammonium salts of the acid:

$$NH_2CO.ONH_4 + 2HCl = 2NH_4Cl + CO_2$$

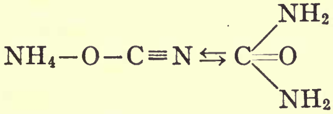
At 60°, the solid carbamate breaks up into ammonia and carbon dioxide; and when it is heated in sealed tubes to 130° – 140°, it is largely converted into urea:

$$NH_2.CO.ONH_4 = NH_2.CO.NH_2 + H_2O$$

Urea, $CO(NH_2)_2$, was discovered in urine in 1773, and is of great physiological interest as it is the most important nitrogen end-product of the metabolism of protein substances in man and the carnivora. The average amount of urea excreted by an adult person in health, is about 30 grams a day, representing about 84 per cent. of the total nitrogen eliminated from the system. In disease, the proportions of urea and other nitrogen compounds may be markedly different.

Preparation from Urine.—Urea may be obtained from urine in the form of its nitrate by evaporating the urine to small bulk and adding nitric acid. Urea nitrate, $CO(NH_2)_2.HNO_3$, is precipitated, and purified by oxidizing agents (nitric acid or potassium permanganate) and recrystallization. Urea is set free from the nitrate by decomposing the salt in a warm solution with barium carbonate. On evaporating the solution of urea and barium nitrate to dryness and extracting with hot alcohol, the urea alone is dissolved.

Formation and Preparation from Other Substances.—1. Urea was first made in the laboratory by Wöhler in 1828. He obtained it as a result of evaporating an aqueous solution of ammonium cyanate:



$$NH_4-O-C\equiv N \leftrightarrows C\begin{array}{l}\diagup NH_2\\ =O\\ \diagdown NH_2\end{array}$$

Ammonium cyanate (p. 150) had not then been prepared from its elements, but it was considered to be essentially an inorganic substance. Up to this time no organic substance had been made from inorganic material and it had been generally thought that transformations of this sort were impossible. Wöhler's discovery is, therefore, of great historical importance, though it was many years before synthetical methods of producing organic substances became a well-established laboratory procedure. The formation of urea from ammonium cyanate evidently involves a considerable rearrangement within the molecule, but we have already noted that the atoms in hydrocyanic and cyanic acids appear to be unusually mobile (p. 151). The reaction is not a complete one, as it is reversible.

Other ways of forming urea are: 2. By leading a mixture of carbon dioxide and ammonia through a tube heated to a faint red, cyanic acid being an intermediate product. 3. From ammonium carbamate at 130°–140°, also essentially a synthesis from carbon dioxide and ammonia. 4. By passing carbonyl sulphide, CO.S (p. 242), into a strong solution of ammonia. Ammonium thiocarbamate, $NH_2.CO.SNH_4$, is first formed but readily breaks down into hydrogen sulphide and urea, especially when shaken with lead carbonate.

1. Like other acid amides, urea is hydrolyzed when its solutions are heated with acids or alkalies, the products being ammonia and carbon dioxide (carbonic acid):

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$

This hydrolysis occurs in urine through the action of certain organisms, so that the urine that is normally acid becomes alkaline, and smells of ammonia.

2. Urea, like other amides, forms salts with strong acids, such as the nitrate, whose formula has been given, and the difficultly soluble oxalate, $2CO.(NH_2)_2,(CO.OH)_2$, only one of the amido groups reacting with acids.

3. Nitrous acid acts on urea, as on the amides and primary amines, with the production of nitrogen and carbonic acid:

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 2H_2O$$

4. A solution of sodium hydroxide and bromine (in which sodium hypobromite is present) effects a like reaction with formation of sodium carbonate and nitrogen. This is often employed for the determination of the amount of urea in solution by measurement of the nitrogen, but in the case of urine it is not a very exact method:

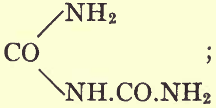
$$CO(NH_2)_2 + 3NaOBr = N_2 + 3NaBr + CO_2 + 2H_2O$$

A test for urea (also given by proteins) is made by heating the solid substance and then treating it with a solution of alkali containing a little copper sulphate. A reddish-violet color is produced. (*Biuret test.*)

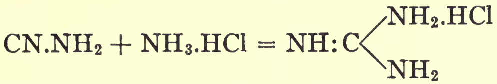
5. By reaction of ammonia with carbonyl chloride—a general reaction of acid chlorides. If instead of carbonyl chloride, diphenyl carbonate, $CO(OC_6H_5)_2$, is first made by the action of the sodium salt of phenol on carbonyl chloride, and this is then treated with ammonia, the reaction is especially successful.

6. Cyanamide (p. 149) is hydrolyzed in the presence of a little inorganic acid to urea: $CN{\cdot}NH_2 + H_2O = CO(NH_2)_2$

The composition of urea and its formation from carbonyl chloride are sufficient evidence for the structure which is represented by its formula.

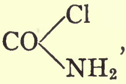
Properties and Reactions.—Urea crystallizes in a form resembling that of saltpeter. It melts at 132° and at a higher temperature decomposes first into ammonia and *biuret*,  $CO\left\langle\begin{matrix}NH_2\\NH.CO.NH_2\end{matrix}\right.$; and gives as a final product cyanuric acid (p. 149). Urea is readily soluble in water and in alcohol.

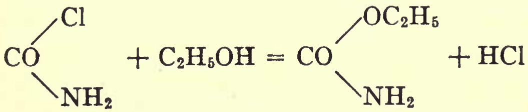
Derivatives of Urea and Related Substances.—*Guanidine*, $HN:C(NH_2)_2$, was first obtained from guanine, a purine base (see p. 235) of complicated structure. Guanidine can be made by heating ammonium thiocyanate to 180°, or by heating an alcoholic solution of cyanamide with ammonium chloride:



$$CN.NH_2 + NH_3.HCl = NH:C\left\langle\begin{matrix}NH_2.HCl\\NH_2\end{matrix}\right.$$

It is a crystalline substance of strong basic properties, which is converted into urea by baryta water.

Carbonyl chloramide,  $CO\left\langle\begin{matrix}Cl\\NH_2\end{matrix}\right.$, or urea chloride is half carbonyl chloride and half amide. It can be made by leading carbonyl chloride over heated ammonium chloride. It reacts vigorously with water to form ammonium chloride and carbon dioxide; with ammonia or amines it gives urea or alkyl-substituted ureas; with alcohols it forms amido-carbonic or carbamic acid esters:



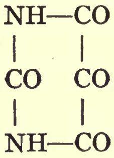
$$CO\left\langle\begin{matrix}Cl\\NH_2\end{matrix}\right. + C_2H_5OH = CO\left\langle\begin{matrix}OC_2H_5\\NH_2\end{matrix}\right. + HCl$$

These esters of carbamic acid are called *urethanes*.

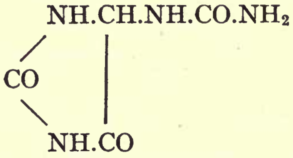
Alkyl derivatives of urea, in which the hydrogen is partly or wholly replaced by alkyl groups, are known in large number.

Uric acid, $C_5H_4O_3N_4$, is a white, crystalline substance, without odor or taste. It is present in small amount in normal human urine, and occurs in large quantities in the excrement of birds (guano) and of reptiles in the form of ammonium urate. It is conveniently prepared from these latter sources. Uric acid is almost insoluble in water. It is a feeble dibasic acid (though containing no carboxyl group). Its alkali salts are sparingly soluble, the lithium salt dissolving more freely than the others.

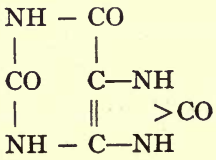
When heated with acids uric acid gives glycocoll (p. 254), ammonia, and carbon dioxide. On oxidation with cold nitric acid there are formed urea and alloxan,



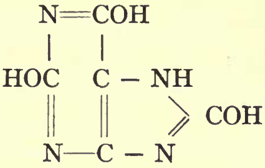
and with alkaline permanganate the product is allantoïn whose formula has been shown to be



On the basis of these reactions Medicus proposed a formula for uric acid which was long in dispute but after many years of investigation by E. Fischer and others was confirmed by successful syntheses. This formula is:



A reaction of the acid with phosphorus oxychloride by which the three oxygen atoms and three hydrogen atoms are replaced by three chlorine atoms suggests an enol tautomeric structure:



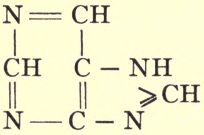
Uric acid and a number of other important natural products such as caffeïne, theobromine, xanthine and guanine all contain the same carbon and nitrogen skeleton in their structural formulas, and may be regarded as derivatives of a hydrogen compound which Fischer called *purine* (from purum and uricum) and succeeded in preparing in 1898.

Purine Bases.—*Guanine* occurs in animal tissues and in guano, and in the form of a calcium salt in fish scales. It is a colorless powder very slightly soluble in water, and combines with both acids and bases. On oxidation it gives guanidine (p. 233) and parabanic acid which hydrolyzes into urea and oxalic acid. Heated with hydrochloric acid it decomposes into glycocoll, formic acid, ammonia, and carbon dioxide. By nitrous acid it is converted into xanthine.

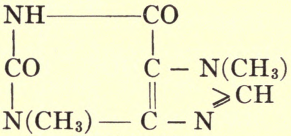
Xanthine is found in all tissues of the body. It unites with both acids and bases. When oxidized it yields alloxan and urea. Theobromine is formed by the reaction of its lead salt with methyl iodide.

Theobromine occurs in cocao beans. It is a white crystalline powder, and is amphoteric in its behavior. Its oxidation products are methyl alloxan and methyl urea. Its silver salt with methyl iodide gives caffeïne.

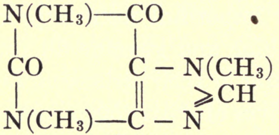
Caffeïne or theïne is a ingredient of coffee and tea and occurs in the cola nuts, etc. It crystallizes with one molecule of water in silky needles, and is weakly basic. It can be oxidized into dimethylalloxan and monomethylurea. When decomposed by hydrochloric acid, its nitrogen appears partly as ammonia and partly as methylamine.



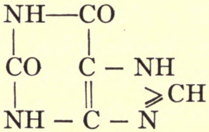
Purine



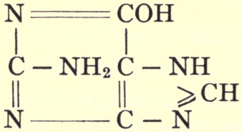
Theobromine



Caffeïne



Xanthine



Guanine

CHAPTER XVII

COMPOUNDS CONTAINING SULPHUR

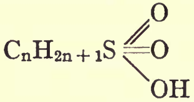
Sulphur is found in only a few natural organic compounds of established chemical constitution, as for instance in the mustard oils (p. 153); but it is usually present in the protein substances which are essential constituents of all living cells, and of whose chemical structure comparatively little is yet known. Many organic compounds containing sulphur have, however, been made by laboratory methods. Some of these in which sulphur is linked to carbon by oxygen, such as the alkyl sulphates, have already been described. We have also noticed a few others where carbon and sulphur are directly united, as in thio and isothiocyanic acids and their esters.

In inorganic chemistry we have learned that sulphur and oxygen form many similar compounds, the sulphides and hydrosulphides generally having formulas which find their analogies in those of the oxides and hydroxides. The same is true in organic chemistry; and sulphur alcohols, esters, aldehydes, ketones, and acids can be readily made in which sulphur takes the place of oxygen in the ordinary compounds of these names. In all these substances sulphur is, like oxygen, divalent. But sulphur in inorganic compounds is also, on occasion, tetravalent or hexavalent, these higher valencies appearing especially in compounds in which it is combined wholly or partly with oxygen, as in its oxides and acids. Similarly, in organic chemistry, tetravalent or hexavalent sulphur appears, often as a linking element between oxygen and alkyl groups. Sulphur atoms also show a tendency to link with each other as oxygen seldom does. Consequently, there are many thio-organic compounds which find no analogies among those of oxygen.

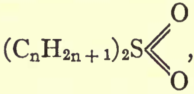
Almost all of the organic sulphur compounds are laboratory products, as already indicated. Those which are of the type of oxygen compounds are made by analogous methods. They are, in general, less stable than the corresponding oxygen compounds, which accords with our knowledge of the inorganic sulphur compounds; and those which are volatile are characterized by most objectionable odors.

When alcohols and ethers are oxidized, the hydrogen of the alkyl groups is at once affected with the production of aldehydes, acids, and ketones. The corresponding sulphur compounds, on the other hand, give a series of oxidation products in which the hydrogen combined with sulphur may be removed, or oxygen added to the sulphur.

The thioalcohols, $C_nH_{2n+1}.SH$, give as their first oxidation product disulphides, $C_nH_{2n+1}.S - S.C_nH_{2n+1}$. On more energetic oxidation, the valence of the sulphur is increased, and *sulphonic acids* are formed, whose formula is probably,

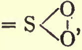


$$C_nH_{2n+1}S\begin{array}{l}{=}O\\{=}O\\{-}OH\end{array}$$

In like manner, the thioethers, $(C_nH_{2n+1})_2S$, are oxidized first to sulphoxides $(C_nH_{2n+1})_2S = O$, in which sulphur is tetravalent, and then to sulphones,  $(C_nH_{2n+1})_2S\begin{array}{l}{=}O\\{=}O\end{array}$, where the valence has become six.[1]

The disposition of sulphur to change from divalency to a higher valence is also shown by the formation of addition compounds.

---

[1] The structure of the sulphur oxygen groups in the sulphonic acids and sulphones is not entirely certain. It may be  $= S\begin{array}{l}{-}O\\ \;|\\{-}O\end{array}$, in which case sulphur is tetravalent.

The alkyl sulphides unite with alkyl halides forming such compounds as $(C_nH_{2n+1})_3SI$.

Thioalcohols are prepared by the action of alcoholic potassium hydrosulphide on alkyl halides or potassium alkyl sulphates:

$$C_2H_5Cl + KSH = C_2H_5SH + KCl$$
$$C_2H_5O.SO_2.OK + KSH = C_2H_5SH + K_2SO_4$$

These reactions are exactly analogous to those for making alcohols. The first is carried out by heating under pressure, the second takes place on distillation.

The thioalcohols are volatile liquids whose boiling points are much lower than those of the corresponding alcohols (methyl thioalcohol boils at 6°). They are almost insoluble in water, but dissolve easily in alcohol and in ether. The products of their oxidation have already been given. As in the case of the alcohols, the hydrogen of the SH-group can be replaced by metals, with the formation of salt-like compounds. But these compounds are more stable than the alcoholates, and are formed with heavy metals such as lead, copper, and mercury. With mercuric oxide, for instance, thioethyl alcohol readily forms $(C_2H_5S)_2Hg$, which can be crystallized from alcohol. On account of the formation of these mercury compounds, the thioalcohols were called *mercaptans* (corpus *mer*curio *apt*um), a name which is still commonly used, and the salts are called *mercaptides*.

The odor of ethyl mercaptan is not only very disagreeable but so intense that it is said that 0.000,000,002 mg. can be detected, an amount about 250 times less than that of sodium which can be recognized by the spectroscope.

Ethyl mercaptan is made commercially, and used in the preparation of sulphonal (p. 240).

Thioethers may be made in a manner analogous to that for making ethers, by the reaction of alkyl halides, or alkali alkyl sulphates with sodium mercaptides:

$$C_2H_5O.SO_2.OK + CH_3SK = C_2H_5.S.CH_3 + K_2SO_4$$

Both simple and mixed thioethers may be thus prepared. The thioethers are also made by the action of potassium sulphide on the above alkyl compounds:

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI$$

The analogous reaction with the alkali oxide does not take place, but can be carried out with dry silver oxide and alkyl halide.

The thioethers are liquids insoluble in water, and having higher boiling points than the corresponding mercaptans. (Compare this with the boiling points of alcohols and ethers.) As has already been stated, they are readily oxidized. They form addition products not only with alkyl halides, but also combine with halogen salts of metals, and with bromine and iodine, with the production of crystalline compounds.

Sulphonium Bases and Salts.—The addition products which the thioethers or alkyl sulphides form with alkyl halides, such as $(C_2H_5)_3SI$, are salt-like compounds, from whose aqueous solutions other salts may be made by reaction with silver salts:

$$(CH_3)_3SI + AgNO_3 = (CH_3)_3SNO_3 + AgI$$

By the action of silver hydroxide, strongly alkaline solutions are obtained, which yield on evaporation deliquescent crystals of *sulphonium hydroxide:*

$$(CH_3)_3SI + AgOH = (CH_3)_3SOH + AgI$$

The sulphonium hydroxide solutions are strongly basic and precipitate hydroxides of metals, set ammonia free from its salts, and absorb carbon dioxide from the air, as do the hydroxides of potassium and sodium.

In the manner of their formation and their behavior they are analogous to the tetra-alkyl ammonium bases (p. 135). On heating, the sulphonium halides decompose into the alkyl sulphides and alkyl halides, reversing the reaction by which they are formed, and behaving in this respect like the tetra-alkyl ammonium salts.

Disulphides, such as $C_2H_5.S - S.C_2H_5$, are formed by careful oxidation (often through oxidation in the air) of the mercaptans. They are also formed by distilling potassium ethyl sulphate with potassium disulphide; and when mercaptans are treated with concentrated sulphuric acid, the product is not the thioether (analogous to ordinary ether formation) but the disulphide.

The disulphides are liquids which boil higher than the corresponding sulphides. They are easily reduced to mercaptans.

Thioacids, in which the SH-group appears in place of the hydroxyl group, can be made by heating oxygen acids with phosphorus pentasulphide, or through the action of potassium hydrosulphide on the acid chlorides. The thioacids have lower boiling points and are less soluble than the corresponding oxygen acids. Their salts with the heavy metals are mostly difficultly soluble and are easily decomposed with the formation of metal sulphides.

Thioaldehydes, and **thioketones** are formed when hydrogen sulphide is passed into solutions of aldehydes or ketones to which hydrochloric acid is added; but these compounds polymerize so readily (the ketones as well as the aldehydes) that the monomolecular substances have not been prepared in the pure state.

Alkyl sulphoxides, such as $C_2H_5.SO.C_2H_5$, are the first product of oxidation of the thioethers by nitric acid. They cannot be distilled without decomposition, and are readily reduced to thioethers again.

Sulphones, of the type of $C_2H_5.SO_2.C_2H_5$, are formed by vigorous oxidation of thioethers or the alkyl sulphoxides. They are not reduced by nascent hydrogen.

Sulphonal, which is employed in medicine as a soporific, is a disulphone, $(CH_3)_2C(SO_2.C_2H_5)_2$, diethyl-sulphon-dimethyl methane. It is made by "condensation" of acetone and ethyl mercaptan through the influence of hydrochloric acid, and oxidation of the product:

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2C_2H_5SH = (CH_3)_2C.(SC_2H_5)_2 + H_2O$$

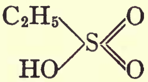
$$(CH_3)_2C(SC_2H_5)_2 + 4O = \underset{\text{Sulphonal}}{(CH_3)_2C.(SO_2.C_2H_5)_2}$$

Other analogous compounds are made in a similar manner.

Sulphonic acids are compounds in which one hydroxyl group in sulphuric acid is replaced by a hydrocarbon radical. They are formed by vigorous oxidation of mercaptans by nitric acid, and their salts can be made by the action of alkyl iodides on an alkali sulphite:

$$C_2H_5I + KSO_3K = C_2H_5.SO_3K + KI$$

By phosphorus pentachloride the sulphonic acids are converted into acid chlorides, *e.g.*, $C_2H_5.SO_2.Cl$, and these are reduced to mercaptans by nascent hydrogen. This fact together with the formation of the sulphonic acids by oxidation of mercaptans, indicates that in them, as in the mercaptans, sulphur is directly united to carbon. Their structure[1] is, therefore, probably



The sulphonic acids are stable, strongly acid compounds which are very soluble in water and give deliquescent crystals. They form alkali salts with solutions of caustic alkalies, but are otherwise unaffected, even on boiling, and they are not acted on by boiling acids. When melted with solid alkalies, however, they are decomposed with the formation of alcohols and alkali sulphites:

$$C_2H_5.SO_2OH + 2KOH = C_2H_5OH + K_2SO_3 + H_2O$$

[1] This conclusion as to the structure of the sulphonic acids, and the fact that they can be made by the reaction of alkali sulphites and alkyl iodide, indicates that the structure of the sulphites is $KSO_2.OK$, rather than $KO.SO.OK$, and that a similar constitution should be assigned to the unstable sulphurous acid.

Esters of sulphonic acids, such as $C_2H_5.SO_2.O.CH_3$ are made by the usual methods of ester formation. The aliphatic sulphonic acids are of comparatively little importance; but the sulphonic acids of the aromatic compounds are extensively employed in synthetical operations both in the laboratory and in chemical manufactures.

Sulphur Compounds Related to Carbonic Acid

Carbon disulphide, CS_2, is the analogue of carbon dioxide, and, like it, is made by the direct union of the elements, when sulphur vapor is passed over red-hot carbon. It is, however, an endothermic compond, absorbing about twenty-five large calories in the formation of the gram-molecular weight, while the formation of the gram-molecular weight of carbon dioxide is attended with the production of about ninety-six calories. Carbon disulphide is a strong refracting liquid, which boils at 46°, and which usually has a very disagreeable odor, due to slight impurities. It is an excellent solvent for phosphorus, iodine, oils, fats, and rubber, and is largely used.

Carbon oxysulphide, CO.S, is formed when a mixture of carbon monoxide and sulphur vapor is passed through a tube heated to a faint red heat. It is also produced by the action of hydrogen sulphide on isocyanic esters:

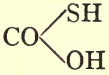
$$\underset{\text{Ethyl isocyanate}}{2C_2H_5NCO} + H_2S = CO.S + \underset{\text{Substituted urea}}{(C_2H_5.NH)_2CO}$$

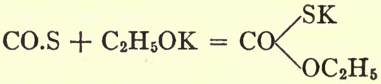
It may also be prepared by the action of strong sulphuric acid on ammonium or potassium thiocyanate:

$$HSCN + H_2O = CO.S + NH_3$$

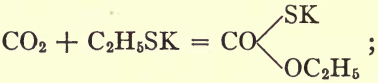
Carbon oxysulphide is an inflammable gas of faint peculiar odor. It is decomposed by alkalies as follows:

$$CO.S + 4KOH = K_2CO_3 + K_2S + 2H_2O$$

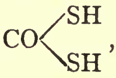
Sulphur Derivatives of Carbonic Acid.—By the replacement of oxygen in carbonic acid it is easily seen that five different sulphur acids might be formed. The acids, themselves, like carbonic acid, are very unstable, and with one exception, $CS(SH)_2$, are not known in the free state; but fairly stable neutral or acid esters, and salts of all of the acid esters have been prepared. Salts of the acid esters of *thiocarbonic acid*,  $CO\begin{matrix}SH\\OH\end{matrix}$, for instance, may be prepared by leading carbon oxysulphide into alcoholic solutions of the alkalies, or by the action of carbon dioxide on mercaptides:

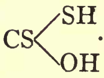
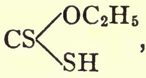


$$CO.S + C_2H_5OK = CO\begin{matrix}SK\\OC_2H_5\end{matrix}$$



$$CO_2 + C_2H_5SK = CO\begin{matrix}SK\\OC_2H_5\end{matrix};$$

and the neutral esters of the *dithiocarbonic acid*,  $CO\begin{matrix}SH\\SH\end{matrix}$, are made by the reaction of alkali mercaptides with carbonyl chloride.

The more important derivatives of these acids are the alkali salts of the acid esters of sulphothiocarbonic acid,  $CS\begin{matrix}SH\\OH\end{matrix}$. When carbon disulphide is shaken with a strong alcoholic solution of potassium hydroxide, yellowish silky crystals of the acid ethyl ester salts are precipitated. The crystals are readily soluble in water, and on adding dilute sulphuric acid to the cold solution, the acid ester itself,  $CS\begin{matrix}OC_2H_5\\SH\end{matrix}$, separates as a colorless oil. Acids of this type are called *xanthic acids* and their salts *xanthates* (ξανθός), from the yellow precipitate of cuprous xanthate which their solutions give with solutions of copper salts. Traces of carbon disulphide can be detected by these reactions.

By treatment of the alkali xanthates with alkyl halides, neutral esters of xanthic acid are formed.

Thiourea, $CS(NH_2)_2$, is formed from ammonium thiocyanate as urea is from the cyanate. It is necessary, however, to melt the solid salt, as the transformation does not occur on simple evaporation of the solution as in the case of the cyanate. It is also a reversible reaction and remains incomplete. Thiourea is converted into urea by adding to its cold solution potassium permanganate as long as this is decolorized. Mercuric oxide added to solutions of thiourea gives cyanamide, mercuric sulphide and water.

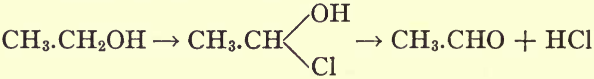
CHAPTER XVIII

SOME HALOGEN AND AMINO DERIVATIVES

Halogen Derivatives

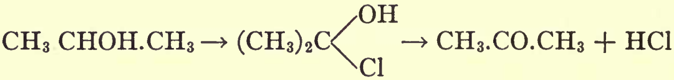
Halogen-substituted Alcohols.—When chlorine (or bromine) acts on an alcohol its attack is first directed to the group containing hydroyxl with the formation of a carbonyl group. Probably the replacement of a hydrogen atom of the alcohol group occurs first and the group thus formed, with halogen and hydroxyl united to the same carbon atom, is too unstable to exist, so that, as in most cases of corresponding dihydroxyl compounds, it at once breaks down.

Thus the action results in an indirect oxidation with the production of the aldehyde group in the case of a primary alcohol:



$$CH_3.CH_2OH \rightarrow CH_3.CH\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix} \rightarrow CH_3.CHO + HCl$$

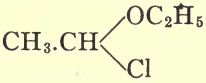
and of the ketone group with a secondary alcohol:



$$CH_3\ CHOH.CH_3 \rightarrow (CH_3)_2C\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix} \rightarrow CH_3.CO.CH_3 + HCl$$

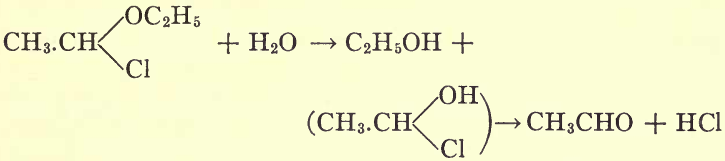
Further action of chlorine causes replacement of hydrogen in the associated alkyl group or groups. Therefore, the product actually obtained is a chloraldehyde (*cf.* chloral, p. 91), from a primary alcohol, or a chloracetone, if a secondary alcohol is used.

Although chloralcohols with chlorine and hydroxyl united to the same carbon atom do not exist, the corresponding esters in which the hydroxyl hydrogen is replaced by an alkyl group are comparatively stable. Thus by the action of chlorine on ethyl ether (kept cool and in the dark to avoid explosive action), there may be obtained as the first product,



$$CH_3.CH\left\langle\begin{matrix}OC_2H_5\\Cl\end{matrix}\right.$$

Substances of this type are called *chlorethers*. The constitution indicated by the formula is proved by the products of hydrolysis with sulphuric acid as a catalytic agent, *viz.*, alcohol, aldehyde, and hydrogen chloride:



$$CH_3.CH\left\langle\begin{matrix}OC_2H_5\\Cl\end{matrix}\right. + H_2O \rightarrow C_2H_5OH + \left(CH_3.CH\left\langle\begin{matrix}OH\\Cl\end{matrix}\right.\right) \rightarrow CH_3CHO + HCl$$

Halogenhydrins.—Halogen-substituted alcohols in which the halogen and hydroxyl are united to different carbon atoms can be obtained indirectly in several ways. They are called halogenhydrins. Chlorhydrins are formed:

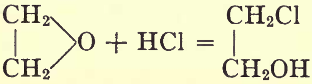
1. By the action of hydrogen chloride on glycols:

$$CH_2OH.CH_2OH + HCl = CH_2Cl.CH_2OH + H_2O$$

2. From olefines by addition of hypochlorous acid (p. 47):

$$CH_2:CH_2 + HClO = CH_2Cl.CH_2OH$$

From alkylene oxides (which are themselves, however, prepared from the chlorhydrins p. 157), by addition of hydrogen chloride:

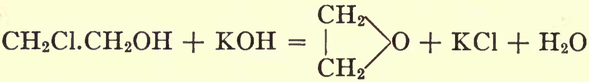


$$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right\rangle O + HCl = \begin{matrix}CH_2Cl\\|\\CH_2OH\end{matrix}$$

The bromhydrins are made by the same methods, but the methods are not effective for iodohydrins. These may be prepared by the action of potassium iodide on the chlorhydrins:

$$CH_2.Cl.CH_2OH + KI = CH_2I.CH_2OH + KCl$$

Properties and Reactions.—The halogenhydrins have the properties and give the reactions of both alkyl halides and alcohols. Since they can be made directly from the polyhydroxyl alcohols, they serve as a means for passing from one such alcohol to others with fewer hydroxyl groups. Both the hydroxyl group and the halogen are affected when a halogenhydrin is treated with alkalies, and alkylene oxides are formed:



$$CH_2Cl.CH_2OH + KOH = \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \!\!> O + KCl + H_2O$$

Of the **halogen-substituted aldehydes,** *chloral,* $CCl_3.CHO$, is the most important representative (*cf.* p. 91). The formation of halogen ketones and ethers has already been alluded to. The chlor and brom-ketones as well as the ethers may be made by direct action of the halogen.

Halogen-substituted Acids.—Chlorine and bromine do not act very readily on the saturated acids, but the action is assisted by sunlight, or by the presence of a catalytic agent, such as iodine or sulphur. The substitution takes place much more rapidly in the acid chlorides or bromides, or the acid anhydride, and is more easily effected the higher the molecular weight of the acid. Since the substituted acid halides or anhydrides are readily converted into the corresponding acids, they are usually employed in making the chlor and brom-acids. Iodine is usually introduced by reaction of the chlor-acids with potassium iodide. Direct chlorination or bromination gives generally α-substitution products, or products in which the halogen is united to the carbon atom standing next to the carboxyl group.

β-, γ,- and δ-compounds are usually formed by the addition of the hydrogen halide to unsaturated acids, the halogen in this case usually entering at a point as far removed from the carboxyl group as possible:

$$\underset{\text{Ethylidene-propionic acid}}{CH_3.CH:CH.CH_2.CO.OH.} + HBr = \underset{\gamma\text{-brompropylacetic acid}}{CH_3.CHBr.CH_2.CH_2.CO.OH}$$

$$\underset{\text{Allylacetic acid}}{CH_2:CH.CH_2.CH_2.CO.OH} + HBr = \underset{\delta\text{-brompropylacetic acid}}{CH_2Br.CH_2.CH_2.CH_2.CO.OH}$$

More than one atom of chlorine or bromine can be substituted by further direct action of the halogen on the monosubstituted acid. Chlorine is allowed to act in solution in carbon tetrachloride when possible, while bromine often acts without a solvent.

It is also possible to obtain the halogen-substituted acids by introduction of the carboxyl group into other halogen-substituted compounds or by oxidation of the substituted alcohols or aldehydes. Thus trichloracetic acid is prepared by oxidizing chloral by means of nitric acid:

$$CCl_3.CHO + O = CCl_3.CO.OH$$

Other methods for introducing the carboxyl group may be employed as, for instance, through the cyanogen group.

Chlorformic acid, $Cl.CO.OH$, can exist only in the form of its esters.

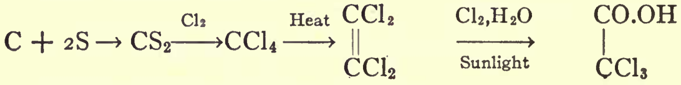
Chloracetic Acids.—*Monochloracetic acid*, $CH_2Cl.CO.OH$, may be prepared by the direct action of chlorine on boiling acetic acid to which some sulphur has been added. It forms crystals which melt at 63°. It is a stronger acid than acetic acid. *Dichloracetic acid*, $CHCl_2.CO.OH$, can be made by further action of chlorine on acetic acid or on the monochloracid, but, as this gives a mixture of chloracetic acids, it is best prepared by boiling chloral hydrate with a solution of potassium cyanide. The reaction occasions a rearrangement which is rather unusual:

$$CCl_3.CH(OH)_2 + KCN = CHCl_2.CO.OH + HCN + KCl$$

This acid is liquid at ordinary temperatures, having a melting point of −4°. *Trichloracetic acid* is made by the oxidation of chloral, as given above. It is a solid, melting at 55°. Though it stands so near to chloral in its structure, it has no trace of the physiological effect of this substance.

The discovery of trichloracetic acid by Dumas in 1839 had a very important influence on chemical theory, the fact that the strongly negative element chlorine could be substituted for hydrogen without changing the essential nature of the compound leading to the overthrow of the dualistic theory of Berzelius.

Trichloracetic acid has also a further historical interest through the demonstration in 1845 by Kolbe of a method of its synthesis from the elements. As the reduction of the trichloracetic acid to acetic acid by potassium amalgam in aqueous solution had already been effected, the synthesis of acetic acid from its elements for the first time was accomplished. Kolbe's synthesis was as follows:



$$C + 2S \rightarrow CS_2 \xrightarrow{Cl_2} CCl_4 \xrightarrow{\text{Heat}} \begin{matrix} CCl_2 \\ \| \\ CCl_2 \end{matrix} \xrightarrow[\text{Sunlight}]{Cl_2,H_2O} \begin{matrix} CO.OH \\ | \\ CCl_3 \end{matrix}$$

The chloracetic acids are all soluble in water. The monochloracetic acid is decomposed by boiling its solutions, with the production of glycollic acid, $CH_2OH.CO.OH$. Dichloracetic acid in solution is decomposed slowly at 100°, more rapidly when heated in a sealed tube to higher temperatures, and yields glyoxylic acid, $CHO.CO.OH$. Trichloracetic acid is more unstable, and on boiling its solution gives chloroform and carbon dioxide:

$$CCl_3.CO.OH = CHCl_3 + CO_2$$

These reactions are effected more rapidly by alkalies or silver hydroxide.

General Properties of the Halogen-substituted Acids.—The substitution of halogen atoms for hydrogen increases the acid character; the influence of chlorine being greater than that of bromine, and that of bromine greater than that of iodine. The position of the substituted halogen also has an influence on the acidity; being less effective the further it is removed from the carboxyl group. The activity of acids is measured by their dissociation-constants, and from determinations of these it appears that the strength of monochloracetic acid is about eighty-six times that of acetic acid. Introduction of a second chlorine atom multiplies this strength by 33, and trichloracetic acid is about 23.5 times as strong as the dichlor-acid, or nearly 67,000 times as strong an acid as acetic acid.

While the presence of the halogen thus influences the acid character, the carboxyl group has a reciprocal influence on the stability of the halogen. In the alkyl halides the halogen can be replaced by hydroxyl, or an unsaturated hydrocarbon produced, by means of alkali hydroxides, but the reaction is slow, and usually requires heating to a high temperature (in sealed tubes) for hours. With the halogen-substituted acids, however, the same reaction takes place much more readily. The influence of the carboxyl group on the reactivity of the halogen, like that of the halogen on the acidity, depends upon the relative position of the halogen and carboxyl in the molecule. With α-compounds, there is substitution of hydroxyl for the halogen; with β-compounds and alcoholic solutions of alkalies the chief product is an unsaturated acid; with γ-compounds, the hydroxyl acids which are first formed break down easily into lactones (p. 172).

The β-halogen-substituted acids enter into a characteristic reaction with sodium carbonate by which the sodium salt which is first formed is decomposed with the formation of an unsaturated hydrocarbon:

$$\underset{\beta\text{-brommethylethyl acetic acid}}{CH_3.CHBr.CH(CH_3).CO.ONa} \xrightarrow{Na_2CO_3} \underset{\text{Butylene}}{CH_3.CH{:}CH.CH_3}$$
$$+ NaBr + CO_2$$

By means of potassium cyanide, the halogen in all monohalogen acids is replaced by cyanogen and the compound thus becomes the half-nitrile of a dibasic acid. Hence the monohalogen acids are a means for building up dicarboxylic acids from monocarboxylic acids.

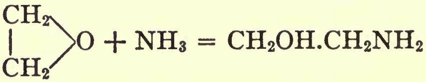
Ammonia reacts with the monohalogen acids with the production of amino-acids.

Amino-compounds

Amino-alcohols.—We have already met with compounds in which the amino-group and hydroxyl are united to the same carbon atom—the aldehyde-ammonias.

Amino-alcohols or *hydramines* in which hydroxyl and the amino group are combined with different carbon atoms of a hydrocarbon radical can be made by the action of ammonia on halogen hydrins or alkylene oxides:

$$CH_2OH.CH_2Cl + NH_3 = CH_2OH.CH_2NH_2 + HCl$$



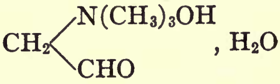
$$\left.\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\right\rangle O + NH_3 = CH_2OH.CH_2NH_2$$

These reactions may give secondary and tertiary derivatives, *e.g.*, $(CH_2OH.CH_2)_2NH$ and $(CH_2OH.CH_2)_3N$, as in the formation of amines (p. 128).

The amino-alcohols are bases which form salts, as the amines do, by direct addition of acids; and the hydrogen of the amino-group may be replaced with alkyl groups as in the amines.

Aminoethyl alcohol, whose formula is used above as an illustration, is of interest as the compound from which the physiologically important *choline* (p. 134) may be considered a derivative.

Amino-aldehydes, the simplest of which is aminoacetaldehyde, CH_2NH_2CHO, and amino-ketones, have been made, but in small number. *Muscarin*, a very poisonous substance, which is found in toad-stools and certain other plants, is apparently a quaternary base related to aminoacetaldehyde, and having the formula,



$$CH_2\left\langle\begin{matrix} N(CH_3)_3OH \\ CHO \end{matrix}\right., H_2O$$

Amino-acids

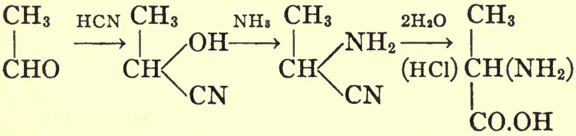
Acids in which the amino group has replaced hydrogen in the alkyl radical of the acid are of great physiological importance, since many of them are natural decomposition products of the proteins (*cf.* p. 405). They may be considered as amines in which alkyl hydrogen has been replaced by the carboxyl group, and, in fact, they show amine as well as acid characteristics: but on the whole it is simpler to view them as substituted acids.

Formation.—They may be made: 1. By the action of ammonia on the monohalogen acid. Thus chloracetic acid yields $NH_2.CH_2.CO.OH$, $NH(CH_2.CO.OH)_2$, and $N(CH_2.CO.OH)_3$. The reactions are like those for forming amines from the alkyl halides, and, as in that case, the immediate products are substituted ammonium salts from which the amino-acids are set free by the action of alkalies.

If amines (substituted ammonias) are used instead of ammonia, the products are correspondingly substituted amino-acids, thus:

$$CH_3NH_2 + CH_2Cl.CO.OH = \underset{\text{Methyl amino-acetic acid}}{(CH_3.NH)CH_2CO.OH}$$

2. α-Amino-acids are also produced from aldehydes or ketones by forming first the hydrocyanic acid addition product of these compounds (p. 78), replacing the hydroxyl group with the amino group by ammonia, and finally converting the cyanogen group into the carboxyl group by hydrolysis:

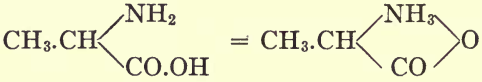


Acetaldehyde Lactonitrile α-Amino-propionitrile α-Amino-propionic acid (alanine)

The amino-acids may be obtained in a pure state by means of their copper salts. These are made by boiling the solutions of the acids with copper carbonate, and crystallize from the hot solutions. The copper is replaced by hydrogen by treatment with hydrogen sulphide.

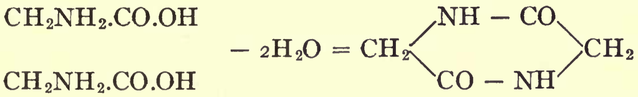
Properties.—The amino-acids are crystalline substances, most of which are readily soluble in water, but insoluble or sparingly soluble in alcohol or ether. Some of them have a sweet taste.

While, as we have seen, the presence of the strongly negative halogens greatly increases the acid character of acids, the decidedly positive amino group opposes the acidity, so that the amino-acids are neutral compounds, forming salts both with bases and with acids. With oxides or hydroxides of the heavy metals they give salts in which the hydrogen of carboxyl is replaced by the metal; but no crystallizable salts with sodium, potassium, or barium are formed. With acids the salts are like those of the amines—substituted ammonium salts. It also appears probable from some of their behavior that the amino-acids may form cyclic salts by reaction between the carboxyl and amino groups:



$$CH_3.CH\left\langle\begin{matrix}NH_2\\CO.OH\end{matrix}\right. = CH_3.CH\left\langle\begin{matrix}NH_3\\CO\end{matrix}\right\rangle O$$

Reactions.—The amino-acids give most of the reactions of the amines. Thus with nitrous acid the amino-group is replaced by hydroxyl as in the case of primary amines (p. 131), and alkyl and acyl chlorides replace the hydrogen of the amino-group with their radicals. Esters of the amino-acids are made by the ordinary method of leading hydrogen chloride into a mixture of the acid and alcohol. The hydrochloride of the amino-ester which is thus produced gives the ester by treatment with a solution of potassium hydroxide at a low temperature and immediately extracting the ester with ether. In other reactions the relative positions of the amino and carboxyl groups influence the result, as in the cases of the hydroxyl and halogen-substituted acids. The α-compounds readily give anhydride compounds by the loss of water from two molecules:



The β-acids easily lose ammonia with the formation of unsaturated acids:

$$\underset{\beta\text{-Amino-propionic acid}}{CH_2NH_2.CH_2.CO.OH} = \underset{\text{Acrylic acid}}{CH_2{:}CH.CO.OH} + NH_3$$

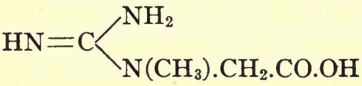
The γ-amino-acids, like the γ-amino-hydroxy acids give inner anhydrides called lactams, on account of their similarity to the lactones (p. 172).

$$\underset{\gamma\text{-Amino-butyric acid}}{CH_2NH_2.CH_2.CH_2.CO.OH} = \underbrace{CH_2NH.CH_2.CH_2CO}_{\text{Lactam}} + H_2O$$

Among the amino-acids and their derivatives the following may be given as examples.

Aminoacetic acid, $CH_2NH_2.CO.OH$, which is also called *glycine* and *glycocoll*, may be made from monochloracetic acid and ammonia. It is obtained from glue and other proteins by boiling with dilute sulphuric acid, and from hippuric acid (p. 359) by hydrolysis. From its aqueous solution crystals are obtained, which melt with decomposition at 232°. Glycine has a sweet taste, which together with its production from glue, was the occasion for the name glycocol (γλυκύς and κόλλα). Like many amino-acids it forms a blue copper salt when its solution is boiled with copper carbonate. This salt is very sparingly soluble in water, and crystallizes with one molecule of water.

Sarcosine is methylaminoacetic acid, $CH_2NH(CH_3).CO.OH$, which was first obtained from *creatine* (κρέας),

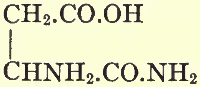


a subtance contained in meat extract, and related to guanidine (p. 233). It can also be obtained from caffeïne, and can be synthesized from methylamine and monochlor-acetic acid. *Betaïne*, which is found in the molasses of beet sugar, is a derivative of trimethyl glycine, being an inner ammonium salt, $\underbrace{\mathrm{N(CH_3)_3.CH_2.CO.O}}$

Betaïne is the source of the "trimethyl amine" obtained by the destructive distillation of vinasse (*cf.* p. 213).

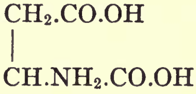
Alanine, $CH_3.CHNH_2.CO.OH$, or α-amino-propionic acid; *leucine*, $CH(CH_3)_2.CH_2.CHNH_2.CO.OH$, or α-amino-isobutyl-acetic acid; *lysine*, $CH_2NH_2.(CH_2)_3.CHNH_2.CO.OH$, α,ε-diamino caproic acid, are illustrations of amino-acids obtained by the hydrolysis of proteins.

Asparagine, which is found in asparagus and often is present in sprouting seeds and in many plants, is at once an amino- and an amido-compound, being amino-succinic acid amide.



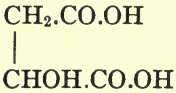
$$\begin{array}{l}\mathrm{CH_2.CO.OH}\\ |\\ \mathrm{CHNH_2.CO.NH_2}\end{array}$$

That this is the structure of asparagine is shown by the fact that on hydrolysis it gives *aspartic acid*,



$$\begin{array}{l}\mathrm{CH_2.CO.OH}\\ |\\ \mathrm{CH.NH_2.CO.OH}\end{array}$$

whose structure is proved by its conversion into *malic acid*, (p. 185),



$$\begin{array}{l}\mathrm{CH_2.CO.OH}\\ |\\ \mathrm{CHOH.CO.OH}\end{array}$$

by nitrous acid.

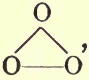
Like many amino-acids and their derivatives, these compounds all contain an asymmetric carbon atom and are optically active.

Asparagine from most natural sources is levo-rotatory; but from one source (the sprouts of vetches) two sets of asparagine crystals are obtained whose solutions have opposite rotatory power. No crystalline racemic form has been obtained. It is noteworthy that the dextro-asparagine has a sweet taste, while that of the levo-compound is disagreeaable and cooling.

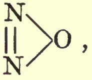
CHAPTER XIX

CYCLO-PARAFFINS

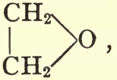
In several instances in inorganic chemistry and also among the organic substances already studied, the student has met with formulas in which the atoms are united in closed rings, such as,



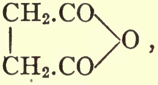
Ozone



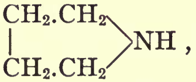
Nitrous oxide



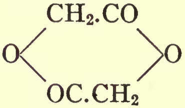
Ethylene oxide



Succinic anhydride



Succinic imide

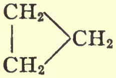
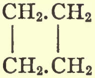
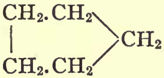
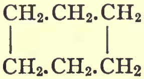
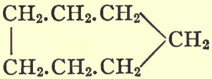
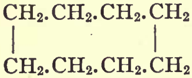
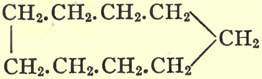


Glycollide

But no compounds have thus far been discussed whose formulas contain a ring of carbon atoms alone. Such compounds, however, are known, and among them are a very large number of the most important substances of organic chemistry—those which form the subject of the second part of this book under the title of the *Aromatic Compounds.*

Compounds which have the closed-ring structure are called *cyclic compounds*—*isocyclic* when the ring is composed of atoms of one element alone as in ozone, and *heterocyclic* if the elements are different as in the other illustrations given above.

Certain carbocyclic (isocyclic) compounds which are intermediate in their deportment between the open-chain aliphatic compounds and those of the aromatic group will be briefly considered here. These carbocyclic hydrocarbons are composed of methylene radicals, CH_2, and are known as the *cycloparaffins.* Their names, formulas, and boiling points are given in the following table, which also includes for comparison the boiling points of the paraffins and olefines having the same number of carbon atoms. It will be noticed that in every case the boiling point of the cyclic compound (polymethylene) is the highest of the three.

		Poly-methylene	Olefine	Paraffin
Trimethylene or cyclopropane		− 35°	− 48°	− 45°
Tetramethylene, cyclobutane		+ 12	− 5	+ 1
Pentamethylene, cyclopentane		49	40	36
Hexamethylene, cyclohexane		81	69	69
Heptamethylene, cycloheptane		117	95	98
Octomethylene, cyclooctane		146	122	126
Nonomethylene, cyclononane		171	......	150

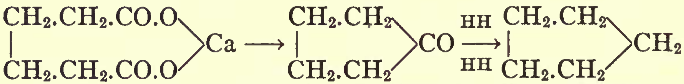
The cycloparaffins are isomeric with the unsaturated hydrocarbons of the ethylene series (olefines), but differ from them in not being readily oxidized by potassium permanganate, and in forming substitution rather than addition products, so that their conduct in general resembles that of the paraffins. Unlike both paraffins and olefines, the series of polymethylenes is apparently limited to the small number given in the table, and there are theoretical considerations which make the existence of larger rings improbable. Much larger heterocyclic rings are, however, known.

The argument for the ring formula of *trimethylene* is as follows. It is formed by the action of sodium on (1,3)-dibrompropane (trimethylene bromide) whose formula is known to be that used in the following equation:

$$\underset{\text{Trimethylene bromide}}{CH_2Br.CH_2.CH_2Br} + 2Na = \underset{\text{Trimethylene}}{CH_2.CH_2.CH_2} + 2NaBr$$

Chlorine forms a substitution product, $C_3H_4Cl_2$. Trimethylene is more stable toward bromine than is its isomer propylene, but in sunlight bromine acts additively, forming, however, trimethylene bromide again, instead of propylene bromide, $CH_2Br.CHBr.CH_3$, which would be the product of bromine on propylene.

Pentamethylene can be made by the following steps which indicate its structure:



$$\begin{array}{l} CH_2.CH_2.CO.O \\ | \\ CH_2.CH_2.CO.O \end{array}\!\!>Ca \longrightarrow \begin{array}{l} CH_2.CH_2 \\ | \\ CH_2.CH_2 \end{array}\!\!>CO \overset{HH}{\underset{HH}{\longrightarrow}} \begin{array}{l} CH_2.CH_2 \\ | \\ CH_2.CH_2 \end{array}\!\!>CH_2$$

Calcium Adipate — Ketopentamethylene — Pentamethylene

Hexamethylene will be discussed later under the aromatic compounds, because of its relationship to benzene. Many derivatives of this hydrocarbon occur in nature, particularly in the terpenes and in camphor.

Numerous derivatives of the cycloparaffins have been prepared and investigated, most of them being made much more readily than the hydrocarbons themselves. The preparation of the tetra-, octo-, and nonohydrocarbons has proved especially troublesome, and it is only quite recently that they have been obtained. The penta- and hexamethylenes are the most stable of the group, and the stability decreases from this maximum, whether the number of carbon atoms in the ring is increased or diminished.

Stereochemistry of the Cycloparaffins.—An explanation of the different degrees of stability of the polymethylene compounds and of the non-existence of rings of more than nine carbon atoms is offered in the "strain theory" of A. v. Baeyer (1885). This theory is in brief as follows: In the tetrahedral structure of which the carbon atom is the center, the valencies or affinities of that atom are supposed to be directed to the solid angles of the figure, along the axes of the tetrahedron. When several carbon atoms are united in chains or in rings, the condition for the greatest stability is when the valencies connecting each pair of neighboring carbon atoms are in a straight line. If this condition is unfulfilled and the directions of the valencies make an angle with each other, the configuration becomes less stable as this angle (of 180°) becomes less, because of the "strain" which results from the deflection that the valencies suffer in coming together.

In open-chain compounds—the paraffins—the linkages occur without deflection of the valencies from their normal directions, but the result is that in these compounds the carbon atoms do not lie in a straight line (as represented in the usual formulas), but in a regular zigzag whose equal angles are those which the edges of a regular tetrahedron subtend at its center, or 109° 28′. Thus the formula for normal pentane would be

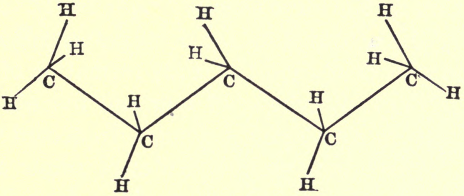


FIG. 1.—Normal pentane.

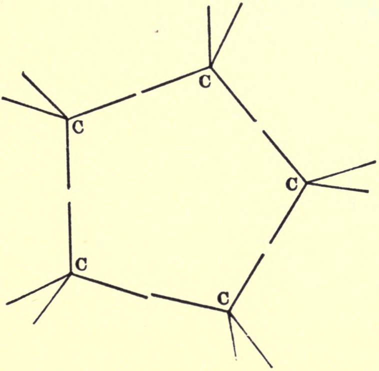


FIG. 2.—Baeyer's strain theory.

Figure 2 gives the normal directions of valencies in ring formations of from three to five atoms of carbon.

Supposing that in trimethylene the centers of the three carbon atoms lie in the angles of an equilateral triangle, the directions of the linking valencies from each carbon atom must be at an angle of 60° with each other. Since the normal directions of the valencies would make an angle of 109° 28′, this configuration requires that each valence shall be "strained" 24° 44′ from its normal direction since $109° 28' - 60° = 49° 28' = 2 \times 24° 44'$. In the tetramethylene ring with the four carbon atoms at the angles of a square, the deviation of each of the valencies is 9° 44′ ($109° 28' - 90° = 19° 28' = 2 \times 9° 44'$). In pentamethylene the angle of strain would be 0° 44′; in hexamethylene, −5° 16′; and becomes larger in the higher cycloparaffins. Thus the greater stability of the five- and six-carbon atom rings is "explained."

This theory also accounts for the non-existence of anhydrides of oxalic and malonic acids, and the ready formation of succinic and glutaric anhydrides with chains of four and five atoms of carbon linked into rings by an atom of oxygen. In accord with the theory, too, is the fact that no anhydrides of adipic acid, $(CH_2)_4$-$(CO.OH)_2$, or of higher dicarboxylic acids exist. The readiness with which γ- and δ-lactones and lactams are produced is also in agreement with the theory.

PART II

AROMATIC COMPOUNDS AND RELATED SUBSTANCES

CHAPTER XX

AROMATIC HYDROCARBONS

Benzene and Its Homologues

The substances that belong to the so-called aromatic group comprise the majority of those known to organic chemistry. The name of the group was first applied to certain natural vegetable substances which possess an agreeable, aromatic odor, such as the oil of bitter almond and of wintergreen. It has persisted like many of the older names, being the common designation of a large group of compounds which, though often without the characteristic aromatic odor, are chemically related to those first classed under this name. Certain well-marked peculiarities in chemical deportment, in which the aromatic compounds differ from those of the aliphatic group, justify a separate classification and treatment. Every aromatic compound contains at least six carbon atoms; and one of the most significant of the peculiarities of these compounds is that, when one of them has more than six carbon atoms, it can be broken down into one which contains six, and at this point farther decomposition is resisted.

Benzene, C_6H_6, is the simplest of the hydrocarbons of this group and may be regarded as the parent substance from which all the others are derived. It was discovered in 1825 by Faraday in the liquid found in compressed oil gas, and found by A. W. Hofmann twenty years later in the mixture of light oils distilled from coal tar, and is obtained from this latter source.

Coal tar is formed in the destructive distillation of bituminous coals in the coal gas and coke industries, which is carried out at temperatures from 980°–1100°. It is a black, viscous oil, owing its color chiefly to the presence of finely divided carbon. When distilled, less than half of it is volatilized, leaving a residue of pitch which is used as a black varnish for metals and, mixed with asphalt, for making pavements. The distillate is collected in separate fractions, the temperature being carried up to about 300°. The substances obtained in this way are of three classes: indifferent hydrocarbons not affected by dilute acids or alkalies, acid compounds which dissolve in alkalies, and bases which dissolve in acids. By successive treatment with alkalies and acids a separation of these classes is effected, and by further operations, more limited groups of substances, or individual compounds are obtained. Of the many compounds contained in the coal tar distillates, only a few—benzene, toluene, naphthalene, anthracene, and phenol—are produced commercially in a pure, or even approximately pure, condition. Mixtures of isomeric compounds are also obtained, known as xylols and cresols; and mixtures of homologues—the pyridine and other bases. Small amounts of other compounds containing oxygen, sulphur, and nitrogen, are also obtained. The amount of benzene and toluene is usually about 1–1.5 per cent. of the tar, of anthracene 0.25–0.45 per cent., of phenol 0.4–0.5 per cent., of cresols 2–3 per cent., and of naphthalene 6–10 per cent.

Benzene obtained from this source contains very small amounts of thiophene (p. 394), which cannot be removed by distillation, but is extracted by shaking the benzene with concentrated sulphuric acid. The final purification of the benzene is effected by crystallizing it in a freezing mixture.

Benzene is a thin oil, lighter than water, which has a slight, not unpleasant odor, melts, when frozen, at 5.4°, and boils at 80.4°. It is insoluble in water.

Formation.—Benzene is formed, together with some related hydrocarbons, when acetylene is led through tubes heated to a dull red. Benzene can in this way be synthesized from the elements, and another synthesis of this sort can be made through mellitic acid (p. 370). In these ways and others, it is possible to convert simple aliphatic compounds into substances of the aromatic group. Benzene can also be made: 1. From benzoic acid, $C_6H_5.CO.OH$, by heating sodium benzoate with sodium hydroxide or soda-lime, a reaction similar to that by which aliphatic hydrocarbons are formed from acids:

$$C_6H_5.CO.ONa + NaOH = C_6H_6 + Na_2CO_3$$

2. From phenol, $C_6H_5.OH$, by distillation with zinc dust. 3. From benzene sulphonic acid, $C_6H_5.SO_3H$, by superheated steam, or boiling with hydrochloric acid. 4. From amidobenzene (aniline), $C_6H_5NH_2$, by conversion into the corresponding diazo compound (p. 315) and boiling with alcohol. 5. From halogen derivatives by the Grignard reaction (*cf.* p. 274).

These four methods are general ones for the exchange of these different groups for hydrogen in the aromatic compounds.

Formula of Benzene.—The molecular formula for benzene, established by analysis and the determination of its vapor density, is C_6H_6. This means that of the twenty-four valencies of the six carbon atoms only sixteen are necessary for the single linkage of these atoms if the atoms form an open chain, or eighteen if the compound is cyclic, and suggests a high degree of unsaturation. The same thing is true of dipropargyl which is also C_6H_6. But while dipropargyl shows itself to be a highly unsaturated compound (p. 50) benzene differs markedly in its chemical conduct from this substance and the other unsaturated compounds we have studied. It is exceedingly indifferent toward oxidizing agents, not decolorizing permanganate, and resisting attacks which would break down ordinary unsaturated hydrocarbons into compounds of a less number of carbon atoms. Further, it does not unite additively with certain reagents as the unsaturated compounds do so readily; for instance, with hydrogen bromide, or hypochlorous or sulphuric acid. With the free halogens, however, it does form addition products in sunlight, but much less readily than the hydrocarbons of unsaturated groups; and hydrogen can also be added to it under certain conditions. But the maximum number of added atoms in either case is six, giving $C_6H_6Br_6$ and C_6H_{12}, while the corresponding aliphatic compounds from unsaturated hydrocarbons are $C_6H_6Br_8$, and C_6H_{14}. In this last respect, therefore, benzene differs both from the unsaturated hydrocarbons, and from the paraffins which form no addition products. It differs from the paraffins also by the readiness with which nitro-substitution products are made by the action of concentrated nitric acid:

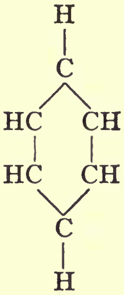
$$C_6H_6 + HONO_2 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

and sulphonic acids by concentrated sulphuric acid:

$$C_6H_6 + HO.SO_2.OH = \underset{\text{Benzene sulphonic acid}}{C_6H_5.SO_2.OH} + H_2O$$

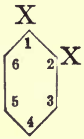
And, further, the behavior of the various derivatives of benzene is quite unlike that of corresponding substitution products of the open-chain hydrocarbons we have studied. The stability and persistence of the benzene *nucleus* of six carbon atoms in aromatic compounds led Kekulé in 1865 to propose a closed-ring formation in explanation of its peculiarities and its differences from the open-chain aliphatic compounds.

Facts helpful in suggesting the structure of the benzene molecule are found in the number of substitution products it forms with a given element or group. 1. It has proved impossible to obtain more than one monosubstitution product, and the results of elaborate experiments have shown that each of the six hydrogen atoms bear the same relation to the rest of the molecule. A formula in which the six carbon atoms are linked in a closed ring is the only one by which this symmetry can be expressed.

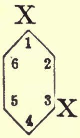


2. If more than one hydrogen atom in benzene is replaced by the same element or group, it is found that three and only three isomeric substitution products can be obtained when two, three, or four atoms of hydrogen are replaced; and only one product when five or six are replaced. These facts are accounted for by the symmetrical ring formula. In the following formulas which show this, we adopt the conventional expression for the benzene molecule as an unlettered hexagon. At each angle the group CH is assumed unless some symbol appears, and in this case it indicates the replacement of the hydrogen alone by some atom or group. The angles (carbon atoms) are numbered for readier reference in the discussion.

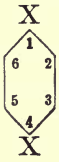
The five possible arrangements with two substitutes are:



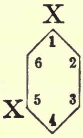
1



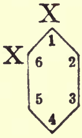
2



3



4

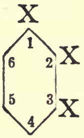


5

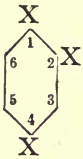
It is evident that the positions 1, 2 and 1, 6 are identical so far as relations of the substituents to each other and the rest of the molecule are concerned. The same is true of the positions 1, 3 and 1, 5. Formulas 1 and 5 are therefore the same, and formulas 2 and 4 also represent the same compound, leaving three different disubstitution products shown by formulas 1 or 5, 2 or 4, and 3.

The three types of disubstitution products are designated as *ortho*, when the substituents are on adjacent carbon atoms, 1, 2 or 1, 6; *meta*, when in the positions 1, 3 and 1, 5, and *para* when on opposite carbon atoms, 1, 4.

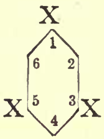
With three *like* substituents the student will readily see that, again, only three distinct structures can be formulated. These are shown in the following formulas with the names which are given them:



Adjacent 1, 2, 3



Unsymmetrical 1, 2, 4



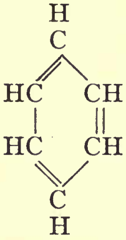
Symmetrical 1, 3, 5

When there are four like substituents, there are also three and only three isomers possible. If in this case we may regard the two remaining hydrogen atoms as the substituents in a molecule of C_6X_6, the demonstration becomes identical with that for the disubstitution products.

With five like substituents, it is evident that there can be but one arrangement, and the same is, of course, true when all the hydrogen is replaced by like atoms or groups.

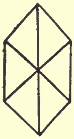
If, however, the substituting atoms or groups are different, it is obvious that the numbers of isomers may be much larger when three or more hydrogen atoms are replaced.

A symmetrical ring formula is thus seen to allow the successful representation of the possibilities and limitations of the isomerism which is established by experiment. The student has probably noticed that the formulas which have been given have represented carbon as a triad, or at least have not indicated the disposal of its fourth valency. In fact, this is still an open question, but in the great majority of aromatic compounds it is a matter of comparatively little importance, since in most of the reactions, the fourth bond, whatever its nature, remains undisturbed. It is only in the halogen and hydrogen addition products that it must be reckoned with, and here it is only necessary to assume that each carbon atom has one additional valence which is disposable under certain conditions. From a theoretical point of view, however, the question is of great interest, and many suggestions have been made, none of which are free from objections. The first structural formula for benzene was proposed by Kekulé in 1865 in the form shown in 1, with alternate double and single bonds,



1

Kekulé



2

Claus

3

Baeyer

The chief objection to this is that the positions 1, 2 and 1, 6 are not identical and that there should therefore be two ortho compounds. To meet this criticism Kekulé assumed that the linkages between the carbon atoms were dynamic instead of static, and that the double and single unions are continually shifting their places. In the Claus formula the fourth valencies are utilized in binding opposite atoms, while in the "centric" formula of Baeyer, they "neutralize" each other without actually uniting, and thus render no service in holding the ring together, but may be utilized in the case of addition products. The objections to these, and to other formulas which have been proposed, gain in force when the spatial arrangement of the atoms is considered.

The solution of the problem of the structure of the benzene molecule, which Kekulé gave in 1865, in his hexagonal formula, has had the most profound influence on the development of organic chemistry. It led at once to an understanding of the relations of the aromatic compounds to benzene and to each other, and has guided the wonderful synthetic achievements in this group of substances. It is probably the most fruitful single idea in the history of chemistry since Dalton's atomic theory.

It has been stated that benzene reacts directly with nitric acid, sulphuric acid, chlorine, and bromine, with the formation of compounds in which one or more hydrogen atoms of the benzene molecule are replaced by the nitro group, NO_2, the sulphonic acid group, SO_3H, or by the halogens. If we add to this that halogen derivatives of the aliphatic hydrocarbons react with benzene in the presence of aluminium chloride with the substitution of the aliphatic radical for hydrogen, the list of direct substitutions is practically exhausted. Other products in which amido, hydroxyl, carboxyl, and other groups are present, may be made from these directly substituted compounds.

The monad group, C_6H_5, which appears in all monosubstituted benzenes, is called **phenyl** (from phenol, $C_6H_5.OH$, in which it is united to hydroxyl), and this term is commonly employed in the naming of compounds; thus, C_6H_5Cl is phenyl chloride, $C_6H_5.C_6H_5$ is diphenyl, etc. The general name **aryl** is used for phenyl and the other homologous monad radicals of the aromatic group. For the sake of convenience in our discussions we will further designate the divalent, trivalent, etc., groups, C_6H_4, C_6H_3, etc., and those in which partial substitution has occurred, such as $Br.C_6H_4$, etc., which appear in benzene derivatives, as *cyclic radicals* in distinction to the "side-chain" or aliphatic radicals which are present in many of the hydrocarbons of the aromatic group.

Homologues of Benzene

A considerable number of hydrocarbons is known which are related to benzene and to each other in such a way that, like the paraffins, they form an homologous series, with the general formula, C_nH_{2n-6}. The empirical formulas of these hydrocarbons are, therefore, C_7H_8, C_8H_{10}, C_9H_{12}, etc., showing an increment from member to member of CH_2, and an increase of fourteen in molecular weight, as in the homologous series of the aliphatic group.

These hydrocarbons all contain the benzene ring with one or more atoms of hydrogen replaced by alkyl groups, so that their structure is given by such formulas as, $C_6H_5.CH_3$, $C_6H_4.(CH_3)_2$, $C_6H_5.C_2H_5$, etc. That these formulas represent their constitution becomes evident from the methods by which they may be formed, and by their reactions.

Formation of the Homologues of Benzene.—The most important methods for the replacement of hydrogen in benzene be alkyl groups are the following:

1. The *Fittig synthesis*, which is an application of the Wurtz method for the synthesis of paraffins (p. 28). It consists, like the latter, in treating a solution of the halides (here a mixture of the halogen substituted benzene and the alkyl halide) with sodium:

$$\underset{\text{Brombenzene}}{C_6H_5Br} + CH_3I + 2Na = \underset{\text{Toluene}}{C_6H_5.CH_3} + NaBr + NaI$$

$$\underset{\text{Dibrombenzene}}{C_6H_4Br_2} + 2CH_3I + 4Na = \underset{\text{Xylol}}{C_6H_4(CH_3)_2} + 2NaBr + 2NaI$$

In a similar way additions may be made to the side chain already present by using halogen derivatives of benzene homologues:

$$\underset{\text{Benzyl bromide}}{C_6H_5.CH_2Br} + \underset{\text{Butylbromid}}{CH_2Br.CH_2.CH_2.CH_3} + 2Na =$$
$$\underset{\text{Amylbenzene}}{C_6H_5.CH_2.CH_2.CH_2.CH_2.CH_3.} + 2NaBr$$

In certain instances zinc or silver may be used in place of sodium. These reactions give the clearest evidence of the constitution of these compounds.

2. *Friedel and Crafts Synthesis.*—In the presence of anhydrous aluminium chloride, halogen derivatives of the aliphatic hydrocarbons react with benzene:

$$C_6H_6 + CH_3Cl \overset{AlCl_3}{=} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

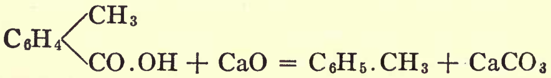
The action is, however, not limited to the formation of a single alkyl benzene, for some of that first formed reacts with the alkyl chloride to form the dialkyl benzene, and this in turn is partly converted into the trialkyl compound. Consequently a single alkyl benzene, as indicated in the above equation, is not obtained by this reaction, but a mixture of the mono, di, tri, etc., substituted benzenes, which, however, can usually be separated by fractional distillation. It is to be noted that this reaction does not occur when the halogen atom is in the benzene ring, but only when it is united to an alkyl group. Indeed, it appears that the explanation of this reaction is to be found in the formation of an addition compound of benzene with the aluminium chloride, as an intermediate step.

The two following reactions may also be employed for making benzene homologues.

3. *Grignard's Synthesis* (p. 36).—Magnesium reacts with halogen substitution compounds of benzene as it does with the corresponding paraffin derivatives, and the magnesium compounds are employed for a variety of syntheses. They react with water with the production of the corresponding hydrocarbons:

$$C_6H_5.MgBr + H_2O = C_6H_6 + MgOH.Br$$
$$C_6H_5.CH_2.MgBr + H_2O = C_6H_5.CH_3 + MgOH.Br$$

4. The homologues of benzene may also be made from the corresponding acids, by the general reaction which the organic acids undergo when heated with lime or sodium hydroxide (p. 28):



$$C_6H_4\begin{cases} CH_3 \\ CO.OH \end{cases} + CaO = C_6H_5.CH_3 + CaCO_3$$

Reactions.—Since the homologues of benzene are compounds which contain hydrocarbon groups of two distinct types—cyclic and alkyl radicals—they give, as we should expect, the reactions of both types, somewhat modified in each case by the presence of the other radical. Such persistence of type characteristics has become familiar from our study of the aliphatic group. The hydrogen of the alkyl groups is replaced by chlorine or bromine in sunlight as in the case of the paraffins, and the hydroxyl, aldehyde, carboxyl, amino, and other groups may be introduced by the same reactions employed in the aliphatic group. The resulting compounds show essentially the same characteristics and behavior as the corresponding derivatives of the paraffins, with the added possibilities of reactions in the cyclic group. In one respect, however, the homologues of benzene show a decided difference from the paraffins: while the paraffins cannot be oxidized readily, and when oxidized do not yield definite fatty acids, the alkyl groups when united to cyclic radicals are easily oxidized. The oxidation usually results in the conversion of the side chain, however long, into a single carboxyl group which remains united to the cyclic radical. Thus both toluene, $C_6H_5.CH_3$, and propyl benzene, $C_6H_5.C_3H_7$, yield benzoic acid, $C_6H_5.CO.OH$. When the hydrocarbon has two or more side chains, a corresponding number of carboxyl groups results from oxidation, and this gives a simple method for determining the number of side chains which were present. When dilute nitric acid is used as the oxidizing agent, if two or more side chains are present, one or more may escape oxidation. Thus ortho and para xylenes, $C_6H_4(CH_3)_2$, give the corresponding toluic acids, $C_6H_4(CH_3)(CO.OH)$. Chromic acid, on the other hand, usually effects the simultaneous oxidation of all side chains, and would give in this case the corresponding dibasic acids, $C_6H_4(CO.OH)_2$. If two or more side chains of different lengths are present, the longer one is usually oxidized first by nitric acid. Thus by the oxidation of cymene (methylisopropyl benzene, $CH_3.C_6H_4.C_3H_7$), para toluic acid, $CH_3.C_6H_4.CO.OH$, is formed, as the first product.

The hydrogen of the cyclic radical can be directly replaced by the same elements or groups as the hydrogen of unsubstituted benzene and in the same way. The reactions, however, generally take place more readily with the homologues of benzene than with benzene itself. This greater reactivity is accounted for by the fact that all the substituents which can be thus directly introduced are negative or acidic in character, while the alkyl groups are positive.

BENZENE AND ITS MOST IMPORTANT HOMOLOGUES

Name			Formula	Melting point	Boiling point	Specific gravity
C_6H_6, Benzene.			C_6H_6	5.8°	80.2°	0.874(20°/4°)
C_7H_8, Toluene.			$C_6H_5.CH_3$	−92.4	111	0.869(16°)
C_8H_{10}	o-Xylene	Dimethyl-benzenes	$C_6H_4\Big\langle\begin{matrix}CH_3\ (1)\\ CH_3\ (2)\end{matrix}$	−28	142	0.893(9°)
	m-Xylene		$C_6H_4\Big\langle\begin{matrix}CH_3\ (1)\\ CH_3\ (3)\end{matrix}$	−53	139	0.881(0°)
	p-Xylene		$C_6H_4\Big\langle\begin{matrix}CH_3\ (1)\\ CH_3\ (4)\end{matrix}$	+15	138	0.880(0°)
	Ethylbenzene		$C_6H_5.C_2H_5$	−92.8	136	0.883(0°)
C_9H_{12}	Hemellithene	Trimethyl benzenes	$C_6H_3\begin{matrix}CH_3\ (1)\\ CH_3\ (2)\\ CH_3\ (3)\end{matrix}$	liquid	175	——
	Pseudocumene		$C_6H_3\begin{matrix}CH_3\ (1)\\ CH_3\ (2)\\ CH_3\ (4)\end{matrix}$	liquid	169.5	0.895(0°)
	Mesitylene		$C_6H_3\begin{matrix}CH_3\ (1)\\ CH_3\ (3)\\ CH_3\ (5)\end{matrix}$	liquid	165	0.865(14°)
	n-Propylbenzene		$C_6H_5.C_3H_7$	liquid	159	0.867(14°)
	iso-Propylbenzene or Cumene		$C_6H_5.CH\Big\langle\begin{matrix}CH_3\\ CH_3\end{matrix}$	liquid	153	0.866(16°)
$C_{10}H_{14}$	Durene, Tetramethylbenzene		$C_6H_2\begin{matrix}CH_3\ (1)\\ CH_3\ (2)\\ CH_3\ (4)\\ CH_3\ (5)\end{matrix}$	80	192	——
	Cymene, Methyl-iso-propyl-benzene		$C_6H_4\Big\langle\begin{matrix}CH_3\ (1)\\ CH(CH_3)_2\ (4)\end{matrix}$	liquid	175	0.856(20°)

All these hydrocarbons (see table), with the exception of n-propyl-benzene and cymene, are found in the distillates from coal tar. With the exception of durene, they are liquids of characteristic but not disagreeable odors.

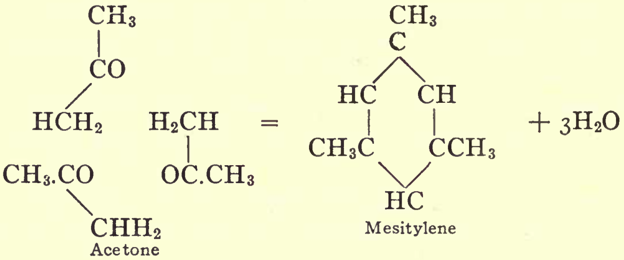
Benzene received its name from benzoic acid from which it was obtained in 1834 by distillation with lime. The acid in turn was named from gum benzoïn from which it was obtained as a sublimate early in the seventeenth century. Benzene is chiefly used for making nitro-benzene as the first step to the manufacture of aniline and a great variety of technical substances.

Commercial benzene is usually a mixture of benzene and toluene with small amounts of other hydrocarbons; and the benzene products which are obtained as fractional distillates from coal tar are known as "90 per cent." and "50 per cent." benzol. These terms mean that 90 or 50 per cent. of the mixture distils below 100°. The "90 per cent. benzol" contains about 70 per cent. of benzene and 24 per cent. of toluene, and the "50 per cent. benzol" a somewhat less amount of benzene with toluene and xylenes.

Toluene, C_7H_8, is so called because it is a product of the dry distillation of tolu balsam. Its use is similar to that of benzene.

The xylenes, C_8H_{10}, are named from their production in the destructive distillation of wood (*ξύλον*). They are now, however, obtained entirely from coal tar. All three isomers occur in coal tar and cannot be separated by fractional distillation. Meta xylene is present in the largest amount and is of technical importance. It can be separated from the others by boiling the mixture with dilute nitric acid, which oxidizes the ortho and para xylenes into toluic acids while it has little effect on the meta compound. Also when the mixture of xylenes is shaken with ordinary sulphuric acid, the ortho and meta xylenes are converted into sulphonic acids from which the para xylene can readily be separated; and then the sodium salts of the sulphonic acids may be more or less completely separated by crystallization and the ortho and meta xylenes recovered from them in comparative purity. The distillate from coal tar, boiling between 140°–170°, known as "solvent naphtha," is chiefly a mixture of the three xylenes with pseudocumene and mesitylene. It is largely used as a solvent of caoutchouc in the waterproofing of fabrics.

Mesitylene, trimethylbenzene, $C_6H_3(CH_3)_3$ (1, 3, 5) is the most important of the eight hydrocarbons of the formula C_9H_{12}, which include three trimethylbenzenes, three methylethylbenzenes, and two (n- and iso-) propylbenzenes. It is a product of the "condensation" of acetone, which occurs when a mixture of acetone and concentrated sulphuric acid is distilled:



This synthesis indicates that the structure of mesitylene is probably symmetrical (1,3,5), and this has been proved to be the case by other evidence (*cf.* p. 280). Its name was suggested by the symmetrical distribution of the methyl groups.

Durene, tetramethylbenzene, $C_{10}H_{14}$ was given its name because it is solid at ordinary temperatures, a property unusual in the aromatic hydrocarbons up to $C_{11}H_{16}$.

Cymene, $C_{10}H_{14}$, p-methyl-iso-propylbenzene, occurs in a number of natural oils, and is named from *cuminium cyminum*, which yields Roman caraway oil. This oil also contains an aldehyde from which *cumene* (iso-propylbenzene), $C_6H_5.CH(CH_3)_2$, may be prepared. Cymene is closely related to the terpenes, $C_{10}H_{16}$, which are constituents of turpentine, and can be obtained from them. It is most readily prepared by treating camphor, $C_{10}H_{16}O$, with phosphorus pentoxide, which withdraws the elements of water.

Aromatic Hydrocarbons With Unsaturated Side Chains

Closely allied to the homologues of benzene are the hydrocarbons which contain unsaturated aliphatic radicals united to phenyl. They, too, show the characteristic reactions of their component radicals, and may be regarded as substituted olefines or acetylenes as well as benzene derivatives. Two compounds typical of this group are:

Styrene, or **Styrolene,** $C_6H_5.CH{:}CH_2$, which is also *vinyl-benzene* or *phenyl-ethylene*, was first obtained from the resin storax, and was named from this. It is present in coal tar, and is formed when a mixture of benzene vapor and ethylene is led through a red hot tube. Styrene may also be made from ethylbenzene by the same reactions which serve for the formation of ethylene from ethane (p. 45). It is best prepared from cinnamic acid (p. 357) by distilling the acid alone or with sodium hydroxide:

$$C_6H_5.CH{:}CH.CO.OH = C_6H_5.CH{:}CH_2 + CO_2$$

Styrene is a liquid which boils at 146°. It polymerizes to $(C_8H_8)_x$ on heating to 200° in a sealed tube, or by treatment with concentrated sulphuric acid. The same change occurs slowly on standing.

Phenyl-acetylene, $C_6H_5.C{\vdots}CH$, may be made from phenyl-propiolic acid, $C_6H_5.C{\vdots}C.CO.OH$, which is obtained from cinnamic acid $C_6H_5.CH{:}CH.CO.OH$ by the usual reactions employed to change a double to a triple bond. When phenyl-propiolic acid is heated with water to 120°, carbon dioxide is evolved and the hydrocarbon is formed. It may also be made from aceto-phenone, $C_6H_5.CO.CH_3$, by replacement of its oxygen with chlorine (by phosporus pentachloride) and heating the acetophenone chloride with alcoholic potash:

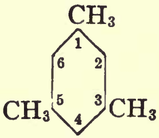
$$C_6H_5.CCl_2.CH_3 + 2KOH = C_6H_5.C\!:\!CH + 2KCl + 2H_2O$$

Phenylacetylene boils at 142° and gives the usual acetylene reactions.

Orientation

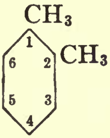
The determination of the relative positions of substituents in the benzene ring is called "orientation." In the case of a given compound this is accomplished, in practice, by converting the compound into another in which the positions are known. This method, of course, assumes that the new substituents which are introduced in place of the original ones occupy the same positions, and this is found to be generally true.

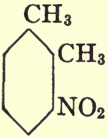
The establishment of reference compounds has been effected by various methods. The synthesis of mesitylene from acetone was taken as presumptive evidence that this hydrocarbon is symmetrical (1, 3, 5) trimethylbenzene and this structure has been proved by various replacements which show that the three unsubstituted hydrogen atoms (2, 4, 6) are of equal value, *i.e.*, each stands in the same relation to the three methyl groups.

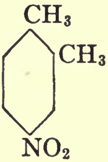


Mesitylene and some of its derivatives may therefore serve as reference compounds.

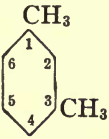
A more general principle is that of Körner. By this it is possible to find whether a compound containing two substituents of the same kind is an ortho, meta, or para compound. The method consists in determining the number of trisubstitution products which can be made from each. For, if another group is introduced into an ortho compound, only two isomers can be formed, since position 6 would give a compound identical with position 3; and 4 and 5 bear the same relation to the original groups.

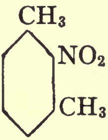


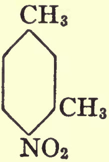


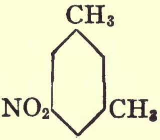


From a meta compound three and only three isomers are possible by the introduction of a new group, 4 and 6 being identical.

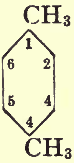


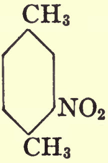






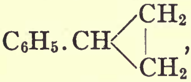
Finally, a para compound can give only one product by the introduction of a new group, as it is easily seen that in the positions 2, 3, 5 and 6, the relations would be the same.



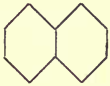


The three xylenes whose formulas have been taken to illustrate this "absolute" method of orientation, may be converted into the three corresponding dibasic acids—the phthalic acids—whose structure thus becomes known, and the positions of the substituents in other compounds can be ascertained by converting them into xylenes or phthalic acids, or into other compounds whose structure has already been determined by these or similar conversions.

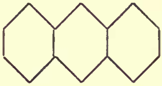
Other Aromatic Hydrocarbons

Besides the hydrocarbons of the types already discussed, there are many others belonging to the aromatic group,which contain two or more cyclic radicals. These may be grouped as follows: 1. Hydrocarbons which may be regarded as aliphatic hydrocarbons (saturated or unsaturated) in which two or more hydrogen atoms are replaced by phenyl, such as triphenylmethane, $(C_6H_5)_3CH$, tetraphenylethane, $(C_6H_5)_2CH.CH(C_6H_5)_2$, and diphenyl ethylene, $C_6H_5.CH:CH.C_6H_5$. 2. Hydrocarbons which consist of a chain of cyclic and aliphatic radicals, such as dibenzyl benzene, $C_6H_5.CH_2.C_6H_4.CH_2.C_6H_5$. 3. Hydrocarbons formed by the union of phenyl with cyclic radicals, such as phenyltrimethylene,  $C_6H_5.CH\left\langle\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right.$, diphenyl, $C_6H_5.C_6H_5$ and triphenylbenzene, $C_6H_3(C_6H_5)_3$. 4. Hydrocarbons which contain "condensed" benzene rings, with carbon atoms common to the adjacent rings. Examples of these are:

Naphthalene, $C_{10}H_8$,



and Anthracene, $C_{14}H_{10}$,



Finally, in many instances, two, four, or a larger even number of hydrogen atoms can be added to usual aromatic hydrocarbons, forming hydro-aromatic hydrocarbons, such as dihydro-, tetrahydro-, and hexahydro-benzene. The last named compound is also called hexamethylene, and was mentioned with the cycloparaffins (p. 257).

The possibilities of substitution of the hydrogen in both the cyclic and aliphatic radicals of these numerous hydrocarbons opens the way for the existence and production of an immense number of aromatic derivatives. As has already been stated, the aromatic compounds now known far outnumber those of the aliphatic group, and new ones are all the time being made.

We shall study here only a very few of these compounds, with the purpose of becoming acquainted with the characteristics of the most important types, and learning something of their practical relations; and shall discuss first the derivatives of those compounds which contain a single cyclic radical.

CHAPTER XXI

HALOGEN DERIVATIVES; SULPHONIC ACIDS; NITRO COMPOUNDS

The three classes of aromatic derivatives which are the subject of this chapter are produced by the direct action of the halogens, or of sulphuric or nitric acid on the hydrocarbons. These compounds can also be made by indirect methods, but except in the case of the halogen derivatives these methods are of minor importance.

Halogen Derivatives

Preparation.—Chlorine and bromine act on benzene under ordinary conditions slowly, and the replacement of the hydrogen is in no case complete. The reaction proceeds much more readily, however, in the presence of certain substances, such as iodine, iron, sulphur, or chlorides of aluminium, antimony, or iron, which are known as "halogen carriers"; and in this way all the hydrogen atoms may be successively replaced with the formation, finally, of C_6Cl_6 and C_6Br_6.

When chlorine or bromine act without carriers, but in direct sunlight, the halogen *adds itself to benzene*, producing the final products, $C_6H_6Cl_6$ or $C_6H_6Br_6$.

Iodine does not act directly on benzene, but iodine substitution products are formed when some substance is present to oxidize the hydriodic acid formed in such a reaction. Such substances are iodic acid, mercuric oxide, etc. Iodine is, however, introduced more conveniently by the diazo-reaction (*cf.* p. 316).

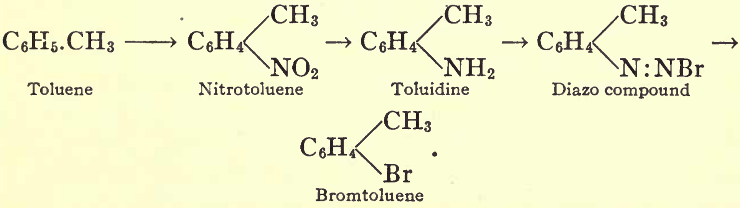
In the case of the homologues of benzene, two classes of halogen derivatives may be obtained: those in which the substitution is in the cyclic radical or "benzene nucleus," and those where it is in the alkyl group. When chlorine or bromine acts on the hydrocarbons in sunlight or at their boiling temperature (in the absence of a carrier) substitution takes place chiefly in the side chains; but in the dark and at ordinary temperatures, it is the hydrogen of the cyclic group which is replaced. The latter reaction occurs more readily in the homologues of benzene than in benzene itself, on account of the presence of the positive alkyl group, but is promoted by the addition of a catalyst.

Both classes of halogen compounds may be made from the corresponding hydroxyl compounds by means of the phosphorus halides. When the hydroxyl group is in the side chain, this reaction generally takes place readily, as in the case of the aliphatic hydroxyl compounds, but hydroxyl in the cyclic radical is less easily replaced. Halogens may also be introduced into side chains by the addition of the halogen or hydrogen halide to unsaturated side chains, as in the aliphatic series.

Halogen substituted hydrocarbons with the halogen in the nucleus can also be obtained indirectly by distilling halogen substituted acids with lime, as in the formation of hydrocarbons from acids:

$$C_6H_4Br.CO.OH + CaO = C_6H_5Br + CaCO_3$$

A most important general method for the preparation of halogen derivatives, containing the halogen in the nucleus, depends on the ready formation and decomposition of diazo compounds (p. 316), and will be discussed later. Starting with the hydrocarbon, the steps are the following,



$$\underset{\text{Toluene}}{C_6H_5.CH_3} \longrightarrow \underset{\text{Nitrotoluene}}{C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown NO_2\end{matrix}} \rightarrow \underset{\text{Toluidine}}{C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown NH_2\end{matrix}} \rightarrow \underset{\text{Diazo compound}}{C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown N{:}NBr\end{matrix}} \rightarrow \underset{\text{Bromtoluene}}{C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown Br\end{matrix}}.$$

When two chlorine or bromine atoms are substituted in the benzene nucleus by direct reaction on benzene, the chief product is the para compound, a small amount of ortho compound being formed at the same time. Similarly, when mono-chlor or brom-toluene is made by direct substitution, the product is mainly the para compound with a little of the ortho derivative. The influence of groups already present on the entrance of other substituents, and how these may be directed to certain positions will be taken up later (p. 298). In the preparation of the halogen derivatives by the direct action of the halogen, the theoretical amount of the halogen necessary to give the special derivative, or a slight excess of it, is added. Bromine is weighed directly before adding it, but the weight of chlorine is usually determined by noting the increase in the weight of the flask in which the reaction takes place.

SOME TYPICAL HALOGEN COMPOUNDS

Name	Formula	Melting point	Boiling point	Specific gravity
Chlorbenzene, Phenyl chloride	C_6H_5Cl	−44.9°	132°	1.106 (20°/4°)
Hexachlorbenzene	C_6Cl_6	227	326°	....
Brombenzene	C_6H_5Br	−30.5	157	1.491 (20°/4°)
o-Dibrombenzene	$C_6H_4Br_2$ (1, 2)	− 1	224	2.003 (0°)
m-Dibrombenzene	$C_6H_4Br_2$ (1, 3)	+ 1−2	220	1.955 (19°)
p-Dibrombenzene	$C_6H_4Br_2$ (1, 4)	89.3	219	1.841 (89°)
Adj-Tribrombenzene	$C_6H_3Br_3$ (1, 2, 3)	87	...	....
Unsym-Tribrombenzene	$C_6H_3Br_3$ (1, 2, 4)	44	275	....
Sym-tribrombenzene	$C_6H_3Br_3$ (1, 3, 5)	120	278	....
Iodobenzene	C_6H_5I	−28.5	188	1.861 (0°)
p-Di-iodobenzene	$C_6H_4I_2$ (1, 4)	129.4	285	....
o-Chlortoluene	$C_6H_4Cl.CH_3$ (1, 2)	−34	159.4	....
p-Chlortoluene	$C_6H_4Cl.CH_3$ (1, 4)	7.4	162.3	....
Benzylchloride, Chlormethylbenzene	$C_6H_5.CH_2Cl$	−43.2	179	1.113 (15°)
Benzalchloride, Dichlormethylbenzene	$C_6H_5.CH.Cl_2$	−16.1	204	1.295 (16°)
Phenylchloroform, Trichlormethylbenzene	$C_6H_5CCl_3$	−22.5	213−214	1.38 (14°)

Properties and Reactions.—Some of the halogen derivatives are liquids, but most of them are solids. They are readily soluble in alcohol, ether, etc., but are usually insoluble or only slightly soluble in water. The compounds containing a halogen in the side chain generally have a pungent and irritating odor, while those in which the halogen is in the nucleus have a much weaker and not unpleasant smell. Like all other organic halogen derivatives they are less inflammable than the corresponding hydrocarbons.

When the halogen is in the nucleus, it is held, as a rule, so firmly that it does not readily enter into reaction. Compounds of this kind may be boiled with alkalies, silver hydroxide, ammonia, potassium cyanide, or acid sulphites without being sensibly affected. But the halogen atom shows a greater reactivity when certain other substituents are present—for instance, o- and p-nitrochlorbenzene, $C_6H_4Cl.NO_2$, give with alcoholic potash the corresponding nitrophenols, $C_6H_4(OH)NO_2$. Sodium, however, removes the halogen, and usually at ordinary temperatures (Fittig's reaction, p. 273), *e.g.*, the syntheses of diphenyl and toluene:

$$2C_6H_5Br + 2Na = \underset{\text{Diphenyl}}{C_6H_5.C_6H_5} + 2NaBr$$

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5.CH_3 + 2NaBr$$

Magnesium also reacts with the halogen compounds as described under Grignard's synthesis (p. 36).

When the halogen is in the side chain it is readily replaced by the hydroxyl, amino, cyanogen, and other groups by the reactions employed with aliphatic halogen compounds. Thus benzylchloride, $C_6H_5.CH_2Cl$, may be converted into benzylalcohol, $C_6H_5.CH_2OH$, benzylamine, $C_6H_5.CH_2NH_2$, or benzylcyanide, $C_6H_5.CH_2CN$, by the action of water or alkalies, ammonia, or potassium cyanide, as in the case of the aliphatic halides.

This difference in reactivity according to the place occupied by the halogen may frequently be made the basis for determining whether the halogen is in the ring or in the side chain. If the substance is boiled with alcoholic potash and the solution is then acidified with nitric acid and tested with silver nitrate, a precipitate of silver halide shows that the halogen has been displaced from the organic compound and hence was probably present in the side chain; while no precipitation indicates that the halogen was in the ring.

Benzalchloride, $C_6H_5.CHCl_2$, and **benzotrichloride** (phenylchloroform), $C_6H_5.CCl_3$, are made commercially by the action of chlorine on toluene, and are employed in the preparation of benzaldehyde, $C_6H_5.CHO$, and benzoic acid, $C_6H_5.CO.OH$, respectively.

Sulphonic Acids

The action of sulphuric acid on aromatic compounds is one of the most striking characteristics of this group of compounds. All aromatic compounds dissolve in concentrated or fuming sulphuric acid with greater or less readiness, and from these solutions compounds are obtained in which hydrogen of the nucleus is found to be replaced by the sulphonic acid group, $-SO_3H$:

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + H_2SO_4 = \underset{\text{Toluenesulphonic acid}}{CH_3.C_6H_4SO_3H} + H_2O$$

Aliphatic compounds react with sulphuric acid much less readily; and prolonged heating results in only a partial and unsatisfactory production of sulphonic acids (p. 241).

Aromatic sulphonic acids may also be made, as the aliphatic sulphonic acids are, by the oxidation of the corresponding sulphhydrogen compounds (thiophenols), and the sulphonic acid group may be introduced by other methods; but the preparation of the sulphonic acids is almost aways effected by the direct action of sulphuric acid. The ease with which this reaction proceeds is markedly influenced by the presence of other substituting groups. In general, alkyl or other positive groups favor the reaction, while carboxyl and other acid groups render it more difficult; and the successive replacement of hydrogen atoms by the sulphonic acid group becomes impossible after three such groups have been introduced. The process of making sulphonic acids is called *sulphonation.*

Preparation.—In the preparation of sulphonic acids the aromatic hydrocarbon or other compound is boiled for some time with concentrated sulphuric acid, or gently heated for a shorter time with fuming acid, and then the mixture of sulphonic acid with the excess of sulphuric acid is poured into water. The sulphonic acids of the hydrocarbons are mostly very soluble in water and may be separated from sulphuric acid in the following way: By neutralizing the mixture with carbonate of calcium, barium or lead, the sulphuric acid is precipitated as an insoluble sulphate, while the calcium, barium, or lead salt of the sulphonic acid remains in solution, and may be obtained by evaporation or converted into other salts by double decomposition, as, for instance, into the sodium salt by adding sodium carbonate. The free acid may be obtained from the calcium or barium salt by exact precipitation with sulphuric acid, or from the lead salt by decomposition with hydrogen sulphide. Another method depends on the fact that many of the sodium salts are difficultly soluble in a solution of sodium chloride, and hence are precipitated when the product of the reaction is poured into a saturated solution of common salt—a result of the changed ionic concentration.

The sulphonic acids of some aromatic compounds are precipitated by ice-water and, in a number of cases, by concentrated hydrochloric acid.

Properties.—Aromatic sulphonic acids are solids which crystallize from water, in which many of them are very soluble. The sulphonic acid salts are also mostly soluble in water and many of them crystallize well.

Reactions.—1. The sulphonic acids are strong acids, forming salts by the replacement of the hydrogen of the $-\ SO_3H$ group by metals; and esters, such as $C_6H_5.SO_3C_2H_5$, with alcohols.

2. Phosphorus pentachloride converts the sulphonic acids or their salts into sulphonic acid chlorides:

$$C_6H_5.SO_3H + PCl_5 = C_6H_5.SO_2Cl + POCl_3 + HCl$$

3. Melted with alkalies, the alkali salts of sulphonic acids have their sulphonic acid group replaced by hydroxyl:

$$C_6H_5.SO_3Na + NaOH = \underset{\text{Phenol}}{C_6H_5.OH} + Na_2SO_3$$

This reaction serves as the best practical method for making certain commercial phenols such as, resorcinol, $C_6H_4(HO)_2$, naphthol, $C_{10}H_7.OH$, alizarin, $C_{14}H_6O_2(OH)_2$, etc.

4. Melted with potassium cyanide, the alkali salts give aromatic cyanides (nitriles) which may be hydrolyzed to acids:

$$C_6H_5.SO_3K + KCN = C_6H_5.CN + K_2SO_3$$

5. Melted with sodium formate, the alkali salts form salts of carboxyl acids,

$$C_6H_5.SO_3Na + HCO.ONa = \underset{\text{Sodium benzoate}}{C_6H_5.CO.ONa} + NaHSO_3$$

6. Heated with sodium amide, the alkali salts give aromatic amines:

$$C_6H_5.SO_3Na + NaNH_2 = \underset{\text{Aniline}}{C_6H_5.NH_2} + Na_2SO_3$$

7. The sulphonic group is replaced by the nitro group in some sulphonic acids by treatment with strong nitric acid.

8. The sulphonic acid group is replaced by hydrogen by distillation of the acid, or most effectively by means of steam under pressure:

$$\underset{\text{Toluenesulphonic acid}}{CH_3.C_6H_4.SO_3H} + H_2O = \underset{\text{Toluene}}{CH_3.C_6H_5} + H_2SO_4$$

This reaction following the sulphonation of a mixture of hydrocarbons and separation of the sulphonic acids is sometimes used for the preparation of pure hydrocarbons; for the sulphonic acids can be separated by crystallization more readily and completely than the hydrocarbons by distillation.

9. *Sulphonic acid chlorides* react: (a) Slowly with water or alkalies, forming the sulphonic acid or its salts. (b) With ammonia or primary or secondary amines with the formation of simple or substituted acid amides:

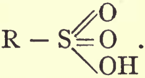
$$C_6H_5.SO_2Cl + CH_3NH_2 = C_6H_5.SO_2.NH.CH_3 + HCl$$

(c) With alcohols, the chlorides give sulphonic acid esters:

$$C_6H_5.SO_2Cl + C_2H_5OH = C_6H_5.SO_2.OC_2H_5 + HCl$$

(d) Nascent hydrogen reduces the chlorides to thiophenols, *e.g.*, $C_6H_5.SH$.

(e) When distilled with phosphorus pentachloride the sulphonic acid group is replaced by chlorine.

The structure of the aromatic sulphonic acids is inferred from the reactions common to these compounds and the sulphonic acids of the aliphatic series (p. 241). The reaction with phosphorus pentachloride shows the presence of the hydroxyl group, and the reduction of the acid chloride to a thiohydride proves that the sulphur atom is united directly to nucleus carbon. The structure is therefore $R - SO_2.OH$ and probably  $\mathrm{R - S}\begin{matrix}\diagup\!\!\diagup \mathrm{O}\\ = \mathrm{O}\\ \diagdown \mathrm{OH}\end{matrix}$. The sulphonic acids may thus be regarded as sulphuric acid in which one hydroxyl has been replaced by an aromatic radical.

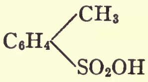
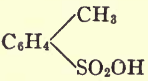
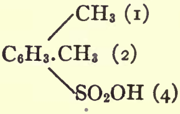
Uses.—On account of the many reactions which they give, and their own ready preparation, the sulphonic acids are largely employed in chemical work. Sulphonation serves also to bring insoluble substances into a soluble condition, so that insoluble dyes, for instance, which cannot be directly employed on account of their insolubility, are made available for dyeing in the form of their sulphonic acids. Further, the sulphonic acid salts, the acid chlorides, and amides are used for the identification of aromatic hydrocarbons. The amides are especially good for this purpose, since they crystallize well from hot water and have well-defined melting points. Benzenesulphonyl chloride, $C_6H_5.SO_2Cl$, may be used to distinguish the three classes of amines. It does not react with tertiary amines; but with primary and secondary amines forms substituted acid amides which are distinguished by the fact that the product from the primary amine is soluble in sodium hydroxide, while that from the secondary amine is insoluble. This difference in solubility is due to the presence in the former compound of hydrogen which is replaced with sodium by the action of sodium hydroxide:

$$C_6H_5.SO_2NH.CH_3 + NaOH \rightarrow C_6H_5.SO_2NNa.CH_3$$

while in the secondary product there is no replaceable hydrogen in the acid amido group: $C_6H_5.SO_2N(CH_3)_2$.

In the following table are given a few typical sulphonic acids with the melting points of their chlorides and amides. "Sulphonic acid" is to be added in each case to the name which is given.

SULPHONIC ACIDS

		Melting Points	
Name	Formula	Chlorides	Amides
Benzene	$C_6H_5.SO_2OH$	14.5°	150°
m-Benzenedi-	$C_6H_4.(SO_2OH)_2$ (1, 3)	63	229
p-Benzenedi-	$C_6H_4.(SO_2OH)_2$ (1, 4)	131	...
Benzenetri-	$C_6H_3(SO_2OH)_3$ (1, 3, 5)	184	306
o-Toluene-	 $C_6H_4\begin{cases}CH_3\\SO_2OH\end{cases}$ (1. 2)	liquid	153
p-Toluene-	 $C_6H_4\begin{cases}CH_3\\SO_2OH\end{cases}$ (1, 4)		96 136
o-Xylene-	 $C_6H_3\begin{cases}CH_3\ (1)\\CH_3\ (2)\\SO_2OH\ (4)\end{cases}$	51–52	144

A substance may be identified as a sulphonic acid or a sulphonic-acid salt by fusing it with sodium hydroxide and treating the product with water and a dilute acid. If the sulphonic-acid group is present, sulphur dioxide is evolved, and a phenol remains in solution which is detected by adding ferric chloride, or bromine water (*cf.* p. 330).

Compounds containing the sulphonic group in the side chains of aromatic compounds may be made by the methods given for forming the alkyl-sulphonic acids (p. 241).

Nitro Compounds

The action of nitric acid on aromatic hydrocarbons has already been noted. The dilute acid when heated with homologues of benzene usually oxidizes one or more of the side chains to the carboxyl group. Occasionally, under certain conditions, hydrogen of the alkyl groups is replaced by the nitro group, NO_2, producing such compounds as $C_6H_5.CH_2.NO_2$; and usually small amounts of compounds are produced which contain the nitro group in place of nucleus hydrogen. With concentrated nitric acid this last reaction becomes the chief one; one, two, or three nitro groups being introduced into the aryl radical. This reaction is called *nitration*, and the resulting substances are nitro compounds:

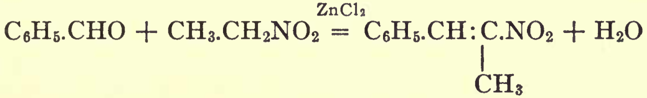
$$\underset{\text{Toluene}}{C_6H_5.CH_3} + HNO_3 = \underset{\text{Nitrotoluene}}{C_6H_4(CH_3)NO_2} + H_2O$$

In nitrating the homologues and other derivatives of benzene, the ease of the reaction is, of course, influenced by the character of the groups which are present; and since the nitro group is a strongly acid group, the statements made in regard to sulphonation (p. 288), apply in general to nitration. It has proved impossible to introduce in this way more than three nitro groups into a compound. In many cases, fuming nitric acid is necessary to effect nitration, and very commonly a mixture of concentrated or fuming nitric acid with sulphuric acid is used, the sulphuric acid uniting with the water formed in the reaction and thus preventing the dilution of the nitric acid. On the other hand, some substances are readily nitrated by dilute acid. Phenol, for instance, can be nitrated by a mixture of concentrated nitric acid with twice its volume of water. The number of nitro groups introduced depends in each case upon the strength of the acid, the temperature, and the nature of the aromatic compound. Nitrobenzene, $C_6H_5.NO_2$, is manufactured in large quantities by allowing a mixture of concentrated nitric and sulphuric acids to flow into benzene which is continually stirred and cooled. Dinitrobenzene, $C_6H_4(NO_2)_2$, results if the mixture is not cooled but allowed to heat from the effect of the reaction; while the formation of trinitrobenzene, $C_6H_3(NO_2)_3$, requires fuming acid and a higher temperature (180°). In general, it is advantageous to carry on the nitration at as low a temperature as is effective, especially when the compounds contain groups subject to oxidation.

Nitro compounds can also be formed from aromatic amines by oxidation or by the replacement of the amino group by the nitro group through diazo compounds; but these methods are only of theoretical interest, practically all nitro compounds being prepared by direct nitration, as the sulphonic acids are by direct action of sulphuric acid.

The introduction of the nitro group into side chains cannot be effected, as one might expect, by the reaction between the halogen compound and silver nitrite (*cf.* p. 142). But the nitration of saturated side chains can be accomplished directly by dilute nitric acid under certain conditions. For example, when ethylbenzene is heated in a sealed tube with weak nitric acid (sp. grav. 1.076) to 105°–108°, a good yield of phenylnitroethane, $C_6H_5.CHNO_2.CH_3$, is obtained. Nitro compounds with the nitro groups in unsaturated side chains may often be made: 1. by the action of nitric or nitrous acid or nitrogen tetroxide on the unsaturated hydrocarbon. Styrene, for example, $C_6H_5.CH:CH_2$, in ethereal solution reacts with nitrous acid to form phenylnitroethylene, $C_6H_5.CH{:}CHNO_2$. 2. Similar compounds can also be made synthetically from nitro paraffins and benzaldehyde, $C_6H_5.CHO$, in the presence of zinc chloride:

$$C_6H_5.CHO + CH_3NO_2 \overset{ZnCl_2}{=} C_6H_5.CH{:}CHNO_2 + H_2O$$



$$C_6H_5.CHO + CH_3.CH_2NO_2 \overset{ZnCl_2}{=} C_6H_5.CH{:}\underset{\substack{|\\ CH_3}}{C}.NO_2 + H_2O$$

The compounds with nitro groups in side chains are, however, of very minor interest, while the importance of the nitro compounds containing the nitro groups in place of nucleus hydrogen can hardly be over-estimated. Their importance lies chiefly in the fact that these nitro compounds form the first step in the introduction of other groups into the cyclic radicals, for the nitro compounds, as such, find only a limited use. In the following, only those compounds which have nitro groups in the ring will be considered.

Properties.—The mononitro derivatives of the lower aromatic hydrocarbons are liquids or crystalline solids having an odor like that of bitter-almond oil. The liquid compounds are pale yellow, and the solids yellow or colorless. They are heavier than water and insoluble in it. They are volatile with steam and can in most cases be distilled without decomposition. Compounds with two or three nitro groups, on the contrary, in most cases do not distil at ordinary pressure without decomposition, and the decomposition is usually the occasion of a more or less violent explosion. They are, however, stable beyond their melting points, and these are often determined for purposes of identification.

Reactions.—1. The most important reaction of the nitro compounds is the reduction they undergo with active reducing agents, with the conversion of the nitro group into the amino group. In the laboratory the reduction is usually effected by means of tin and hydrochloric acid, while iron filings and hydrochloric acid are commonly employed in technical operations (*cf.* p. 303). Various other reducing agents may, however, be used:

$$\underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + 6H = \underset{\text{Aniline}}{C_6H_5.NH_2} + 2H_2O$$

The *amines* which are products of these reductions form the second step in the introduction of various groups in place of nucleus hydrogen, the third being the conversion of the amine into a diazo compound (p. 313).

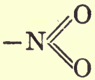
2. By the use of milder reducing agents several intermediate reduction products can be produced (p. 321). All of these substances are converted into amines, *e.g.*, aniline, by further reduction, and some of them at least, form transition steps in the active reduction which yields the amines directly, and are also produced by oxidation of the amines.

3. The direct replacement of the nitro group by other groups cannot usually be effected. This is especially true of the mononitro compounds. When two nitro groups are present in the ortho or para position to each other, one of them can be exchanged for hydroxyl by boiling with a solution of sodium hydroxide; or for the amino group when heated with an alcoholic solution of ammonia. These reactions do not occur when the groups have the meta positions. Trinitro compounds, however, give similar reactions whatever the positions. Thus symmetrical trinitrobenzene (1, 3, 5) is converted slowly at ordinary temperature by sodium methoxide, CH_3ONa, into dinitro anisol, $C_6H_3(NO)_2(O.CH_3)$.

4. The influence of the presence of the nitro group is seen in many reactions, and we may note here that hydrogen situated in the ring between nitro groups is rendered more active, so that, for instance, symmetrical trinitrobenzene is oxidized by potassium ferricyanide to trinitrophenol, $C_6H_2(OH)(NO_2)_3$.

Structure of Nitro Compounds.—Two facts indicate that the nitro group is $-NO_2$ and not the nitrous acid radical $-ONO$.

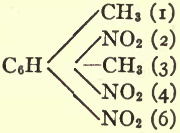
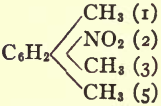
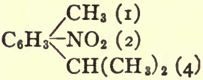
These are: 1. That the mononitro compounds cannot be saponified as a nitrous ester would be, and 2. The reduction of the group to an amino group, instead of to hydroxyl, which would be the probable result if the compound had the ester formation. Hence the nitrogen of the nitro group is directly united to the ring carbon, and the structure is



NITRO COMPOUNDS

Name	Formula	Melting point	Boiling point	Specific gravity
Nitrobenzene	$C_6H_5.NO_2$	5.7°	210.9°	1.204 (20°)
o-Dinitrobenzene	$C_6H_4(NO_2)_2$ (1, 2)	117°	319°	....
m-Dinitrobenzene	$C_6H_4(NO_2)_2$ (1, 3)	90°	303°	1.369 (98°)
p-Dinitrobenzene	$C_6H_4(NO_2)_2$ (1, 4)	172°	299°	....
unsym.-trinitrobenzene	$C_6H_3(NO_2)_3$ (1, 2, 4)	57.5°	....	....
sym-trinitrobenzene	$C_6H_3(NO_3)_3$ (1, 3, 5)	122°	....	....
o-nitrotoluene	$C_6H_4\begin{cases} CH_3\ (1) \\ NO_2\ (2) \end{cases}$	−13.8°	222.3°	1.168 (15°)
m-nitrotoluene	$C_6H_4\begin{cases} CH_3\ (1) \\ NO_2\ (3) \end{cases}$	16°	230°	1.168 (22)
p-nitrotoluene	$C_6H_4\begin{cases} CH_3\ (1) \\ NO_2\ (4) \end{cases}$	54°	237.7°	1.123 (54°)
Dinitrotoluene	$C_6H_3\begin{cases} CH_3\ (1) \\ (NO_2)_2 (2,\ 4) \end{cases}$	70°	....	1.321 (70°)
Trinitrotoluene (T.N.T.)	$C_6H_2\begin{cases} CH_3\ (1) \\ (NO_2)_3\ (2,\ 4,\ 6) \end{cases}$	82°	....	....
Nitroorthoxylene	$C_6H_3\begin{cases} (CH_3)_2\ (1,\ 2) \\ NO_2\ (4) \end{cases}$	29°	258°	1.139 (30°)
Dinitrometaxylene	$C_6H_2\begin{cases} (CH_3)_2\ (1,\ 3) \\ (NO_2)_2\ (2,\ 4) \end{cases}$	82°	....	....

NITRO COMPOUNDS *(Continued)*

Name	Formula	Melting point	Boiling point	Specific gravity
Trinitrometaxylene	 $C_6H\left\langle\begin{array}{l}CH_3\ (1)\\NO_2\ (2)\\CH_3\ (3)\\NO_2\ (4)\\NO_2\ (6)\end{array}\right.$	182°	....	....
Nitromesitylene	 $C_6H_2\left\langle\begin{array}{l}CH_3\ (1)\\NO_2\ (2)\\CH_3\ (3)\\CH_3\ (5)\end{array}\right.$	44°	255°	....
Nitrocymene	 $C_6H_3\left\langle\begin{array}{l}CH_3\ (1)\\NO_2\ (2)\\CH(CH_3)_2\ (4)\end{array}\right.$	liquid	....	1.085 (15°)

Nitrobenzene, $C_6H_5.NO_2$, is technically the most important of the nitro compounds of the aromatic hydrocarbons. It was discovered by Mitscherlich, in 1834. Its first practical use was as a substitute for oil of bitter almonds in perfumery. While it is still used to scent many commercial substances, this is of quite minor importance as compared with the employment of nitrobenzene for making aniline for the manufacture of coal tar dyes.

The Influence of Substituents on Each Other

The fact that the presence of a substituent in the benzene ring influences both the readiness with which a second atom or group can be introduced, and the position which it occupies, has been noticed. Sulphonation and nitration proceed more easily with compounds which contain alkyl or hydroxyl groups than with benzene or derivatives in which a nitro or sulphonic group is already present; and not only is the position of the entering group affected by the character of the group attached to the nucleus, but also the reactivity of both groups in the resulting compound. A second nitro or sulphonic group enters chiefly in the meta position to the first, while a second chlorine or bromine atom gives principally a para compound.

The following rules are found to be generally applicable:

1. When an alkyl group, a halogen atom, or either of the groups NH_2 or OH, is present, a second alkyl group (by Friedel and Craft's synthesis), halogen atom, or the sulphonic or nitro group, enters in the para or ortho position, the chief product being generally the para compound.

2. Compounds containing one of the groups, NO_2, SO_3H, CN, CO.OH, or CHO give on a second substitution chiefly meta compounds.

These statements may conveniently be put in the form of a table, in which the positions are indicated by the conventional numbers, bracketed numbers meaning that these compounds are produced in relatively small amounts.

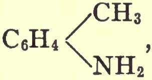
Element or group	Positions of substitutes					
in position 1	Alkyl	Cl	Br	I	SO_3H	NO_2
Alkyl	4 (2)	4 (2)	4 (2)	....	4 (2)	4 (2)
Cl	4 (2)	4 (2)	4	4	4	4 (2)
Br	4 (2)	....	4 (2)	....	4	4 (2)
I	....	....	....	....	....	4 (2)
OH	4 (2)	4 (2)	4 (2)	4 (2)	4 (2)	4 (2)
NH_2	4 (2)	4	4	4	4	4 (2)
SO_3H	4 (2)	....	3	....	3 (4)	3 (2, 4)
NO_2	4 (2)	3	....	....	3 (2, 4)	3 (2, 4)
CO.OH	4 (2)	3	3	3	3 (4)	3 (2, 4)
CN	....	....	4	....	....	3

To the illustrations already given may be added the great readiness with which phenol, $C_6H_5.OH$, reacts with bromine, giving symmetrical tribromphenol; and with nitric acid, with the production of ortho and para nitrophenol, ortho-para and diortho-nitrophenol, and para diorthonitrophenol (p. 337).

As regards the activity of the products, the meta compounds, as a class, are more stable toward reagents than the ortho or para compounds. Ortho and para bromnitrobenzene, $BrC_6H_4.NO_2$, react with ammonia to form the corresponding nitranilines, $NH_2.C_6H_4.NO_2$, while meta bromnitrobenzene, and brombenzene itself, are not affected by ammonia. Many further illustrations of the reciprocal influence of substituents on reactions will be met with in the course of our study.

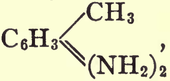
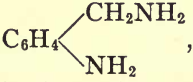
CHAPTER XXII

AROMATIC AMINES

All aromatic amines contain, of course, one or more aryl (or substituted aryl) radicals. Considering them as substituted ammonias, we may distinguish the following types of simple aromatic amines: 1. Those in which one or more cyclic radicals are substituted for hydrogen in NH_3, nitrogen being united to nucleus carbon. Of this type are aniline $C_6H_5NH_2$, triphenylamine $(C_6H_5)_3N$, toluidine  $C_6H_4\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right.$, etc.

2. Those in which the nitrogen of the substituted ammonia is combined with carbon in a side chain, such as $C_6H_5.CH_2NH_2$, etc.

3. *Mixed amines* which contain both phenyl and alkyl groups combined directly with nitrogen as in $C_6H_5.NH.CH_3$; phenyl and phenyl-alkyl groups, such as $C_6H_5.CH_2.NH.C_6H_5$; and, finally, amines containing alkyl and phenyl-alkyl groups such as $C_6H_5.CH_2.NH.CH_3$. These mixed amines are necessarily secondary and tertiary amines, while all three classes, primary, secondary, and tertiary may be represented in the first two types.

4. Aromatic amines containing two or more amino groups are also known, and may be of the type of $C_6H_4(NH_2)_2$,  $C_6H_3\left\langle\begin{array}{l}CH_3\\(NH_2)_2\end{array}\right.$, etc., with the amino groups all united to nucleus carbon; or such as  $C_6H_4\left\langle\begin{array}{l}CH_2NH_2\\NH_2\end{array}\right.$, with an amino group in the side chain as well as in the nucleus.

There is, therefore, rather a bewildering variety of aromatic amines; but we need consider here only the general characteristics of the several types and give special attention to a few individuals which illustrate these types and are of practical importance.

In the first place, we may observe that in contrast with the aliphatic amines, the aromatic amines, in which the amino group is united with nucleus carbon, are neutral in reaction instead of strongly alkaline, and do not absorb carbon dioxide. The amines containing one or two phenyl groups form additive salts with acids, but these salts are less stable than the salts of the aliphatic amines, being more or less hydrolyzed in solution so that the reaction of their solutions is acid; and tertiary amines like triphenylamine have no basic properties at all. The aliphatic amines, on the contrary, form stable salts, and their alkalinity and basicity is greater with the increase in the number of alkyl groups.

These differences between the aromatic nucleus amines and the alkyl amines show that the phenyl radical has a negative character as compared with the rather strongly positive alkyl radicals. This is again very markedly in evidence in the aromatic hydroxyl compounds—the phenols (p. 327)—which have distinctly acid properties as compared with the alkyl hydroxides—the alcohols; and is also more or less marked in all the aromatic derivatives.

Aromatic amines which have the amino group in side chains are very similar to the alkyl amines in their properties, and may be regarded as alkyl amines in which aryl groups have been substituted for hydrogen in the alkyl radical.

The presence of the positive amino group in the nucleus increases the reactivity of the hydrogen atoms of the ring, which are now readily replaced by chlorine or bromine and yield easily to sulphonation and nitration.

Primary Amines

Preparation.—1. Aromatic amines with the amino group united with nucleus carbon—aryl amines—cannot usually be made, like the alkyl amines, by the action of ammonia on the halogen derivatives of the aromatic hydrocarbons—the halogen in this position having, as we have seen, little reactivity. The reaction becomes possible, however, when the nitro group is also present in the ortho or para position relative to the halogen; and ortho-dinitrobenzene, and ortho and para nitrophenols also give nitro-amido compounds when heated with ammonia. Meta compounds do not react. Some phenols also are converted into amines by heating to 300°–350° with ammonia-zinc chloride.

But the method generally employed for the preparation of these amines is by the reduction of the corresponding nitro compounds. The reduction is usually effected by means of tin or iron and hydrochloric acid, though quite a variety of other reducing agents are sometimes employed. Among these ammonium sulphide in alcoholic solution is especially useful for the reduction of a single nitro group in a compound containing two or three such groups.

2. Aromatic aryl-alkyl amines with the amino group in the side chain are prepared by the methods used for alkyl amines (*cf.* p. 128).

Aniline, $C_6H_5.NH_2$, received its name from the Spanish term for indigo, *anil*, as it was first obtained by the destructive distillation of this substance in 1826. In 1834 it was discovered in coal tar, and shortly before had been made by the reduction of nitrobenzene. It was not till 1843, however, that the identity of these products with that from indigo was established. Its constitution is determined by its formation from compounds of known structure and by the products of its reactions.

The amount of aniline in coal tar is too small to make this source of any importance. The very large amounts that are used, chiefly in the dye-stuff industry, are obtained from coal tar benzene through nitrobenzene. The reduction of the nitrobenzene is effected by means of iron-filings and hydrochloric acid:

$$\underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + 3Fe + 7HCl = \underset{\text{Aniline hydrochloride}}{C_6H_5.NH_2.HCl} + 3FeCl_2 + 2H_2O$$

This reaction is accomplished, however, with the use of a very much smaller amount (about $\frac{1}{40}$) of hydrochloric acid than is indicated in the above equation. The probable explanation of this fact is that iron filings and water effect the reduction, the small amount of ferrous chloride formed at first acting as a catalyzer.

$$C_6H_5.NO_2 + 2Fe + 4H_2O = C_6H_5.NH_2 + 2Fe(OH)_3$$

When the reduction is ended, lime is added and the aniline is distilled with steam. Since the aniline is only slightly soluble in water and is a little heavier, the greater part of it separates as an oil and is purified by redistillation, while the "aniline-water" is used in the boiler which furnishes steam for the first distillation.

In the laboratory, tin and strong hydrochloric acid are usually employed for the reduction. In this case double salts of tin and aniline are formed, which are decomposed by adding caustic soda before distilling with steam. Common salt added to the distillate reduces the solubility of the aniline, which is then extracted with ether and distilled.

Properties.—Aniline is an oily liquid of a slight and characteristic odor, and is poisonous. When freshly distilled it is colorless, but turns yellowish-brown on exposure to light and air. This change in color is apparently due to the presence of traces of sulphur compounds, which can be removed by heating with acetone. Aniline thus treated remains colorless. Its specific gravity is 1.024 (16°). It boils at 183.7°. In water it dissolves in the proportion of about one part to 30 of water; and it dissolves water in a slightly larger proportion. Aniline is dried by means of solid potassium hydroxide or carbonate (calcium chloride combines with ammonia and amines, and is consequently not suitable for drying these compounds). Aniline is miscible in every proportion with alcohol. ether, benzene, etc. It is readily volatile with steam.

Reactions.—1. Aniline, like most amines, unites additively with acids, forming crystalline salts which are mostly soluble in water.

The normal sulphate, $(C_6H_5.NH_2)_2.H_2SO_4$, and the oxalate, $(C_6H_5.NH_2)_2.H_2O_4C_2$, however, are only slightly soluble in cold water. The solutions have an acid reaction from hydrolysis; and the salts with fatty acids are converted by heating into the more stable substituted acyl amides (anilides):

$$C_6H_5NH_2.HO.OC.CH_3 = C_6H_5NH.OC.CH_3 + H_2O \div HCl$$

Aniline also forms double salts such as $(C_6H_5.NH_2)_2ZnCl_2$, $(C_6H_5.NH_2.HCl)_2PtCl_4$, and $(C_6H_5.NH_2.HCl)_2SnCl_4$.

2. Like ammonia and the alkyl amines, aniline enters into reaction with alkyl halides with the formation of mono- and dialkyl anilines, such as $C_6H_5.NH.CH_3$ and $C_6H_5N(CH_3)_2$; and with alkyl iodides the reaction proceeds to the formation of the salt of the quaternary ammonium base, *e.g.*, trimethylphenylammonium iodide, $C_6H_5(CH_3)_3NI$, which is not decomposed by cold solutions of alkalies, and from which silver hydroxide sets free the strongly alkaline base, $C_6H_5(CH_3)_3NOH$.

3. Aniline reacts with acid chlorides with the formation of anilides corresponding to the amides:

$$\underset{\text{Aniline}}{C_6H_5.NH_2} + CH_3.CO.Cl = \underset{\text{Acetanilide}}{C_6H_5.NHOC.CH_3} + HCl$$

4. When warmed with nitrous acid, solutions of salts of aniline and other primary aryl amines evolve nitrogen with the exchange of the amino group for the hydroxyl group, as in the case of the alkyl amines; but at room temperature or in ice water no nitrogen is set free, but a *diazo compound* is formed which contains two atoms of nitrogen:

$$C_6H_5.NH_2.HCl + HNO_2 = \underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5.N_2Cl} + 2H_2O$$

The diazo compounds are quite unstable, as is indicated by the statements just made in regard to their preparation, and they enter into many important reactions (p. 315).

5. The nucleus hydrogen of aniline is more readily replaced than that of benzene by halogens, and by the sulphonic acid and nitro groups. In an aqueous solution of an aniline salt, chlorine or bromine readily give trichlor or tribromaniline, (1, 2, 4, 6).

6. Aniline like all primary amines gives the carbylamine test (*cf.* p. 132).

7. Special tests for aniline are: Dilute solutions of aniline or its salts give (a) a violet color with a solution of bleaching powder; (b) a precipitate of tribromaniline with bromine water; (c) a green, blue, or black precipitate when treated with sulphuric acid and a little potassium dichromate.

Some Derivatives of Aniline

Acetanilide, $C_6H_5NH.OC.CH_3$, is the most important of a group of compounds which may be regarded as amides in which hydrogen of the amido group is replaced by aromatic radicals—in this case by phenyl. Acetanilide (or phenyl-acetamide) is usually prepared by boiling a mixture of glacial acetic acid and aniline for some hours. The aniline acetate first formed loses the elements of water under this treatment, leaving the acetanilide:

$$C_6H_5.NH_2.HO.OC.CH_3 = C_6H_5.NH.OC.CH_3 + H_2O$$

It may also be made by the other methods used for the formation of amides (p. 137): treatment of aniline with acetyl chloride, acetic anhydride, or acetic esters.

Acetanilide melts at 116° and boils at 304°. It is much more soluble in hot water than in cold, and crystallizes well from its solution in glistening plates. It is not hydrolyzed by water alone, but when boiled with alkalies or acids is converted into its components, aniline and acetic acid (or acetate):

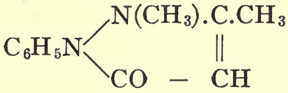
$$C_6H_5.NH.OC.CH_3 + KOH = C_6H_5.NH_2 + CH_3CO.OK$$

The hydrogen of the amido group can be replaced by a second acetyl group by the action of acetyl chloride at 170°–180°, giving *diacetanilide,* $C_6H_5.N(OC.CH_3)_2$. This melts at 37°, is decomposed on boiling, and is readily hydrolyzed to acetanilide and acetic acid by very dilute alkalies or acids.

Acetanilide and the corresponding derivatives of other aromatic amines are often employed in the preparation of aryl amine substitution products, since the presence of the negative acetyl group renders the nucleus hydrogen less reactive and so makes it possible to control the reaction to some extent. Thus, while with aniline, bromine water produces principally tribromaniline, acetanilide yields monobromacetanilide (para) from which monobromaniline can be obtained by hydrolysis.

Acetanilide, formerly known as "antifebrine," is used in medicine, especially in headache tablets.

"Antipyrine" is a derivative of aniline whose formula is



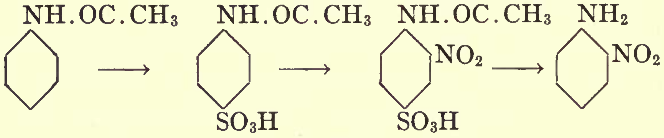
$$C_6H_5N\left\langle\begin{array}{ll}N(CH_3).C.CH_3 & \\ \qquad\qquad\ \ \| & \\ CO\ -\ CH & \end{array}\right.$$

Sulphanilic Acid, $NH_2.C_6H_4.SO_3H(1, 4)$, or para aminobenzenesulphonic acid, is prepared by heating aniline and concentrated sulphuric acid to 180°–190° for four or five hours. Sulphanilic acid separates from its solution in hot water in crystals which contain two molecules of water and are efflorescent. It has no definite melting point, and chars when heated to about 300°. Sulphanilic acid, unlike the sulphonic acids of the hydrocarbons, is only slightly soluble in cold water. It dissolves readily, however, in alkaline solutions from the formation of alkali salts. It forms no salts with acids, the basic character of the amino group being neutralized by the negative sulphonic group.

It is oxidized by chromic acid into quinone, $C_6H_4O_2$ (1, 4) (p. 350). When fused with caustic potash, instead of yielding aminophenol, $HO.C_6H_4NH_2$, it gives aniline. The diazo compound formed from it by the action of nitrous acid is used in the preparation of certain dyes.

The ortho and meta isomers of sulphanilic acid can be made by the reduction of the corresponding nitrosulphonic acids.

Nitranilines, $NO_2.C_6H_4.NH_2$. It is difficult to control the reaction of concentrated nitric acid on aniline so as to obtain a mononitraniline, but nitration of acetanilide gives a mixture of para and ortho nitroacetanilide from which the para and ortho nitranilines are obtained by hydrolysis. The nitro group may be directed to the ortho position by first sulphonating acetanilide. This gives the para sulphonic acid, and when this is nitrated the nitro group enters the position which is ortho to the acetylamino group; and then by splitting off the sulphonic and acetyl groups, ortho-nitraniline is obtained:



Meta nitraniline is readily prepared by partial reduction of meta dinitrobenzene (p. 294) by means of ammonium sulphide, or stannous chloride and hydrochloric acid in alcoholic solution:

$$\underset{\text{m-Dinitrobenzene}}{NO_2.C_6H_4.NO_2} \rightarrow \underset{\text{m-Nitraniline}}{NO_2.C_6H_4.NH_2}$$

The nitranilines are yellow solids which crystallize well and are very slightly soluble in water, but dissolve readily in alcohol. They are weak bases, the presence of the nitro group not quite neutralizing the basicity of the amino group. The basic character varies with the relative positions of the nitro and amino groups: being least in the ortho compound and greatest in the meta nitraniline. Their melting points are 71.5°, 114°, and 147° for the ortho, meta, and para, respectively.

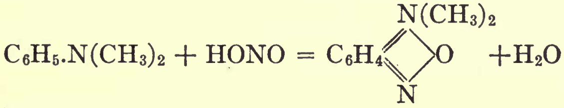
Para nitraniline, and to a less extent, meta nitraniline, are employed in the manufacture of azo-dyes.

Tetranitro-aniline is one of the most powerful explosives known, and another similar compound, tetranitro-methylaniline, called "tetryl," is used for detonators in place of mercuric fulminate.

Alkyl Derivatives of Aniline.—By the replacement of one or both hydrogen atoms of the amino group in aniline by alkyl groups, mixed secondary and tertiary amines are produced. These may be prepared by the direct action of alkyl halides on aniline; but in the technical manufacture they are made by heating aniline with hydrochloric or sulphuric acid and the appropriate alcohol to about 200°:

$$C_6H_5.NH_2.HCl + CH_3OH = C_6H_5.NH.CH_3.HCl + H_2O$$
$$C_6H_5.NH.CH_3.HCl + CH_3OH = C_6H_5.N(CH_3)_2.HCl + H_2O$$

These alkyl derivatives are oily liquids which smell like aniline. They are neutral in reaction, but are stronger bases than aniline, as one would expect from the presence of the positive alkyl groups, and are very similar to the secondary and tertiary alkyl amines. Many of these tertiary amines differ, however, from the tertiary aliphatic amines, in reacting very readily with nitrous acid forming paranitroso derivatives which are of importance as intermediate compounds in the preparation of certain dyes:



$$C_6H_5.N(CH_3)_2 + HONO = C_6H_4\overset{N(CH_3)_2}{\underset{N}{\Diamond}}O + H_2O$$

Dimethyl-aniline p-Nitroso-dimethyl-aniline

Another peculiar reaction of these amines is that which occurs when their hydrochloric acid salts are heated to about 300°. Under these conditions the alkyl groups are transferred from the amino group to the nucleus, with the formation of homologues of aniline, aniline and alkyl chloride being perhaps intermediate products:

$$\underset{\text{Ethyl-aniline hydrochloride}}{C_6H_5.NH(C_2H_5).HCl} \rightarrow C_6H_5.NH_2 + C_2H_5Cl$$
$$\rightarrow \underset{\text{Aminoethylbenzene chloride}}{C_2H_5.C_6H_4.NH_2.HCl}$$

This is an important technical method for preparing the homologues of aniline.

The quaternary ammonium salts undergo a like transformation:

$$\underset{\text{Trimethyl-phenylammonium iodide}}{C_6H_5.N(CH_3)_3I} \rightarrow CH_3.C_6H_4.N(CH_3)_2.HI \rightarrow$$

$$(CH_3)_2.C_6H_3NH.(CH_3)HI \rightarrow \underset{\substack{\text{Tri-methyl-animobenzene iodide} \\ 1:2:4:6}}{(CH_3)_3.C_6H_2.NH_2.HI}$$

By this reaction it has proved possible to prepare a homologue of aniline in which all five of the nucleus hydrogen atoms are replaced by methyl, $(CH_3)_5C_6NH_2$.

The most important of these alkyl derivatives is dimethylaniline, $C_6H_5.N(CH_3)_2$, which is employed in the manufacture of a number of dyes. Monomethyl, monoethyl, and diethyl anilines are also prepared in the industry, but their use is far less than that of the dimethylaniline.

Novocaine, a local anæsthetic, is the hydrochloride of diethylamino-ethyl-p-aminobenzoate:

$$NH_2.C_6H_4.CO.OC_2H_4.N(C_2H_5)_2HCl$$

Homologues of Aniline.—These are usually prepared from the corresponding nitro compounds when the hydrocarbon is obtainable for nitration. In many instances they are conveniently made from the phenols, whose hydroxyl group is replaced by the amino group by heating with ammonia in the presence of zinc chloride, etc:

$$\underset{\text{Thymol}}{(CH_3)(C_3H_7)C_6H_3OH} + NH_3 \overset{ZnCl_2}{=} \underset{\text{Thymylamine}}{(CH_3)(C_3H_7)C_6H_3.NH_2} + H_2O$$

A third method is by heating the halogen salts of the alkylanilines (p. 309).

The homologues of aniline have the same general characteristics as that substance and require no further description here. Important from a practical standpoint on account of their employment in the color industry are: the three *toluidines*, $CH_3.C_6H_4NH_2$, ortho and para toluidines being used almost as much as aniline itself. The *xylidines*, $(CH_3)_2.C_6H_3.NH_2$, and *pseudocumidine*, $(CH_3)_3.C_6H_2.NH_2$ (1,2,4,5), are also employed.

Secondary and Tertiary Aromatic Amines.—*Diphenylamine*, $(C_6H_5)_2NH$, is made on a large scale for the color industry by heating aniline with aniline hydrochloride to about 200°;

$$C_6H_5.NH_2 + C_6H_5NH_2.HCl = (C_6H_5)_2NH + NH_4Cl$$

It can also be made by heating phenol with aniline in the presence of zinc chloride:

$$C_6H_5.NH_2 + C_6H_5.OH \overset{ZnCl_2}{=} (C_6H_5)_2NH + H_2O$$

The tertiary *triphenylamine* $(C_6H_5)_3N$, cannot be made by these methods. It is formed, but in small amount, when the sodium compound of diphenylamine is heated with brombenzene:

$$(C_6H_5)_2.N.Na + C_6H_5Br = (C_6H_5)_3N + NaBr$$

The basic character of aniline is much weakened by the introduction of the negative phenyl group. Diphenylamine forms salts with strong acids, but they are at once decomposed by water; while in triphenylamine the basic properties have wholly disappeared. A solution of diphenylamine in concentrated sulphuric acid serves as a delicate test for nitric acid, giving a blue color with traces of this acid.

Benzylamines

Aromatic amines which have the amino group in a side chain have received the name of benzylamines from the simplest member of this type, $C_6H_5.CH_2.NH_2$ ($C_6H_5.CH_2$ = benzyl). They can be made by the methods for forming the aliphatic amines, and show the general behavior of these amines, modified, of course, by the presence of the phenyl group. Benzylamine, and the other primary amines of this class, are isomeric with the homologues of aniline. They are of comparatively little importance.

Benzylamine, $C_6H_5.CH_2NH_2$, isomeric with toluidine, is an alkaline liquid which absorbs carbon dioxide from the air. It boils at 185°, and is miscible with water in every proportion.

Dibenzylamine, $(C_6H_5.CH_2)_2NH$, is a liquid which boils above 300° but decomposes when slowly distilled. It is insoluble in water and does not absorb carbon dioxide.

Tribenzylamine, $(C_6H_5.CH_2)_3N$, crystallizes from hot alcohol, melts at 91°, and combines with methyl iodide to tribenzyl-methyl-ammonium iodide.

Derivatives of these amines, such as benzyl aniline, $C_6H_5.CH_2.NH.C_6H_5$, and dibenzylaniline, $(C_6H_5.CH_2)_2N.C_6H_5$, can also be obtained.

SOME AMINO DERIVATIVES OF BENZENE

		Melting point	Boiling point
Aniline	$C_6H_5.NH_2$	−6.2°	183–184°
o-Toluidine	$CH_3.C_6H_4.NH_2$ (1, 2)	liquid	199.7
m-Toluidine	$CH_3.C_6H_4.NH_2$ (1, 3)	liquid	203.3
p-Toluidine	$CH_3.C_6H_4.NH_2$ (1, 4)	45	200.4
p-Ethylphenylamine	$C_2H_5.C_6H_4.NH_2$ (1, 4)	−5	214
Benzylamine	$C_6H_5.CH_2.NH_2$	.....	185
Methylaniline	$C_6H_5.NH(CH_3)$	.....	193.5
Dimethylaniline	$C_6H_5.N(CH_3)_2$	2.5	193
o-Phenylene diamine	$C_6H_4(NH_2)_2$ (1, 2)	102–103	257
m-Phenylene diamine	$C_6H_4(NH_2)_2$ (1, 3)	63	283
p-Phenylene diamine	$C_6H_4(NH_2)_2$ (1, 4)	140	267
Toluylene diamine	$CH_3.C_6H_3(NH_2)_2$ (1, 3, 4)	88.5	265
Diphenylamine	$(C_6H_5)_2NH$	54	302
Triphenylamine	$(C_6H_5)_3N$	127	...
Acetanilid	$C_6H_5.NH.CO.CH_3$	116	304
Diacetanilide	$C_6H_5.N(CO.CH_3)_2$	37	145 (15 mm.)

CHAPTER XXIII

DIAZO COMPOUNDS

Attention has already been called to the existence of a class of compounds which are formed by the action of nitrous acid on the salts of the primary aromatic amines (*cf.* p. 305). The immediate products of this reaction are unstable, very reactive substances whose composition is of the type, $C_6H_5.N_2Cl$ or $C_6H_5.N_2NO_3$. They were called diazo compounds from the fact that they contain two united atoms of nitrogen (French, *azote*). These compounds were discovered in 1858 by Peter Griess, and the many useful reactions which they give quickly established their importance in synthetic and technical chemistry.

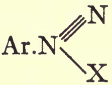
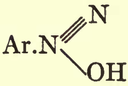
Preparation.—Although diazo compounds can be made in other ways, the method which is of the first importance is by means of nitrous acid acting on the salt of the amine:

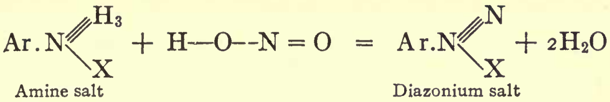
$$\underset{\text{Aniline hydrochloride}}{C_6H_5.NH_2.HCl} + HONO = \underset{\substack{\text{Phenyldiazonium}\\ \text{chloride}}}{C_6H_5.N_2Cl} + 2H_2O$$

The reaction is carried out by adding sodium nitrite or amyl nitrite to an acid solution of the amine; or less often by leading into a solution of the amine salt oxides of nitrogen evolved by the action of nitric acid on arsenic trioxide or starch. The operation is conducted in solutions cooled by ice on account of the instability of the diazo compounds at higher temperatures. The diazo compounds made in this way are usually not isolated, but immediately employed in solution for various reactions. The solid compounds can, however, be prepared by taking advantage of their small solubility in alcohol and their insolubility in ether.

Properties.—Since the isolation of these substances is seldom necessary, for the purposes to which they are applied, comparatively little is known of their individual properties, in spite of the fact that almost every known primary aromatic amine has been "diazotized." They are colorless, crystalline solids which are easily soluble in water. In the dry solid state they are very explosive when heated, and in some cases when struck. Diazobenzenenitrate, in particular, is more violently explosive than nitrogen iodide or mercury fulminate.

They are well characterized salts, and they form double salts, such as $(C_6H_5N_2)_2PtCl_6$, which are analogous to those of the alkalies. The chlorides and nitrates are not hydrolyzed in solution, as is shown by their neutral reaction, and they are ionized to the same high degree as potassium chloride and nitrate. The carbonates, which are formed in solution by digesting diazonium halides with silver carbonate, are, like potassium carbonate, soluble, and have a strong alkaline reaction. On treatment of a solution of the chlorine compound with silver oxide, silver chloride is precipitated and the solution becomes strongly alkaline from the formation of the diazonium hydroxide.

Structure.—The facts that have just been stated show that the solutions of these compounds contain a highly positive ion, $C_6H_5N_2$, resembling in character the potassium or ammonium ion, and in which one nitrogen atom probably has the valence of five, as in ammonium. This ion or radical is, by analogy, called *diazonium* and the structure of the diazonium salts is represented by the formula,  $\mathrm{Ar.N}\genfrac{}{}{0pt}{}{\equiv \mathrm{N}}{- \mathrm{X}}$ (in which Ar stands for the aryl radical). The strong base which is produced by the action of silver oxide (hydroxide) on a diazonium salt is  $\mathrm{Ar.N}\genfrac{}{}{0pt}{}{\equiv \mathrm{N}}{- \mathrm{OH}}$, analogous to ammonium hydroxide. This structure of the diazonium compounds accords with the simplest explanation of the reaction by which they are formed:



$$\mathrm{Ar.N}\begin{smallmatrix}\equiv H_3 \\ \diagdown X\end{smallmatrix} + H{-}O{-}N = O \;=\; \mathrm{Ar.N}\begin{smallmatrix}\equiv N \\ \diagdown X\end{smallmatrix} + 2H_2O$$

The nitrogen atom in the amine salt has the valence of five, that in nitrous acid is a triad, and the formation of the diazonium salt is the result of simple replacement of three hydrogen atoms by triad nitrogen.

Reactions.—The diazo group can be replaced by:

1. *Hydroxyl.*—This usually takes place on warming the aqueous solution of a diazonium salt, or allowing it to stand at ordinary temperature:

$$C_6H_5.N_2Cl + H_2O = C_6H_5.OH + N_2 + HCl$$

If a diazonium nitrate is used, the resulting phenol is liable to be nitrated by the nitric acid liberated in the reaction.

2. *Alkoxyl.*—In many cases an alkoxyl group may be substituted by boiling the dry diazonium salt with absolute alcohol:

$$(CH_3)_3C_6H_2.N_2.SO_4H + C_2H_5OH = (CH_3)_3C_6H_2.OC_2H_5 + N_2 + H_2SO_4$$

The reaction with alcohol in other cases results in the substitution of:

3. *Hydrogen.*—In this reaction the alcohol is oxidized to aldehyde:

$$C_6H_5.N_2Cl + C_2H_5OH = C_6H_6 + N_2 + CH_3.CHO + HCl$$

Which of these two reactions with alcohol occurs, depends on the nature of the diazonium compound and of the alcohol, as well as on the conditions of the reaction. The hydrogen replacement is favored by the presence of negative groups in the aryl ring, especially if they are in the ortho position. Hydrogen can also be substituted for the diazo group by treatment of the diazonium salt with an alkaline stannous solution; or indirectly, by formation of diazonium iodide and reduction of this by distillation from zinc dust; or through the hydrazine (p. 318).

4. *Halogens* can be introduced in place of the diazo group in several ways: (a) By heating with the halogen acids. (b) By distilling the platinum double salt with sodium carbonate. (c) By treating the solution of the corresponding diazonium halide with finely divided copper, which usually decomposes it in the cold (Gattermann's reaction). (d) Most conveniently by heating the diazonium chloride or bromide with cuprous chloride or bromide (Sandmeyer's reaction). (e) Iodine is introduced most simply by pouring a strongly acid solution of diazonium sulphate into a solution of potassium iodide.

5. *Cyanogen* is substituted by means of Sandmeyer's reaction, using a hot solution of potassium cuprous cyanide. Since the resulting cyanide (nitrile) is readily hydrolyzed to the corresponding acid, this reaction serves as a useful method for introducing the carboxyl group into aromatic compounds.

6. *Aromatic hydrocarbon groups*, such as toluyl, can be introduced by warming the dry diazonium salt with an excess of the corresponding hydrocarbon—the reaction being aided, if necessary, by the presence of aluminium chloride:

$$C_6H_5N_2Cl + C_6H_5.CH_3 = C_6H_5.C_6H_4.CH_3 + N_2 + HCl$$

7. *Nitro Group.*—This replacement is seldom made, but is occasionally useful, as in making β-nitronaphthalene which cannot be obtained by direct nitration, while the corresponding amine is easily prepared. The nitro group is introduced by treating the diazonium solution with an equivalent amount of sodium nitrite and then decomposing the diazonium nitrite with cuprous oxide.

Other replacements can be made, but these which have been described are the most important ones.

Reactions in which the diazo group is not replaced are:

8. The formation of *diazoamino and aminoazo compounds.*

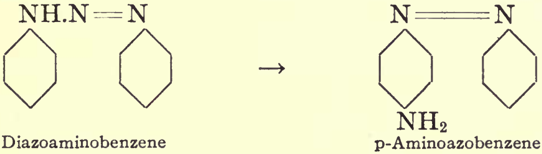
By the action of a diazonium salt on amines (aromatic or aliphatic) the first product is a diazoamino compound:

$$C_6H_5N_2Cl + C_6H_5.NH_2 = \underset{\text{Diazoaminobenzene}}{C_6H_5.N_2.NH.C_6H_5} + HCl$$

These compounds are very weak bases. They are converted into diazonium chlorides or bromides and the corresponding amine salts by the action of concentrated hydrochloric acid, or by hydrobromic acid in ethereal solution:

$$\underset{\text{Diazoaminonitrobenzene}}{NO_2.C_6H_4.N_2.NH.C_6H_4.NO_2} + HCl = \underset{\text{Nitrobenzene diazonium chloride}}{NO_2.C_6H_4.N_2Cl} + \underset{\text{Nitraniline hydrochloride}}{NO_2.C_6H_4.NH_2.HCl}$$

The most remarkable property of the diazoamino compounds is that of molecular rearrangement which occurs in their solutions in the free amines when a little of the amine salt is also present, and under some other conditions. If the para position in the amine group is unsubstituted, a *para aminoazo compound* is formed:



The aminoazo compounds are of great importance in the dyestuff industry.

9. Diazonium salts react with phenols in alkaline solutions to form para *hydroxyazo compounds:*

$$C_6H_5.N_2Cl + C_6H_5OH = \underset{\text{Hydroxyazobenzene}}{C_6H_5.N_2.C_6H_4.OH} + HCl$$

A great variety of dyes are made by similar reactions.

10. By partial reduction of diazonium salts *hydrazines* are

produced, which may be regarded as hydrazine, $NH_2.NH_2$, in which a hydrogen atom is replaced by an aryl group. *Phenylhydrazine hydrochloride*, $C_6H_5.NH.NH_2.HCl$, for instance, can be made by treating benzenediazonium chloride with the proper amount of stannous chloride and hydrochloric acid:

$$C_6H_5.N_2Cl + 4H = C_6H_5.NH.NH_2.HCl$$

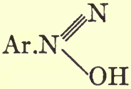
The hydrazines are pronounced mono-acid bases. They are set free from their salts by sodium hydroxide in the form of oils or solids which are sparingly soluble in water and nearly insoluble in strong alkalies; but they dissolve readily in alcohol and ether. They are very sensitive to oxidizing influences, and hence are strong reducing agents, even dilute solutions reducing Fehling's solution in the cold. The first product of the oxidation of primary hydrazines is the corresponding diazo compound. Treatment with copper sulphate or ferric chloride under certain conditions results in the replacement of the hydrazine group by hydrogen, and this reaction serves as a means for converting amines into the corresponding hydrocarbons, and also for the quantitative determination of the hydrazine by measurement of the nitrogen which is evolved:

$$C_6H_5.NH.NH_2 + 2CuSO_4 + H_2O = C_6H_6 + Cu_2O + N_2 + 2H_2SO_4$$

Phenylhydrazine is a poisonous oil. It is made commercially for the preparation of "antipyrine" and certain dyes.

The hydrazines react with compounds containing the carbonyl group, forming with aldehydes and ketones, *hydrazones*, whose service in the characterization of carbonyl compounds—especially the sugars—has already been noticed (p. 208).

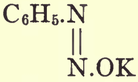
Further Discussion of the Structure of Diazo Compounds.—We have seen that diazonium hydroxide is a strong base whose constitution is like that of ammonium hydroxide. Its solutions, nevertheless, react with potassium hydroxide forming a *potassium diazoate* by replacement of the hydroxyl hydrogen by potassium.

In this relation, therefore, it behaves as an acid. Now while we know several metal hydroxides which play the double part of base and acid, such as the hydroxides of zinc, aluminium, and tin—their compounds are weak bases and very weak acids, and the alkali salts they form are usually very unstable. But here we have a very strong base which also forms a distinct alkali salt. The explanation is found in a probable rearrangement of the diazo group, so that in acting as a weak acid toward potassium hydroxide its structure becomes Ar.N:N OH, isomeric with the base,  . The hydroxyl group has shifted, and the valence of the pentad nitrogen atom has dropped to three, with the change from strong base to weak acid.

Potassium benzenediazoate, $C_6H_5N:NOK$, when heated with strong potassium hydroxide is changed to a more stable iso-form which is considered to be a stereoisomer of the first. The arrangements of the groups in these two salts may be represented by projection formulas which are similar to those for maleïc and fumaric acids (p. 186), the "anti" arrangement being the stable one,

$$\begin{array}{r} C_6H_5.N \\ \| \\ KO.N \end{array}$$

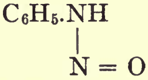
Normal or syn-diazoate



$$\begin{array}{l} C_6H_5.N \\ \| \\ N.OK \end{array}$$

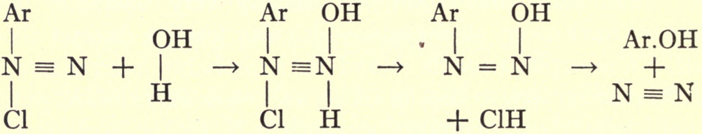
Iso- or anti-diazoate

The only hydroxide which can be isolated is the anti-diazo hydroxide, which is obtained in the form of unstable crystals by precipitating an anti-diazoate with acetic acid at a low temperature. On dissolving in water it changes into another isomeric form, nitrosamine,



$$\begin{array}{l} C_6H_5.NH \\ \quad\quad | \\ \quad\quad N = O \end{array}$$

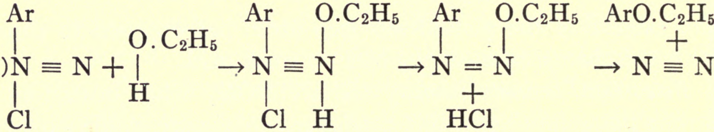
This theory as to the structure of the diazo compounds explains the reactions which result in the replacement of the diazo group as follows: The diazonium salts first form addition products with the reagent employed, and then these break down into syn-diazo compounds, which in turn decompose with loss of nitrogen. In the replacement by hydroxyl, for instance, the steps would be:



$$\begin{array}{l}\mathrm{Ar}\\ |\\ \mathrm{N}\equiv\mathrm{N}\\ |\\ \mathrm{Cl}\end{array} + \begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{H}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{OH}\\ | & |\\ \mathrm{N}\equiv & \mathrm{N}\\ | & |\\ \mathrm{Cl} & \mathrm{H}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{OH}\\ | & |\\ \mathrm{N} = & \mathrm{N}\\ & \\ \multicolumn{2}{c}{+\ \mathrm{ClH}}\end{array} \rightarrow \begin{array}{c}\mathrm{Ar.OH}\\ +\\ \mathrm{N}\equiv\mathrm{N}\end{array}$$

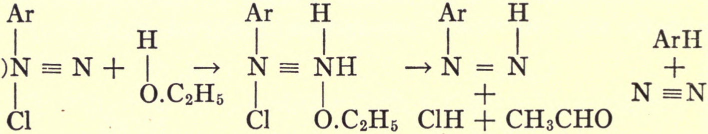
In the case of the reaction with alcohol, which sometimes substitutes alkoxyl and sometimes hydrogen, two different addition products can be formed, and the formation of one or the other determines the final product.

(1)



$$\begin{array}{l}\mathrm{Ar}\\ |\\ \mathrm{N}\equiv\mathrm{N}\\ |\\ \mathrm{Cl}\end{array} + \begin{array}{c}\mathrm{O.C_2H_5}\\ |\\ \mathrm{H}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{O.C_2H_5}\\ | & |\\ \mathrm{N}\equiv & \mathrm{N}\\ | & |\\ \mathrm{Cl} & \mathrm{H}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{O.C_2H_5}\\ | & |\\ \mathrm{N} = & \mathrm{N}\\ \multicolumn{2}{c}{+}\\ \multicolumn{2}{c}{\mathrm{HCl}}\end{array} \rightarrow \begin{array}{c}\mathrm{ArO.C_2H_5}\\ +\\ \mathrm{N}\equiv\mathrm{N}\end{array}$$

(2)



$$\begin{array}{l}\mathrm{Ar}\\ |\\ \mathrm{N}\equiv\mathrm{N}\\ |\\ \mathrm{Cl}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{O.C_2H_5}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{H}\\ | & |\\ \mathrm{N}\equiv & \mathrm{NH}\\ | & |\\ \mathrm{Cl} & \mathrm{O.C_2H_5}\end{array} \rightarrow \begin{array}{cc}\mathrm{Ar} & \mathrm{H}\\ | & |\\ \mathrm{N} = & \mathrm{N}\\ \multicolumn{2}{c}{+}\\ \multicolumn{2}{c}{\mathrm{ClH} + \mathrm{CH_3CHO}}\end{array} \quad \begin{array}{c}\mathrm{ArH}\\ +\\ \mathrm{N}\equiv\mathrm{N}.\end{array}$$

The other reactions may be explained in a similar way.[1]

---

[1] For a good exposition of Hantzsch's theory of the structure of diazo compounds, see Sidgwick's "Organic Chemistry of Nitrogen."

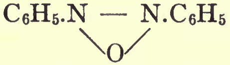
CHAPTER XXIV

AZO AND OTHER NITROGEN COMPOUNDS — DYES

In discussing the reactions of the nitro compounds, we have noticed that while the amines—anilines—are the final products of the reduction of these substances, the reduction can be controlled by the use of certain mild reducing agents, so that intermediate compounds are obtained. These are illustrated by the following, which are products of different reductions of nitrobenzene:

Phenylhydroxylamine, $C_6H_5.NH.OH$

Azoxybenzene,



$$C_6H_5.N \underset{\diagdown O \diagup}{—} N.C_6H_5$$

Azobenzene, $C_6H_5.N{:}N.C_6H_5$

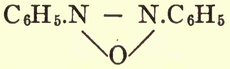
Hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$

All of these substances are converted into the corresponding amines—*e.g.*, aniline—by strong reducing agents, and they usually do not appear at all when acid reducing agents act on the nitro compounds.

Phenylhydroxylamine is formed when nitrobenzene is reduced by a neutral reducing agent, such as aluminium amalgam or zinc dust and hot water.

It forms white crystals which melt at 81°. It reduces an ammoniacal solution of silver nitrate and Fehling's solution in the cold, and in aqueous solution is quickly oxidized by the air into azoxybenzene. By chromic acid it is oxidized to nitrosobenzene, $C_6H_5.NO$, which is readily reduced to aniline. Phenylhydroxylamine acts toward acids as a base, but when warmed with inorganic acids suffers a transformation by rearrangement, into the isomeric p-aminophenol, $NH_2.C_6H_4.OH$.

Azoxy compounds are formed by reduction of the nitro compounds with weak alkaline reducing agents, such as an alcoholic solution of sodium hydroxide. *Azoxybenzene,*



$$C_6H_5.\underset{\diagdown O \diagup}{N - N}.C_6H_5$$

is a light yellow crystalline substance, which melts at 36°.

Azo compounds can be prepared from the nitro compounds by the use of somewhat stronger alkaline agents—sodium amalgam, alcoholic solutions of an alkali with zinc dust, or stannous chloride with an excess of sodium hydroxide. The azo compounds can also be prepared by further reduction of the azoxy compounds by the agents just mentioned, or, very conveniently, by their distillation from iron filings; or by oxidation of the primary aromatic amines (by alkaline permanganate or hydrogen peroxide):

$$C_6H_5NH_2 + H_2N.C_6H_5 + 2O \rightarrow C_6H_5.N:N.C_6H_5.$$

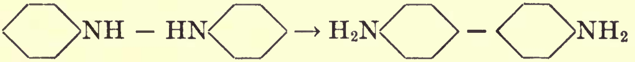
The azo compounds are strongly colored substances. They are insoluble in water, acids, and alkalies, but dissolve in benzene, alcohol and ether. They are very stable, and in this respect form a striking contrast to the diazo compounds, which also contain two united nitrogen atoms. By reducing agents, however, the azo compounds are readily changed, being converted, according to the conditions, into hydrazo compounds or into the amines. *Azobenzene* forms orange red crystals, melts at 68° and boils at 295°. While the azo hydrocarbons are not themselves dyes, a large number of the most important dyes are derivatives of these compounds and are known as the azo dyes (p. 325).

Hydrazo compounds, such as *hydrazobenzene,* $C_6H_5.NH.NH.C_6H_5$, are formed in the last step before the amine in the reduction of nitro compounds. They are formed by the reduction of nitro, azoxy, or azo compounds by an alcoholic solution of ammonium sulphide, or other alkaline reducing agents, and also by electrolytic reduction of the nitro compounds in the presence of an alkali.

The hydrazo compounds are colorless substances, which are neutral in character. In the air they suffer a partial oxidation, especially when moist, into the strongly colored azo compounds, and this change occurs readily with other mild oxidizing agents. When strongly heated they are converted into a mixture of azo compounds and amines:

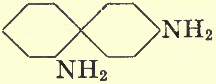
$$2C_6H_5.NH.NH.C_6H_5 = C_6H_5.N{:}N.C_6H_5 + 2C_6H_5NH_2.$$

Strong acids cause a molecular rearrangement, *hydrazobenzene* being transformed into *benzidine* with some of the isomeric diphenyline,



and

Hydrazobenzene Benzidine



Diphenyline

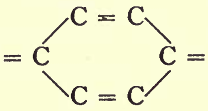
Benzidine, p-diaminodiphenyl, crystallizes in colorless plates which melt at 122°. It is a diacid base, and is the starting point for the manufacture of a large group of dyes of the Congo series.

Dyes

The azo dyes exceed in number those of any other class, and are perhaps the most important of the manufactured dyes. The first commercial dye made from coal tar products was prepared by W. H. Perkin in 1857 by the oxidation of an impure aniline sulphate with chromic acid. The manufacture of this dye, "mauve," and, soon after, of a number of others from aniline and its homologues, led to their designation as "aniline dyes," a term which is now often used for all of the dyes which are made from the aromatic substances distilled from coal tar. Many of these dyes, however, are in no way derived from, or related to, aniline, so that the general name of "coal tar dyes" is a more appropriate one.

A dye must be soluble in water, or readily brought into a soluble form, and have the property of adhering to the fiber either directly, or after the fiber has been treated with certain agents called "mordants." Dyes which color the fiber permanently without a mordant are called "direct" or "substantive" dyes, while those which require a mordant are "mordant" or "adjective" dyes. Many dyes are either substantive or adjective according to the character of the fiber. Substantive dyes for wool or silk are more common than for cotton and linen. Many different substances serve as mordants; those most used being, for basic dyes, tannic acid and compounds of it with antimony; and for acid dyes, acetates of aluminium, chromium, or iron, from which the hydroxides of the metals are separated on the cloth by passing through a weak basic bath or steaming. The cloth prepared by treatment with the mordant is dyed by the formation of insoluble compounds of the dye with the hydroxides. The mordant frequently modifies the color produced by the dye. In some cases, a fabric is dyed by developing the dye on the fibers by the use of appropriate reagents in the dye-bath. The results are called "ingrain" colors and are remarkably "fast," *i.e.*, resistant to washing and acids.

There are certain groups which are almost always present in colored organic compounds. The most important of these "chromophore" groups are: The nitro group, $-NO_2$, the azo group, $-N=N-$, and the quinoid group (p. 352):

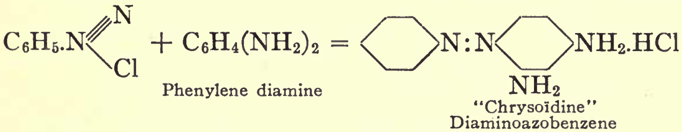


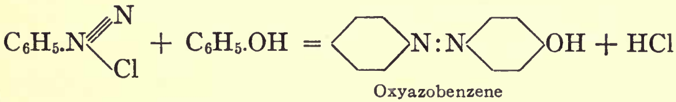
The colors of the compounds containing these groups are often much modified by the further introduction of atoms or groups which of themselves produce no color; such as phenyl, alkyl groups or bromine. With the increase in molecular weight which is brought about in this way there is in general a deepening of the shade, or a change in color, usually in the order yellow, orange, red, violet, blue, black.

But the presence of a chromophore group does not of itself make the compound a dye. There must be also a basic or acid group which will enable it to combine with the fiber or mordant. Such groups are called "auxochrome" groups, and the most important of them are the amino and hydroxyl (phenol) groups. Thus nitrobenzene, which is pale yellow, is not a dye, but p-nitraniline, $NO_2.C_6H_4.NH_2$, and p-nitrophenol, $NO_2.C_6H_5.OH$, are dyes; and azobenzene, though deeply colored, is incapable of dyeing cloth, while aminoazobenzene and derivatives of it form a large number of well-known dyes.

The acid groups $-CO.OH$ and $-SO_3H$ do not have the power of changing a colored compound into a dye, but the sulphonic group is often introduced to give an insoluble dye the solubility necessary for use in dyeing.

Azo dyes are aminoazo or oxyazo compounds and are made by treating diazonium salts with aromatic amines or phenols:





In the reaction between the diazonium salt and the amine. diazoamino compounds are sometimes the immediate products, but are readily converted into the aminoazo compounds in the presence of the amine and its hydrochloride (*cf.* p. 317).

As indicated in the equation just given, a para-hydrogen atom in the amine or phenol is the one which is first replaced.

Since practically all aromatic primary amines can be diazotized and the resulting diazonium salts react with all aromatic amines, primary, secondary, and tertiary, and with all phenols (hydroxyl derivatives), the number of azo dyes that are theoretically possible is enormous. The first of these dyes which was made commercially was chrysoïdine (1876), an orange dye, whose formation is given in the first of the equations above.

These dyes, and colored organic substances generally, are converted by reducing agents into colorless substances, the so-called leuco compounds, which usually return readily to their original color even on exposure to the air. The leuco compounds of the azo dyes are the corresponding hydrazo compounds.

The simplest of the azo dyes are yellow. With increase of molecular weight through the presence of substituents they become darker, changing through the range of colors already given (p. 325). They are crystalline substances, and most of them are insoluble, so that they are frequently employed in the form of their sulphonic acids which are made by treatment with concentrated sulphuric acid.

Methyl orange (helianthine) is the sodium salt of dimethylamino-azobenzene sulphonic acid, $HSO_3.C_6H_4.N_2.C_6H_4.N(CH_3)_2$. It is prepared by "condensing" dimethyl aniline with the diazo compound of sulphanilic acid (p. 307). It dyes silk and wool a bright orange, and is much used as an indicator in volumetric analysis, the orange being changed sharply to red by acids.

Congo red is described on page 387.

CHAPTER XXV

PHENOLS—AROMATIC ALCOHOLS—ETHERS

As in the case of other derivatives of the aromatic group, the hydroxyl compounds fall into two classes. The *phenols* are compounds in which the hydroxyl group or groups are united to nucleus carbon, while substances containing this group in a side chain are *aromatic alcohols.* The aromatic alcohols are very much like the alcohols of the aliphatic series in their general behavior, but the phenols are quite different from alcohols in most of their properties. The differences between these two classes of hydroxyl compounds are, in general, of the kind already noticed in other derivatives of the aromatic hydrocarbons in which aryl and alkyl groups both are present.

The aromatic *ethers* are compounds in which two aryl radicals or an aryl and alkyl radical are linked together by oxygen.

Phenols

A number of phenols are among the products of the destructive distillation of various natural organic substances. Thus *phenol, hydroxybenzene*, C_6H_5OH, the simplest of the phenols, and the cresols, C_7H_7OH, formed thus from coal, are obtained from coal tar; and *pyrogallol*, a trihydric phenol, $C_6H_3.(OH)_3$, is obtained by heating gallic acid, which occurs naturally in oak-galls and is also prepared from tannin. The characteristics of the phenols may be best learned by a study of the first member of the group. All the phenols have names ending in "ol."

Phenol, $C_6H_5.OH$, was discovered in coal tar in 1834, and is to-day one of the most important of the immediate products of the coal tar industry. In the form of the sodium salts of their sulphuric acid esters, phenol and several other members of this group occur in considerable amounts in the urine of herbivora. "Carbolic acid," the name first given to phenol, is still employed in common usage. Later it was called "phenyl hydrate" or "phenic acid" (from φαίνω, to illuminate), apparently because of its appearance as a by-product in the making of illuminating gas. As has been noticed, it is from this rather fanciful naming that we have the term *phenyl* for the benzene radical, C_6H_5.

Properties.—Phenol forms long colorless crystals which melt at 42°, and usually become reddish on exposure to light and air. The boiling point is 183°. It has a very characteristic odor, is highly poisonous, blisters the skin, and has strong antiseptie properties. Water dissolves about one-fifteenth of its weight of phenol at 20°, and in turn phenol dissolves about one-third of its weight of water. The presence of water in phenol lowers its melting point, so that even small amounts of water cause it to remain liquid at and below the ordinary temperature. Phenol was formerly much used in surgery as an antiseptic, and is employed in the preparation of picric acid, dyes, and some medicines.

Chemically, phenol acts as a weak acid whose salts are decomposed at ordinary temperatures by carbonic acid—though carbon dioxide is evolved when sodium carbonate is brought into boiling phenol. In both phenol and alcohols the hydrogen of the hydroxyl group can be replaced by metals, but the "phenolates" are more salt-like in character than the alcoholates. The latter are at once decomposed by water, and consequently, alcohols insoluble in water (*i.e.*, amyl alcohol), do not dissolve in aqueous solutions of alkalies. Phenolates are more stable, and phenol dissolves freely in alkaline solutions. The weakness of the acid character of phenol is shown, however, by the alkaline reaction of solutions of the alkali phenolates. The acid properties of phenol, like the absence of alkalinity in the aromatic amines is evidence of the essentially negative character of phenyl. When this negative character is increased by the introduction of negative atoms or groups into the phenyl radical, the acidity becomes much more pronounced; trinitrophenol, for example, is a comparatively strong acid, and is called picric acid.

Reactions.—1. Phenol reacts *like an alcohol* with: (a) Metals, forming salts, phenolates. (b) Acyl chlorides, to form esters:

$$\underset{\text{Phenol}}{C_6H_5.OH} + \underset{\text{Acetyl chloride}}{CH_3.CO.Cl} = \underset{\text{Phenyl acetate}}{C_6H_5O.OC.CH_3} + HCl$$

Nitric and sulphuric acid esters are not formed, as with alcohols, by the direct action of these acids on phenol, nitro or sulphonic acid substitution products being produced instead. Phenylsulphuric acid in the form of its potassium salt can, however, be obtained by warming a concentrated solution of potassium phenolate with potassium pyrosulphate:

$$C_6H_5OK + K_2S_2O_7 = C_6H_5O.SO_2.OK + K_2SO_4$$

But on heating this salt in the dry state, it suffers molecular rearrangement into $KO.SO_2.C_6H_4.OH$, the potassium salt of phenolsulphonic acid.

(c) With alkyl halides the alkali salts of phenol form mixed aryl-alkyl ethers (*cf.* p. 74):

$$\underset{\substack{\text{Sodium}\\\text{phenolate}}}{C_6H_5.ONa} + CH_3I = \underset{\text{Anisol}}{C_6H_5.OCH_3} + NaI$$

(d) With phosphorus pentachloride or bromide the hydroxyl group is replaced by chlorine or bromine. But this reaction is not very satisfactory as the yield of chlor or brombenzene is small, various other compounds being formed at the same time.

2. *Unlike alcohols*, phenol is

(a) Reduced to the corresponding hydrocarbon (benzene) by distillation with zinc dust.

(b) Changed to an amine (aniline) by heating with ammonia in the presence of zinc chloride.

(c) In the form of alkali phenolate, it is converted by carbon dioxide into the unstable salt of the carbonic acid ester:

$$C_6H_5.ONa + CO_2 = C_6H_5.O.CO.ONa$$

This sodium phenyl carbonate, on heating under pressure, undergoes a molecular rearrangement into the salt of hydroxybenzoic or salicylic acid, $HO.C_6H_4.CO.ONa$ (1, 2); hence this reaction gives a means for making hydroxy acids from phenols (*cf.* p. 362).

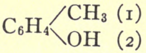
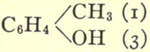
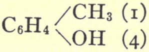
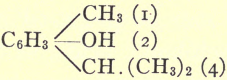
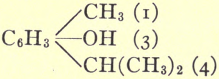
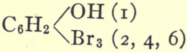
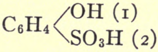
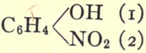
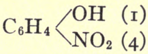
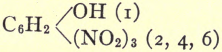
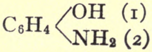
3. Phenol is more easily oxidized than benzene. As the carbon atom to which the hydroxyl is united is not combined with hydrogen atoms, phenol is analogous to a tertiary alcohol and cannot yield aldehydes or acids on oxidation. Under certain conditions the dihydric phenols, catechol, and quinol are formed, but the oxidation products are, in general, quite various, including both simpler and more complex compounds.

4. The hydrogen of the phenyl group is rendered particularly reactive by the presence of the hydroxyl group. Tribrom and trinitrophenol and phenoltrisulphonic acid are readily formed by the direct action of bromine, nitric or sulphuric acids.

Dilute aqueous solutions of phenol give a violet color with ferric chloride, and bromine water precipitates yellowish tribromphenol. These reactions do not serve, however, to *identify* phenol, since other members of this group and some other substances show a similar behavior.

Formation of Phenols.—The hydroxyl group can be introduced (a) in place of the sulphonic acid group by melting the compound with solid alkali (pp. 290, 334). This is the method used in the commercial production of phenol. (b) In place of the amino group by the diazo reaction (p. 315). Phenols can also be prepared (c) from hydroxy-acids by replacement of the carboxyl group with hydrogen, through fusion with sodium hydroxide or lime (p. 274); and (d) by means of the Grignard reagents (p. 37).

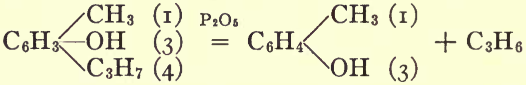
PHENOLS AND SUBSTITUTED PHENOLS

Name	Formula	Melting point	Boiling point
Phenol	C_6H_5OH	42.5°	181.5
o-Cresol	 $C_6H_4\left<\begin{matrix}CH_3 & (1)\\ OH & (2)\end{matrix}\right.$	30°	188°
m-Cresol	 $C_6H_4\left<\begin{matrix}CH_3 & (1)\\ OH & (3)\end{matrix}\right.$	4°	200.5°
p-Cresol	 $C_6H_4\left<\begin{matrix}CH_3 & (1)\\ OH & (4)\end{matrix}\right.$	36°	201°
Carvacrol	 $C_6H_3\left<\begin{matrix}CH_3 & (1)\\ OH & (2)\\ CH.(CH_3)_2 & (4)\end{matrix}\right.$	0.5°	237°
Thymol	 $C_6H_3\left<\begin{matrix}CH_3 & (1)\\ OH & (3)\\ CH(CH_3)_2 & (4)\end{matrix}\right.$	50°	232°
Pyrocatechol	$C_6H_4(OH)_2$ (1, 2)	104°	240°
Resorcinol	$C_6H_4(OH)_2$ (1, 3)	111°	276.5°
Quinol (hydroquinone)	$C_6H_4(OH)_2$ (1, 4)	169°	285°
Pyrogallol	$C_6H_3(OH)_3$ (1, 2, 3)	132°	....
Phloroglucinol	$C_6H_3(OH)_3$ (1, 3, 5)	219°	....
Hexahydroxybenzene	$C_6(OH)_6$	....	....
Sym.-tribromphenol	 $C_6H_2\left<\begin{matrix}OH & (1)\\ Br_3 & (2, 4, 6)\end{matrix}\right.$	92°	....
o-Phenolsulphonic acid	 $C_6H_4\left<\begin{matrix}OH & (1)\\ SO_3H & (2)\end{matrix}\right.$	....	....
o-Nitrophenol	 $C_6H_4\left<\begin{matrix}OH & (1)\\ NO_2 & (2)\end{matrix}\right.$	44.3°	214°
p-Nitrophenol	 $C_6H_4\left<\begin{matrix}OH & (1)\\ NO_2 & (4)\end{matrix}\right.$	114°	....
Sym.-trinitrophenol (picric acid)	 $C_6H_2\left<\begin{matrix}OH & (1)\\ (NO_2)_3 & (2, 4, 6)\end{matrix}\right.$	112.5°	....
o-Aminophenol	 $C_6H_4\left<\begin{matrix}OH & (1)\\ NH_2 & (2)\end{matrix}\right.$	170°	....

Homologues of Phenol

Among the phenols containing a single hydroxyl group, the following are of especial importance and serve as types of the homologues of phenol.

Cresols, $CH_3.C_6H_4.OH$. All three of the isomeric cresols are obtained among the products of the distillation of coal tar and of beech wood. The separation of the three cresols by distillation is difficult because of the nearness of their boiling points (see table), but sometimes the ortho cresol is thus isolated from the other two. They can be prepared in pure form from the corresponding toluenesulphonic acids, or from the toluidines by the diazo reaction. Meta cresol can also be made by heating thymol with phosphorus pentoxide:

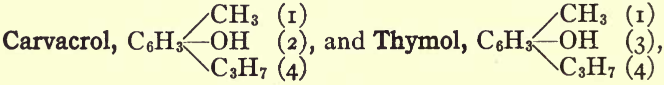


$$C_6H_3\left\langle\begin{array}{ll}CH_3 & (1)\\ OH & (3)\\ C_3H_7 & (4)\end{array}\right. \overset{P_2O_5}{=} C_6H_4\left\langle\begin{array}{ll}CH_3 & (1)\\ OH & (3)\end{array}\right. + C_3H_6$$

Thymol Meta cresol Propylene

This reaction by which a long side-chain is replaced by hydrogen with the formation of an olefine can be applied in making other phenols.

The cresols resemble phenol in most of their properties. They are more strongly antiseptic than phenol, and the crude mixture of them from coal tar is used for disinfecting purposes. They give a bluish coloration with ferric chloride. It is a curious fact that the hydroxyl group in cresols protects the methyl group from oxidation by chromic acid. This is also the case with similar phenols. If, however, the hydrogen of the hydroxyl group is replaced by an alkyl or acyl group, oxidation occurs.



Carvacrol, $C_6H_3\left\langle\begin{array}{ll}CH_3 & (1)\\ OH & (2)\\ C_3H_7 & (4)\end{array}\right.$, and **Thymol,** $C_6H_3\left\langle\begin{array}{ll}CH_3 & (1)\\ OH & (3)\\ C_3H_7 & (4)\end{array}\right.$,

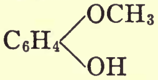
are the two possible monohydric phenol derivatives of cymene

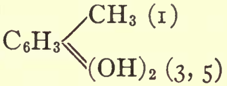
(p. 278). Both of them occur in a number of essential vegetable oils, and are obtained from these sources. The positions of the hydroxyl group with reference to the methyl group is proved by the conversion of carvacrol into o-cresol, and of thymol into m-cresol, when they are heated with phosphorus pentoxide. Carvacrol can be prepared by heating camphor with iodine, or made from cymenesulphonic acid. Thymol is made commercially from the oil of thyme where it exists together with cymene, by shaking the oil with caustic soda. It has a thyme-like odor, is very sparingly soluble in water, and is not poisonous like phenol and the cresols. It finds employment in medicine as an antiseptic. Carvacrol is colored green by ferric chloride, but thymol gives no coloration.

As an illustration of a phenol with an unsaturated side chain may be noted **chavicol,** p-allylphenol, $HO.C_6H_4.CH_2.CH:CH_2$, which occurs in the betel leaves that are chewed by natives in the East.

Phenols with More Than One Hydroxyl Group

The polyhydric phenols differ from the simpler phenols chiefly in their greater solubility in water and in the fact that most of them are strong reducing agents. Several of them are found in wood tar, especially in the form of their methyl ethers. They can be made by the usual methods for introducing hydroxyl groups. Their behavior in some particulars depends markedly on the relative positions of the hydroxyl groups.

Catechol, or *pyrocatechol,* $C_6H_4(OH)_2$ (1, 2), is named from *catechu,* a product from certain Indian trees, having been first made by the dry distillation of this substance. It can be made by the usual synthetical methods, but is conveniently prepared from its methyl ether, *guaiacol,*  $C_6H_4\left\langle\begin{matrix}OCH_3\\OH\end{matrix}\right.$, which is obtained from wood tar. Catechol is readily soluble in water. It is a stronger reducing agent than either of its two isomers. An alkaline solution absorbs oxygen from the air and turns green and then black. Catechol in aqueous solution gives a green color with ferric chloride, which turns violet on addition of a solution of sodium carbonate or acetate. This reaction is characteristic for aromatic orthodihydroxyl compounds.

Resorcinol, $C_6H_4(OH)_2(1, 3)$, derives its name from the related and previously known substance *orcin*  $C_6H_3\begin{cases} CH_3\ (1) \\ (OH)_2\ (3, 5) \end{cases}$ which in turn was named from its discovery in the investigation of the so called "lichen orcina." Resorcinol is formed by melting benzenedisulphonic acids, halogen-benzenesulphonic acids, or halogen-phenols with potassium hydroxide. Many ortho and para compounds of these classes, as well as the meta compounds, yield in this way the meta compound resorcinol. Two things are to be noted in this connection: That halogen atoms when substituted in phenols can be replaced by hydroxyl directly, and second, that in the transformations of ortho and para compounds given above the relative positions of groups are changed, the greater stability of the meta configuration usually determining the final result. Reactions of this character evidently cannot be employed for the determination of position.

Resorcinol is prepared industrially from benzene-m-disulphonic acid. It gives a dark violet with ferric chloride, which disappears on addition of sodium acetate (compare with catechol). When it is heated with phthalic anhydride (p. 369) and the product is dissolved in dilute sodium hydroxide, the yellow solution shows a beautiful green fluorescence. Other meta diphenols give this reaction, which may therefore serve as a test for these compounds, and also for certain dicarboxylic acids, like phthalic acid.

Resorcinol is largely used in making the dyes *fluoresceïn* and *eosin* (p. 370), other phthaleïn dyes, and certain azo colors.

Quinol, or *hydroquinone*, $C_6H_4(OH)_2$ (1, 4), so-called because first obtained by the dry distillation of quinic acid $C_6H_7(OH)_4.CO.OH$ (p. 375), occurs in the leaves of the bearberry as a glucoside. It is usually prepared by reducing quinone $C_6H_4O_2$ (p. 350) by sulphurous acid. With ferric chloride quinol gives a dark green solution which turns yellow from its oxidation to quinone:

$$\underset{\text{Quinol}}{C_6H_4(OH)_2} + O = \underset{\text{Quinone}}{C_6H_4O_2} + H_2O$$

Other mild oxidizing agents effect the same change, and this reaction is characteristic of quinol and its homologues, the p-dihydric phenols or hydrochinones—which are thus converted into the corresponding yellow quinones.

The three isomeric dihydric phenols are colorless crystalline substances. The solubility of resorcinol is the greatest and that of quinol the least (5.85:100 at 15°). The melting points increase from catechol to quinol; and in reducing power quinol lies between the other two. Cathechol and quinol are used as developers in photography.

Pyrogallol, or *pyrogallic acid*, $C_6H_3(OH)_3$ (1, 2, 3), is prepared by heating gallic acid (p. 366):

$$\underset{\text{Gallic acid}}{(OH)_3C_6H_2.CO.OH} = \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + CO_2$$

It forms colorless crystals which dissolve in about two parts of water. Its alkaline solutions absorb oxygen rapidly from the air or other gaseous mixtures and turn dark brown. On account of this property pyrogallol solutions are used in the analysis of gases. This behavior marks it as an energetic reducing agent. It precipitates gold, silver, and mercury from solutions of their salts, and is extensively used as a photographic developer. Among the oxidation products of pyrogallol which are formed in these reductions of other substances, are acetic acid and carbon dioxide.

The two isomers of pyrogallol, *phloroglucinol* (1, 3, 5), and *hydroxyquinol* (1, 2, 4), are of little importance.

The three possible *tetrahydricphenols* are well known, as such, or in the form of derivatives. *Pentahydricphenols* are unknown.

Hexahydroxylbenzene, $C_6(OH)_6$, has been made synthetically. It is a crystalline substance which is not very soluble in water and very slightly soluble in alcohol and ether. Its solutions rapidly become violet-red in the air, and reduce silver nitrate instantaneously in the cold. With acetic anhydride it forms a hexa-acetyl derivative, $C_6(O.OC.CH_3)_6$. The potassium salt of this hexaphenol, $C_6(OK)_6$, is formed by the action of carbon monoxide on melted potassium, and from this the phenol can be set free by dilute acid. Since by the distillation of hexaphenol with zinc dust benzene is formed, an interesting synthesis of benzene from the elements can thus be effected. The potassium compound, which is a gray, crystalline substance, acquires in the air an explosive property, which had to be reckoned with in the older process for making potassium (see Inorganic Chemistry).

The homologues of the polyhydricphenols are not important.

Derivatives of Phenols

Halogen derivatives of the phenols are readily formed by the direct action of chlorine and bromine, and iodine replaces hydrogen when brought into an alcoholic solution of the phenol in the presence of mercuric oxide. The halogen atoms enter in the ortho or para positions relative to the hydroxyl groups. The halogen derivatives can also be made from the aminophenols by the diazo reaction.

They are colorless crystalline substances which are more strongly acid than the phenols. On melting with potassium hydroxide the halogen is exchanged for hydroxyl, molecular rearrangement often occurring in the reaction with chlor and bromphenols, so that p-bromphenol yields not only quinol (1, 4), but considerable amounts of resorcinol (1, 3).

Phenolsulphonic Acids.—By the action of concentrated sulphuric acid on phenol, the orthosulphonic acid is the chief product in the cold; but if the mixture of acid and phenol is heated, the para compound alone is formed. The orthosulphonic acid is unstable when heated, suffering rearrangement into the para compound, and this even occurs in evaporating its aqueous solution. The chemical properties of the phenol sulphonic acids are those which are characteristic of both phenol and sulphonic acids. Ortho phenolsulphonic acid is a stronger disinfectant than phenol, and has been used for this purpose under the name of "aseptol."

Nitrophenols.—Ortho and para nitrophenol are formed by the action of dilute nitric acid on phenol, and are easily separated, since the ortho compound alone is volatile with steam. They are both crystalline solids. The para compound is not only non-volatile with steam but is colorless and odorless, while ortho nitrophenol is yellow, and has a strong odor resembling that of nitrobenzene. They are used industrially in the preparation of dyes and medicines. Meta nitrophenol cannot be made directly, but is prepared from m-nitraniline by the diazo reaction.

Picric Acid, (1) $HO.C_6H_2(NO_2)_3(2, 4, 6)$, is symmetrical trinitrophenol. This important substance is the end-product in the nitration of phenol. It is usually prepared by dissolving phenol in concentrated sulphuric acid, then adding the phenolsulphonic acid to concentrated nitric acid, and finally heating for some time at 100°. On cooling, the picric acid separates as in a mass of pale yellow crystals. It dissolves rather slightly in hot water, and at 20° its solubility is 1.03:100. It is freely soluble in alcohol, ether, etc., and its aqueous solutions have a bitter taste, and a strong acid reaction. The presence of three nitro groups makes trinitrophenol a stronger acid—more highly ionized—than acetic acid. The sodium and the ammonium salts are quite soluble, but the potassium salt dissolves very slightly. With many hydrocarbons, such as naphthalene and anthracene, picric acid forms crystalline molecular compounds well suited for the separation and the identification of these hydrocarbons. These compounds are resolved into their components by ammonia. In a similar way picric acid is often used in the laboratory to precipitate and purify organic bases through the formation of difficultly soluble salts. Its solutions and those of its alkali salts have a much deeper color than would be expected from the appearance of the crystals. Picric acid is a substantive dye for wool and silk and is largely used, especially in mixture with other dyes. It is the oldest of the manufactured organic dyes.

Picric acid is detonated by mercury fulminate or guncotton, but does not explode when struck. Its alkali and other salts, however, explode violently on percussion, or when heated, and are used in various explosives (*e.g.*, "*melinite*").

Dinitrocresols, $CH_3.C_6H_2.(NO_2)_2.OH$, were formerly used in the form of alkali salts for dyes, under the names of "Victoria yellow," etc.

Aminophenols can be made by reduction of nitrophenols. Of especial interest is their formation by molecular rearrangement of aromatic hydroxylamines (p. 321). In consequence of this reaction many aminophenols are conveniently prepared from nitro compounds by electrolytic reduction. Thus, from nitrobenzene dissolved in sulphuric acid, p-aminophenol is prepared:

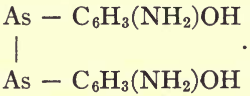
$$C_6H_5NO_2 + 4H \rightarrow C_6H_5.NH.OH \rightarrow HO.C_6H_4.NH_2$$

The aminophenols are basic through the presence of the amino group and form stable salts with acids; and the acidity of the hydroxyl group is so weakened that although they dissolve in caustic alkalies, they do not form definite alkali salts.

The aminophenols are mostly quite soluble in water, and their solutions oxidize in the air and consequently are reducing agents. A number of them are employed as photographic developers: "*Rodinal*" is the hydrochloric acid salt of p-aminophenol; "*Amidol*" a salt of o-p-diaminophenol; "*Reducin,*" a salt of diortho-para triaminophenol; and "*Metol*," the sulphate of methylaminophenol,

$$C_6H_4(OH)NH(CH_3).$$

Salvarsan, or 606, recently introduced into medicine as a specific for syphilis, is the dihydrochloride of a derivative of aminophenol containing arsenic,



$$\begin{array}{l}As - C_6H_3(NH_2)OH \\ | \\ As - C_6H_3(NH_2)OH\end{array}.$$

Esters of Phenols.—Of these only certain phenylsulphuric acids need be mentioned, which occur as sodium salts in urine.

Bakelite.—By a "condensation" of phenols and formaldehyde under certain conditions, a hard, infusible product is obtained, which under the name of "bakelite" is finding many applications. It resembles amber in appearance, burns with difficulty, is insoluble in all solvents and withstands almost all chemical reagents. If made from phenol its formula is represented by $C_{43}H_{38}O_7$, and it has received the chemical name of oxybenzylmethyleneglycolanhydride. In the form of a transition product it is softened by heat and can be molded. It is mostly used compounded with other substances such as wood pulp, for the manufacture of a great variety of articles for which celluloid, hard rubber, and amber have been employed, for insulating purposes, etc.

Aromatic Alcohols

The aromatic compounds which contain hydroxyl in a side chain can be made by the synthetic methods employed for the preparation of the aliphatic alcohols. When the corresponding aldehydes are available, as in some cases, the primary alcohols are conveniently prepared from them by the usual methods of reduction, or by shaking the aldehyde with an aqueous solution of an alkali. Aliphatic aldehydes (except formaldehyde) are converted into resins by alkalies, but aromatic aldehydes undergo a reaction of a different nature in which one half of the aldehyde is reduced to alcohol and the other half oxidized to an acid (salt) (*cf.* p. 84):

$$\underset{\text{Benzaldehyde}}{2C_6H_5.CHO} + KOH = \underset{\text{Benzyl alcohol}}{C_6H_5.CH_2OH} + \underset{\text{Potassium benzoate}}{C_6H_5.CO.OK}$$

Alcohols in which the group $-CH_2OH$ is directly united to ring carbon can also be obtained by reduction of the corresponding acid amides:

$$C_6H_5.CO.NH_2 + 4H = C_6H_5.CH_2OH + NH_3$$

The aromatic alcohols completely resemble the aliphatic alcohols, and differ from the phenols in the greater readiness with which they form esters, and are oxidized to aldehydes, acids or ketones, as well as by the fact that they do not form stable salts with bases.

Benzyl Alcohol, $C_6H_5.CH_2OH$ (phenylcarbinol), occurs as benzoic and cinnamic esters in the balsams of Peru and Tolu, and in liquid storax. It is a liquid of faint aromatic odor, boiling at 204°. On oxidation it gives benzaldehyde and benzoic acid and it can be reduced to toluene. Benzyl alcohol may be considered as methyl alcohol in which one hydrogen atom of the CH_3 group is replaced by phenyl. If two of these atoms are thus replaced the compound is **diphenylcarbinol** (or benzhydrol) $(C_6H_5)_2CHOH$, a secondary alcohol. This alcohol may be made, like the secondary alcohols of the aliphatic series, by reduction of the corresponding ketone, benzophenone or diphenylketone $C_6H_5.CO.C_6H_5$. It is a solid, melting at 68° and boiling at 298°. **Triphenylcarbinol,** $(C_6H_5)_3COH$, is a tertiary alcohol, which can be obtained by the oxidation of triphenylmethane, $(C_6H_5)_3CH$, a reaction peculiar to aromatic compounds. It is a solid, melting at 159°.

Cinnamyl Alcohol, $C_6H_5.CH{:}CH.CH_2OH$, (γ-phenyl-allyl alcohol), occurs in storax as the ester of cinnamic acid, and serves as an illustration of an unsaturated aromatic alcohol. It melts at

33°, boils at 254°, and has the odor of hyacinths. It may be reduced to phenylpropyl alcohol, $C_6H_5.CH_2.CH_2.CH_2OH$, and when oxidized gives cinnamic aldehyde, $C_6H_5.CH:CH.CHO$, cinnamic acid, $C_6H_5.CH:CH.CO.OH$, or benzoic acid, $C_6H_5.CO.OH$ according to the oxidizing agent employed.

Phenol-Alcohols.—Certain compounds which are hydroxy aromatic alcohols, or phenol-alcohols, since they contain hydroxyl both in the ring and in a side chain, occur as glucosides in nature. The simplest of these is *o-hydroxybenzylalcohol*, or *salicyl alcohol*, $HO.C_6H_4.CH_2OH$, whose glucoside is salicin which is found in the bark of the willow. The alcohol can be obtained by splitting off the sugar of the glucoside with mineral acids or emulsin. Salicyl alcohol melts at 86°, and is quite soluble in water. It gives a blue color with ferric chloride, and it shows both phenol and alcohol reactions.

Aromatic compounds containing sulphur in place of oxygen can be prepared, but these thiophenols, aromatic mercaptans, thioethers, etc., present no very important points of interest.

Aromatic Ethers

Diphenyl Ether, $C_6H_5.O.C_6H_5$, is the simplest ether containing two aryl groups. It can be made by heating phenol with anhydrous zinc chloride, or by the dry distillation of aluminium phenolate, $Al(O.C_6H_5)_3$. It has a geranium-like odor, and melts at 28° and boils at 252°.

Anisol, $C_6H_5.OCH_3$, phenyl-methyl ether, is produced by distilling anisic acid, $CO.OH.C_6H_4.OCH_3$ (which is obtained by oxidation of anethol, the chief constituent of anise oil) with lime, or by heating guaiacol with zinc dust. Anisol, and other ethers of this type, can be made by the action of alkali phenolates on alkyl halides:

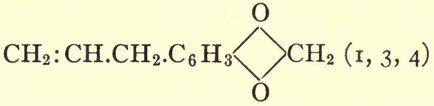
$$C_6H_5.ONa + CH_3I = C_6H_5.OCH_3 + NaI$$

Their formation from aryl halides and sodium alkoxides is also possible, but more difficult, because of the smaller reactivity of the halogen atom when united to a cyclic radical.

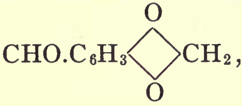
Guaiacol, $C_6H_4(OH)(OCH_3)(1, 2)$, was first obtained from gum guaiacum. It is among the products of wood tar, and can be made from catechol (p. 333) of which it is the methyl ether.

Eugenol, or allyl-guaiacol, $C_6H_3(OH)(OCH_3)(CH_2.CH{:}CH_2)$ (1, 2, 4), occurs in oil of cloves which is obtained by distilling cloves with steam, and in other essential oils. In oil of cloves it is associated with a terpene of the formula, $C_{15}H_{24}$, and it is separated from this as an alkali salt by its solubility in an alkaline solution. It has a strong odor of cloves, and unites the properties of a phenol, an ether and an unsaturated compound. It is a colorless oil which boils at 247°, and is used for perfumery and for making vanillin (p. 347).

Safrol, the chief constituent of sassafras oil, has the constitution,



$$CH_2{:}CH.CH_2.C_6H_3\overset{O}{\underset{O}{\diamond}}CH_2 \ (1, 3, 4)$$

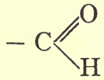
which is that of methylene ether of propylene dihydroxybenzene. It is very poisonous, but has been used to cover the unpleasant fatty odor of soaps. It also serves for the preparation of *piperonal,*  $CHO.C_6H_3\overset{O}{\underset{O}{\diamond}}CH_2$, the methylene ether of dihydroxybenzaldehyde (1, 3, 4) which is a product of its oxidation; and is employed, on account of its heliotrope odor, in perfumery under the name of "heliotropin." Safrol melts at 8° and boils at 232°, piperonal at 37° and 263°.

Phenacetin, the well-known drug, is an ethereal derivative of p-hydroxyacetanilide, having the formula, $C_6H_4(OC_2H_5)(NH.OC.CH_3)$ (1,4). It forms colorless crystals which melt at 135°, and is very slightly soluble in cold water. It is made by boiling the ethyl ether of p-aminophenol with glacial acetic acid.

CHAPTER XXVI

AROMATIC ALDEHYDES, KETONES AND QUINONES

Aldehydes

The aldehyde group,  $-C\begin{matrix}{}^{\displaystyle /\!\!/ O}\\ {}_{\displaystyle \diagdown H}\end{matrix}$, requiring two valencies for oxygen and one for hydrogen, cannot be developed on nucleus carbon. The aromatic aldehydes are, therefore, compounds in which this group is directly or indirectly united to an aryl radical in place of hydrogen. There are thus two varieties of aromatic aldehydes, both of which may be regarded as aliphatic aldehydes in which aryl groups have been substituted for hydrogen in formaldehyde, or in the radicals of higher aldehydes.

Preparation.—Aromatic aldehydes can be made from the alcohols, as in the case of formaldehyde and acetaldehyde, but the corresponding alcohols are generally not readily accessible. In the aromatic series, as we have seen, the hydrocarbons form the most important sources for the preparation of other compounds, hence a method much employed for making aldehydes which have the aldehyde group immediately attached to the benzene ring, is by first forming, directly from the hydrocarbons, derivatives having chlorine in a side chain, and then converting the alkyl halogen group into the aldehyde group. In this way benzaldehyde is prepared commercially from toluene. The toluene is chlorinated with the production of benzalchloride, $C_6H_5.CHCl_2$, as the chief product, and then the chlorine is replaced by oxygen by heating under pressure with milk of lime:

$$C_6H_5.CHCl_2 + Ca(OH)_2 = C_6H_5.CHO + CaCl_2 + H_2O$$

The reaction can be effected with other agents, even with water.

Benzaldehyde may also be made from benzylchloride, $C_6H_5.CH_2Cl$, by oxidation with lead or copper nitrate; or direct from toluene by an oxidation effected by chromyl chloride, CrO_2Cl_2 (Étard's method). This method of oxidizing a methyl group to an aldehyde group may also be used for the preparation of other aromatic aldehydes.

The aldehyde group may also be introduced in place of a hydrogen atom of the aryl nucleus by Gattermann's reaction. Thus benzaldehyde is prepared directly from benzene by passing into it a mixture of hydrogen chloride and carbon monoxide in the presence of anhydrous cuprous chloride and aluminium chloride. It may be assumed that the unstable formyl chloride, HCO.Cl is an intermediate product:

$$C_6H_6 + HCO.Cl = C_6H_5.CHO + HCl$$

Aldehydes, in which the aldehyde group is linked to the cyclic radical by other groups, are made by distillation of a mixture of calcium formate and the calcium salt of the corresponding acid—a general method for both aliphatic and aromatic aldehydes:

$$C_6H_5.CH_2.CO.Oca + H.CO.Oca = C_6H_5.CH_2.CHO + CaCO_3$$

Properties.—The aromatic aldehydes are very like the aliphatic aldehydes in behavior, but differ from these in some respects. They form no addition products with ammonia, though they unite with acid sodium sulphite and hydrocyanic acid; they do not reduce Fehling's solution, though ammoniacal silver nitrate is reduced; and they do not polymerize in the manner characteristic of the aliphatic aldehydes, or form resins when treated with caustic alkalies. With ammonia, they form condensation products such as hydrobenzamine, $(C_6H_5.CH_3)N_2$, from benzaldehyde, resembling in this respect formaldehyde (p. 84); and again like formaldehyde, they are converted by concentrated alkalies into a mixture of the corresponding alcohol and the alkali salt of the corresponding acid:

$$\underset{\text{Benzaldehyde}}{2C_6H_5.CHO} + KOH = \underset{\text{Benzyl alcohol}}{C_6H_5.CH_2OH} + \underset{\text{Potassium benzoate}}{C_6H_5.CO.OK}$$

With chlorine the aromatic aldehydes, unlike the aliphatic aldehydes, yield the corresponding acid chlorides (*cf.* p. 358); but like the aliphatic aldehydes they form hydrazones with phenylhydrazine (*cf.* p. 80).

Although the aldehyde group is, in general, readily oxidized to the carboxyl group, aromatic aldehydes can be successfully nitrated without such oxidation by working at temperatures below 0°.

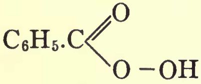
Aromatic aldehydes form condensation products with many varieties of aliphatic and aromatic compounds, the combination taking place with the loss of the elements of water, thus:

$$C_6H_5.CHO + 2C_6H_5.CH_3 = C_6H_5.CH(C_6H_4.CH_3)_2 + H_2O$$

$$C_6H_5.CHO + CH_3.CO.ONa = C_6H_5.CH:CH.CO.ONa + H_2O$$

Benzaldehyde, $C_6H_5.CHO$, is one of the products of the hydrolysis of *amygdaline*, a glucoside which is present in bitter almonds and the kernels of other fruits, hydrocyanic acid and glucose being formed at the same time. Some of the many methods proposed for its commercial preparation have been described above.[1] It is commonly called "oil of bitter almonds," and is used for flavoring, and for making dyes.

Benzaldehyde is a colorless oil which boils at 179° and is slightly heavier than water. It is very easily oxidized to benzoic acid, the change taking place slowly in contact with air. In the atmospheric oxidation of benzaldehyde it has been found that an intermediate product, benzoyl-hydrogen peroxide,



$$C_6H_5.C\begin{matrix}\diagup O \\ \diagdown O-OH\end{matrix}$$

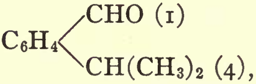
is formed. This is an active oxidizing agent, and in oxidizing other substances, *e.g.* unchanged benzaldehyde, is itself reduced to benzoic acid. This conversion of half of the absorbed oxygen to the "active" state is observed in the atmospheric oxidation of various other substances (*e.g.* turpentine).

---

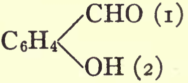
[1] For an account of the various methods by which benzaldehyde can be made see Thorpe's Dictionary of Applied Chemistry.

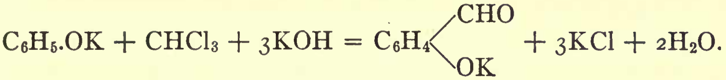
When chlorine is led into benzaldehyde it converts it into benzoyl chloride, $C_6H_5.CO.Cl$. Derivatives which contain a halogen atom in the benzene ring are made from the corresponding derivatives of benzalchloride (*cf.* p. 288). Sulphuric and nitric acids act on benzaldehyde with the formation of the meta sulphonic acid and meta nitrobenzaldehyde.

The only other aromatic aldehydes of special interest are the following:

Cuminic Aldehyde,  $C_6H_4\left<\begin{matrix}CHO\ (1)\\ CH(CH_3)_2\ (4)\end{matrix}\right.$, p-isopropyl benzaldehyde, occurs in caraway oil and other essential oils. Its constitution is proved by its oxidation to terephthalic acid (p. 368). It can be obtained from the essential oils which contain it by taking advantage of the small solubility of the addition product it forms with acid sodium sulphite, and then distilling this product with a solution of sodium carbonate. This is a general method for isolating naturally occurring aldehydes.

Cinnamic Aldehyde, $C_6H_5.CH:CH.CHO$, is found in oil of cinnamon, oil of cassia, and other oils, and can be isolated by the method just described. It is formed by the oxidation of cinnamyl alcohol (p. 340), and can be prepared by condensing benzaldehyde and acetaldehyde (p. 82), a reaction which takes place in the presence of a dilute solution of sodium hydroxide. Cinnamic aldehyde is an oil of aromatic odor which is volatile with steam, but cannot be distilled alone at ordinary pressures without decomposition.

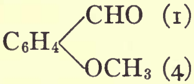
Salicylic Aldehyde,  $C_6H_4\left<\begin{matrix}CHO\ (1)\\ OH\ (2)\end{matrix}\right.$, occurs in the volatile oils from varieties of spiræa, and can be obtained by the oxidation of salicin (a glucoside found in willow bark) or salicyl alcohol. It is prepared by the action of chloroform on phenol when this is dissolved in an excess of potassium hydroxide:



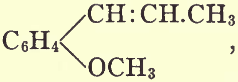
$$C_6H_5.OK + CHCl_3 + 3KOH = C_6H_4\left\langle\begin{matrix}CHO\\OK\end{matrix}\right. + 3KCl + 2H_2O.$$

This reaction, which is known as the Reimer-Tiemann reaction, serves to introduce the aldehyde group into phenol in the ortho and para positions. Probably an intermediate product containing the group $-CHCl_2$ is first formed, which is then converted into the aldehyde group, as in the making of benzaldehyde (p. 343). Salicylic aldehyde is a pleasant smelling liquid which boils at 196.5°. It gives an intense violet with ferric chloride, and has the general properties of a phenol and an aldehyde, but does not reduce Fehling's solution.

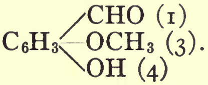
Anisaldehyde is the methyl ether of p-hydroxybenzaldehyde,



$$C_6H_4\left\langle\begin{matrix}CHO\ (1)\\OCH_3\ (4)\end{matrix}\right.$$

It is prepared by oxidation of *anethol*,  $C_6H_4\left\langle\begin{matrix}CH:CH.CH_3\\OCH_3\end{matrix}\right.$, which is the chief constituent of oil of aniseed. Anisaldehyde has an agreeable aromatic odor and is used in perfumery. It is an oil which boils at 245°.

Vanillin is the principal substance in the much-used extract of vanilla which is extracted from vanilla beans by alcohol. Its formula is



$$C_6H_3\left\langle\begin{matrix}CHO\ (1)\\OCH_3\ (3).\\OH\ (4)\end{matrix}\right.$$

It may be made from guaiacol (p. 342) by the Reimer-Tiemann reaction, and is prepared commercially chiefly from eugenol (p. 342) by oxidation. Vanillin, thus prepared, has largely supplanted the natural extract.

Vanillin forms white crystals which melt at 81°, and is sparingly soluble in cold water. It has a strong vanilla-like odor and taste. Its solutions have an acid reaction and are colored blue by ferric chloride. If the solution containing ferric chloride is heated, a characteristic white crystalline precipitate is formed.

Aromatic Ketones

The compounds of this class may be divided into two groups: Those in which the ketone group—carbonyl—unites an aryl and an aliphatic radical, and those in which two aryl radicals are thus linked.

Ketones of both groups can be obtained by the general method for making aliphatic ketones—the distillation of the calcium salts of the corresponding acids; or more advantageously, from the aromatic hydrocarbon and the appropriate acid chloride by the Friedel and Crafts method (p. 274).

Acetophenone, $C_6H_5.CO.CH_3$, the simplest of the mixed aryl-aliphatic ketones, will serve as an illustration of this group. It is best prepared by the condensation of benzene and acetyl chloride by the Friedel and Crafts reaction:

$$CH_3.CO.Cl + C_6H_6 \xrightarrow{AlCl_3} CH_3.CO.C_6H_5 + HCl$$

Acetophenone melts at 20.5° and boils at 202°. It is used as medicine under the name of "hypnone," as a hypnotic.

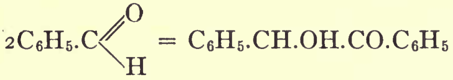
Its general chemical behavior is like that of the aliphatic ketones, but it does not unite with acid sodium sulphite. By reduction with sodium amalgam, it yields, in part, methylphenyl carbinol $CH_3.CHOH.C_6H_5$, a secondary alcohol. When oxidized with alkaline permanganate it is converted into a ketone-acid, phenylglyoxylic acid, $C_6H_5.CO.CO.OH$, and then into benzoic acid, $C_6H_5.CO.OH$.

Chlorine under all conditions (temperature, light, chlorine carriers) acts almost entirely on the methyl group with replacement of its hydrogen, and not on the phenyl radical.

Benzophenone, $C_6H_5.CO.C_6H_5$, the first of the diaryl ketones, can be made by heating calcium benzoate, $(C_6H_5.CO.O)_2Ca$; or from benzene and benzoyl chloride, $C_6H_5.CO.Cl$ by the Friedel and Crafts reaction. It melts at 48° and boils at 306°. Under certain conditions benzophenone is obtained in an unstable form which melts at 27°. This variety slowly changes to the other on standing, and in contact with a trace of the stable form the change takes place rapidly with evolution of heat. This appears to be a case of allotropy due to molecular arrangement, as with phosphorus and sulphur.

Benzophenone is reduced by sodium amalgam to *diphenylcarbinol*, $(C_6H_5)_2CH.OH$, or by zinc and sulphuric acid to a *pinacone*, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, and by hydriodic acid to *diphenylmethane*, $(C_6H_5)_2CH_2$.

Benzoïn, $C_6H_5.CH.OH.CO.C_6H_5$, is a ketone-alcohol, formed by the union of two molecules of benzaldehyde, which occurs with molecular rearrangement when the aldehyde is heated in dilute alcoholic solution with potassium cyanide:



$$2C_6H_5.C\begin{matrix} \nearrow O \\ \searrow H \end{matrix} = C_6H_5.CH.OH.CO.C_6H_5$$

Benzaldehyde Benzoïn

Benzoïn melts at 137°. In virtue of the group, CHOH.CO, which it contains, it is, like certain ketoses (p. 199) which contain the same group, easily oxidized by Fehling's solution even in the cold, and forms a hydrazone and an osazone with phenylhydrazine.

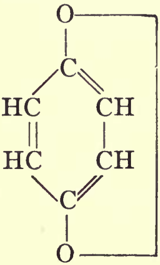
It is oxidized by nitric acid to benzil (diphenyldiketone), $C_6H_5.CO.CO.C_6H_5$ (melting point 95°), and can be reduced by suitable agents to desoxybenzoïn (phenylbenzylketone), $C_6H_5.CH_2.CO.C_6H_5$, hydrobenzoïn, $C_6H_5.CH.OH.CH.OH.C_6H_5$, or dibenzyl $C_6H_5.CH_2.CH_2.C_6H_5$.

Quinones

A considerable number of para derivatives, such as diamines, dihydroxyl compounds (hydrochinones), aminosulphonic acids, phenolsulphonic acids, aminophenols, when oxidized with chromic acid or certain other acid oxidizing agents, are converted into well-crystallizing compounds of an intense yellow color, and a pungent, characteristic odor. These substances, which are called quinones, withstand the action of acid oxidizing agents as is evident from the manner of their formation, but are readily reduced with the production of hydrochinones.

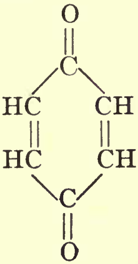
Benzoquinone, usually called simply **quinone,** $C_6H_4O_2$, is the simplest representative of the quinones. It was discovered in 1838 as the oxidation product of quinic acid, a by-product obtained in the extraction of quinine and allied alkaloids from cinchona bark.

Structure.—Quinone is a para derivative of benzene, as its formation from many para compounds and its relation to quinol (hydrochinone) indicates. It behaves like a diketone in forming both a monoxime and a dioxime with hydroxylamine; but on reduction, the carbonyl groups are converted into $\equiv$ C.OH group (quinol) instead of $=$ CH.OH groups as in the case of ordinary ketones. Further, by phosphorus pentachloride, quinone, $C_6H_4O_2$, is changed into $C_6H_4Cl_2$, one chlorine atom taking the place of each oxygen atom, instead of a replacement with two chlorine atoms, as in ketones. Two structures are suggested by these reactions which in the Kekulé formulation are:



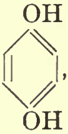
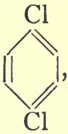
1.

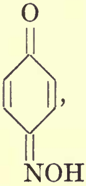
and



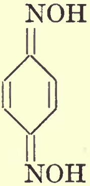
2.

The first formula shows the usual benzene ring with two linking atoms of oxygen replacing two hydrogen atoms. In the second, two carbonyl groups appear, and the valence requirements are met by the omission of one of the double linkages, and the shifting of a second one.

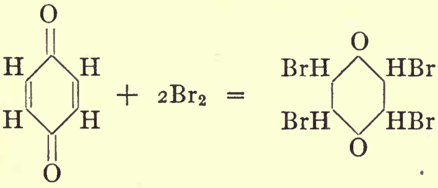
The first formula explains in a simple manner the reduction to quinol , and the formation of para-dichlorbenzene,  by the action of phosphorus pentachloride; while the second formula requires rearrangement of valencies in the benzene ring. On the other hand the formulas for the oximes,



and

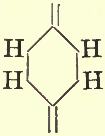


are derived naturally from the second formula. Further, in a chloroform solution of quinone, two or four atoms of bromine may be added, forming $C_6H_4Br_2O_2$, and $C_6H_4Br_4O_2$. This is a reaction characteristic of an unsaturated compound, and is explained by assuming that the two double bonds between carbon atoms in the second formula are like the double bond in ethylene, and are easily resolved into single bonds:

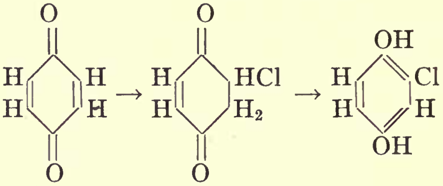


These and other considerations have led to the adoption of the diketone formula—the second one—for the quinones.

Quinone is usually prepared by oxidizing aniline with potassium dichromate and sulphuric acid, and extracting with ether. It is purified by distillation with steam. The golden-yellow crystals melt at 116°, and are quite soluble in hot water.

The "quinoid configuration,"  ,is a "chromophore" group, since all of the quinones and their derivatives are colored compounds. The most important dyes containing this group are, however, derivatives of aromatic hydrocarbons with two or more "condensed" benzene rings, such as naphthalene and anthracene, and among them are both natural and artificial dyes.

Quinone is easily converted into quinol by sulphurous acid and other reducing agents. Hydrogen chloride and hydrogen bromide effect a peculiar reaction, changing quinone into chlor or bromquinol, $C_6H_3Br(OH)_2$. The steps in this reaction and the rearrangements involved are probably,



Tetrachlorquinone or *chloranil*, $C_6Cl_4O_2$, is produced by the chlorination of quinone, but is usually prepared by the simultaneous oxidation and chlorination (potassium dichromate or chlorate and hydrochloric acid) of many aromatic substances. It is a yellow substance which melts at 290°, and is insoluble in water. It is readily reduced to tetrachlorquinol, $C_6Cl_4(OH)_2$, and is hence a strong oxidizing agent, and employed as such in the production of certain dyes.

CHAPTER XXVII

AROMATIC ACIDS

The carboxyl group which is characteristic of all organic acids cannot be developed on an atom of nucleus carbon, and hence, as in the case of the aldehydes, the aromatic acids are compounds in which the carboxyl group is united directly or by linking groups to the aryl radical. Of these two classes of acids, those with directly united carboxyl groups are much the more important.

Many of the aromatic acids occur in nature in the free condition, or as esters, in resins, balsams, and essential oils. The acids are solid crystalline substances, which are generally somewhat soluble in hot water, but almost insoluble at ordinary temperatures. Many of them are volatile with steam, and those of smaller molecular weight can be distilled without decomposition. In solution they are ionized to some extent and usually redden litmus. They decompose carbonates, and are, in general, "stronger" than the aliphatic acids.

Preparation.—1. Both classes of aromatic acids can be made by the methods employed for the formation of aliphatic acids: oxidation of alcohols, or hydrolysis of nitriles or esters.

2. A more important method for the preparation of many acids with carboxyl united to the nucleus is by oxidation of the hydrocarbons with side chains. All side chains can be oxidized to carboxyl groups. When side chains of different lengths are present the longer is usually oxidized first, and it is possible to control the oxidation so that one or more carboxyl groups shall be formed.

3. A useful method is by the oxidation of aryl-alkyl ketones

(p. 348), which are readily formed from the aromatic hydrocarbons and acyl chlorides by the Friedel-Crafts reaction. Thus from mesitylene and acetyl chloride, acetomesitylene, $(CH_3)_3C_6H_2.CO.CH_3$, is made, and then oxidized to the corresponding acid, $(CH_3)_3C_6H_2.CO.OH$.

4. The carboxyl group can be introduced into the hydrocarbon in place of hydrogen by the action of carbonyl chloride in the presence of aluminium chloride (Friedel-Crafts) and hydrolysis of the resulting chloride; or, with better results, by carbonyl chloramide (p. 233), followed by hydrolysis:

$$CH_3.C_6H_5 + Cl.CO.NH_2 \xrightarrow{AlCl_3} CH_3C_6H_4.CO.NH_2 + HCl$$

5. The aromatic acids can also be prepared by the Grignard reaction (p. 37). The immediate product of the reaction, *e.g.*, $C_6H_5.MgBr$, absorbs carbon dioxide giving $C_6H_5.CO.OMgBr$, and this on treatment with hydrochloric acid yields the aromatic acid, $C_6H_5.CO.OH$, and MgBrCl. The yield is nearly that indicated by the equation.

6. Halogen can be replaced by carboxyl by the action of carbon dioxide in the presence of sodium:

$$C_6H_5Br + CO_2 + 2Na = C_6H_5.CO.ONa + NaBr$$

Acids which have the carboxyl group in a side chain may be prepared by the acetoacetic ester synthesis (p. 174).

Reactions.—Salts are of course formed by the action of the acids on hydroxides or carbonates. The alkali salts are readily soluble in water, and the acids are precipitated from them by inorganic acids. The silver salts are frequently employed in determining the molecular weight of the acid, since on ignition the silver is left in a pure state.

The formation of esters, acid chlorides, amides and anilides, and the replacement of the carboxyl group by hydrogen, are accomplished by reactions similar to those employed with the aliphatic acids (p. 99).

Chlorine or bromine, or the sulphonic acid or nitro group can be introduced into the aryl radical of acids directly, and these negative substituents enter chiefly the meta position with reference to the carboxyl group. Other derivatives may be made by the usual methods.

An unusual reaction is that which produces hydrogen addition products of the acids. In alkaline solution into which carbon dioxide is led, sodium amalgam converts benzoic acid into *tetrahydrobenzoic acid*, $C_6H_9.CO.OH$, and in boiling amyl alcohol, benzoic acid is reduced to *hexahydrobenzoic acid*, $C_6H_{11}.CO.OH$. Such additions of hydrogen take place more easily as the number of carboxyl groups is larger. These hydroaromatic compounds are discussed in Chapter XXVIII.

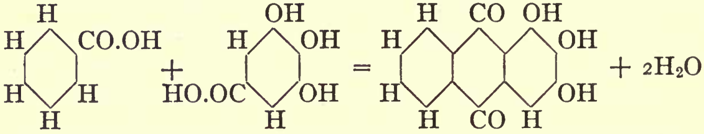
Benzoic acid, $C_6H_5.CO.OH$ (phenylformic acid), has been known since the beginning of the seventeenth century, having been originally obtained as a sublimate from gum benzoïn. It is present in gum benzoïn chiefly in the form of esters, and is also found in other plant products, such as balsams of Peru and Tolu, and in cranberries. A derivative of benzoic acid, the hippuric acid (p. 359), is present in the urine of herbivora.

While it may be made by any of the methods which have been given, it is usually prepared for pharmaceutical purposes by sublimation from gum benzoïn; and manufactured on a large scale from toluene by converting this hydrocarbon into benzyl chloride, $C_6H_5.CH_2Cl$, and then oxidizing the latter with nitric acid. The direct oxidation of toluene gives the acid, but in such small amounts that its preparation through the chlorine derivative is more advantageous.

Benzoic acid is also made from benzotrichloride, $C_6H_5.CCl_3$, which is a by-product in the production of benzaldehyde, by heating this with milk of lime:

$$2C_6H_5.CCl_3 + 3Ca(OH)_2 = 2C_6H_5.CO.OH + 3CaCl_2 + 2H_2O$$

Benzoic acid is nearly odorless when perfectly pure, but that made from gum benzoïn has a slight odor of the aromatic gum. It sublimes readily and its vapors are very irritating to the nose and throat. Benzoic acid is used in medicine, in the preparation of dyes, aniline blue and *anthragallol*. The latter is an anthracene derivative formed from benzoic and gallic acids by elimination of water:



Benzoic acid Gallic acid Anthragallol

Sodium benzoate is well known as a food preservative.

AROMATIC ACIDS

Name	Formula	Melting point
Benzoic	$C_6H_5.CO.OH$	121.4°
o-Toluic	$C_6H_4\left\langle\begin{matrix}CH_3 & (1)\\ CO.OH & (2)\end{matrix}\right.$	104°
m-Toluic	$C_6H_4\left\langle\begin{matrix}CH_3 & (1)\\ CO.OH & (3)\end{matrix}\right.$	109°
p-Toluic	$C_6H_4\left\langle\begin{matrix}CH_3 & (1)\\ CO.OH & (4)\end{matrix}\right.$	180°
Cuminic	$C_6H_4\left\langle\begin{matrix}CH(CH_3)_2 & (1)\\ CO.OH & (4)\end{matrix}\right.$	116°
Phenylacetic	$C_6H_5.CH_2.CO.OH$	76°
Cinnamic	$C_6H_5.CH:CH.CO.OH$	133°
o-Phthalic	$C_6H_4(CO.OH)_2$ (1, 2)	231
m-(Iso)Phthalic	$C_6H_4(CO.OH)_2$ (1, 3)	330°+
p-(Tere)Phthalic	$C_6H_4(CO.OH)_2$ (1, 4)	sublimes
Trimellitic	$C_6H_3(CO.OH)_3$ (1, 2, 4)	228°
Pyromellitic	$C_6H_2(CO.OH)_4$ (1, 2, 4, 5)	265°
Benzenepentacarboxylic	$C_6H(CO.OH)_5$	....
Mellitic	$C_6(CO.OH)_6$	287°

Toluic acids, $CH_3.C_6H_4.CO.OH$. The three isomeric acids of this formula can be made by partial oxidation of the three xylenes with nitric acid, or from the toluidines by conversion into nitriles by the diazo reaction and subsequent hydrolysis. Paratoluic acid is also readily prepared from cymene $CH_3.C_6H_4.C_3H_7$, by oxidation of the isopropyl group. These acids present no especial points of interest, nor is it necessary to discuss further the homologues of benzoic acid.

Phenylacetic acid, $C_6H_5.CH_2.CO.OH$, which is isomeric with the toluic acids, is best obtained by the hydrolysis of benzylcyanide, $C_6H_5.CH_2.CN$, its nitrile, which is made by the reaction of benzylchloride, $C_6H_5.CH_2Cl$, with potassium cyanide. It is a slightly weaker acid (less ionized) than benzoic acid, though stronger than acetic acid; and illustrates the general fact that with wider separation of the phenyl and carboxyl groups by intermediate hydro-carbon groups the acids become weaker.

Phenylacetic acid can yield, of course, two classes of derivatives, according as substitution takes place in the nucleus or in the side chain. On oxidation it gives benzoic acid, while the toluic acids give dibasic phthalic acids.

Cinnamic acid, $C_6H_5.CH{:}CH.CO.OH$, β-phenylacrylic acid, is a type of the unsaturated aromatic acids and the most important of the group. It occurs free, and in esters of various aromatic alcohols, in many gums and balsams, and in the leaves of certain plants. It has been known for a long time, and was formerly confused with benzoic acid.

It is prepared from storax, or is synthesized by Perkin's reaction. This reaction, which is the most important method for making many unsaturated aromatic acids (and also applicable to the formation of unsaturated aliphatic acids), consists in the condensation of an aromatic aldehyde and a salt of an aliphatic acid, which occurs in the presence of acetic anhydride:

$$C_6H_5.CHO + CH_3.CO.ONa = C_6H_5.CH{:}CH.CO.ONa + H_2O$$

(Benzalchloride may be used here in place of benzaldehyde.)

When slowly distilled, or more readily when heated with lime, cinnamic acid gives *styrene*, $C_6H_5.CH:CH_2$, and carbon dioxide (calcium carbonate).

When cinnamic acid is oxidized, the double bond becomes the point of attack; a mild oxidation ($KMnO_4$) yielding phenylglyceric acid, $C_6H_5.CHOH.CHOH.COOH$, and a stronger oxidation (HNO_3) giving benzaldehyde and benzoic acid.

As an unsaturated compound it unites with halogens to form dihalogen derivatives, *e.g.*, $C_6H_5.CHCl.CHCl.CO.OH$; and by reduction with sodium amalgam it gives *hydrocinnamic acid*, or *phenylpropionic acid*, $C_6H_5.CH_2.CH_2.CO.OH$.

By the usual reactions for producing unsaturation (p. 45) cinnamic acid may be converted into *phenylpropiolic acid*, $C_6H_5\text{-}C \equiv C.CO.OH$, and from this, *phenylacetylene*, $C_6H_5.C \equiv CH$, can be prepared (p. 279).

Derivatives of the Monobasic Acids

Benzoyl Chloride, $C_6H_5.CO.Cl$, is formed like other acyl chlorides by the action of phosphorus pentachloride on benzoic acid or its sodium salt; but it is usually prepared in quantity by treating benzaldehyde with chlorine (p. 346), a reaction that differs from that of chlorine with aliphatic aldehydes (*cf.* p. 80).

Benzoyl chloride is a liquid of disagreeable, tear-compelling odor that boils at 198°. It is insoluble in water but is slowly decomposed by it with the formation of benzoic and hydrochloric acids (*cf.* p. 115). It reacts with practically all alcohols and phenols, primary or secondary amines, with the formation of benzoyl compounds which are useful in the identification and characterization of these substances. These reactions are greatly facilitated by the presence of an alkali (Schotten-Baumann reaction):

$$C_6H_5.CO.Cl + C_2H_5OH + NaOH = C_6H_5CO.OC_2H_5 + NaCl + H_2O$$

$$C_6H_5.CO.Cl + C_6H_5NH_2 + NaOH = C_6H_5.CO.NHC_6H_5 + NaCl + H_2O$$

Benzamide, $C_6H_5.CO.NH_2$, is readily prepared by bringing together benzoyl chloride and ammonia or ammonium carbonate. It crystallizes from hot water in glistening plates that melt at 128°. One hydrogen atom of the amido group is replaceable by metals (*cf.* p. 140), and the metal may in turn be replaced by alkyl radicals by the action of alkyl halides. Like the aliphatic amides benzamide appears to exist in two forms (*cf.* p. 141).

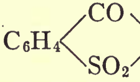
Benzonitrile, $C_6H_5.CN$, can be formed by the withdrawal of water from benzamide, (P_2O_5), but is best prepared from anilin by the Sandmeyer reaction (p. 316). It is a liquid with the odor of bitter almonds and boils at 191°. It has all the properties of the aliphatic nitriles (p. 153).

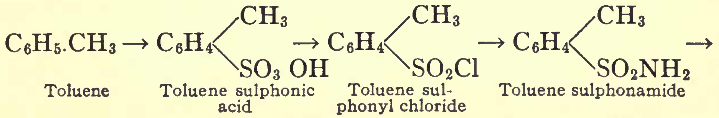
Hippuric Acid, $C_6H_5.CO.NH.CH_2.CO.OH$, which occurs in the urine of herbivora, is *benzoylglycine*, and can be made by shaking a mixture of benzoylchloride and aminoacetic acid (glycine) with sodium hydroxide:

$$\underset{\text{Benzoyl chloride}}{C_6H_5.CO.Cl} + \underset{\text{Glycine}}{NH_2CH_2.CO.OH} =$$

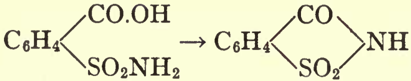
$$\underset{\text{Hippuric acid}}{C_6H_5.CO.NH.CH_2.CO.OH} + HCl$$

Benzoic acid was formerly obtained to some extent from the natural hippuric acid, which was discovered in 1776 in the urine of cows and camels. Hippuric and benzoic acids were not clearly distinguished until 1829 (Liebig).

Saccharin,  $C_6H_4\left\langle {CO \atop SO_2} \right\rangle NH$ (1, 2), is o-sulphobenzoic-acid-imide and a derivative of the ortho sulphonic acid of benzoic acid. Since the chief product of the sulphonation of benzoic acid is the meta compound, the starting point for the preparation of saccharin is toluene. The steps are:



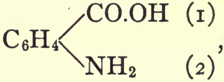
$$\underset{\text{Toluene}}{C_6H_5.CH_3} \rightarrow \underset{\text{Toluene sulphonic acid}}{C_6H_4\left\langle {CH_3 \atop SO_3\,OH} \right.} \rightarrow \underset{\text{Toluene sulphonyl chloride}}{C_6H_4\left\langle {CH_3 \atop SO_2Cl} \right.} \rightarrow \underset{\text{Toluene sulphonamide}}{C_6H_4\left\langle {CH_3 \atop SO_2NH_2} \right.} \rightarrow$$



Toluic acid sulphonamide   Saccharin

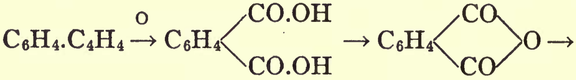
In the sulphonation of toluene, both ortho and para sulphonic acids are produced. These are converted into the acid chlorides, and as the para chloride is a solid and the ortho a liquid, they may be largely separated. The ortho compound is then converted into the amide by ammonia and the amide oxidized by potassium permanganate in neutral solution. On adding hydrochloric acid to the solution, saccharin is obtained. It was discovered in 1879 by Fahlberg and Remsen.

It is a colorless, crystalline substance, which melts with some decomposition at 224°. It is only slightly soluble in water. Its most striking property is its intensely sweet taste, which is said to be more than 500 times that of cane sugar. On this account it is manufactured and used for sweetening purposes, and as a substitute for sugar by sufferers from diabetes.

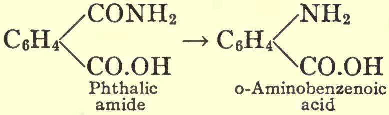


Anthranilic Acid, $C_6H_4\left\langle\begin{matrix}CO.OH & (1)\\ NH_2 & (2)\end{matrix}\right.$, *o-aminobenzoic acid,* is of especial interest on account of its relation to indigo and its use in the artificial preparation of this dye. It was first obtained from indigo (anil) by boiling this substance with potassium hydroxide.

The three aminobenzoic acids can be made by reduction of the corresponding nitro compounds; but the o-nitrobenzoic acid is a minor product of direct nitration of benzoic acid. Anthranilic acid is prepared for making indigo from naphthalene by the series of reactions shown by the following formulas:



Naphthalene   o-Phthalic acid   Phthalic anhydride



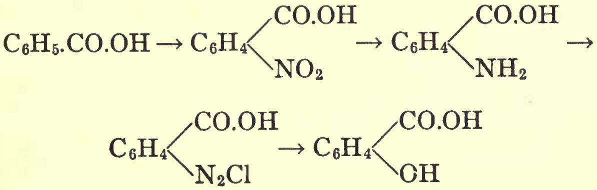
$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CONH_2}\\\mathrm{CO.OH}\end{matrix} \rightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{CO.OH}\end{matrix}$$

The last reaction is accomplished by bleaching powder and is Hofmann's reaction for the formation of amines (*cf.* p. 129).

Anthranilic acid melts at 145° and decomposes, on distillation, into aniline and carbon dioxide. By reaction with chloracetic acid, and fusion of the product with sodium hydroxide, *indoxyl* is produced, which in dilute solution is oxidized to indigo by the air (p. 400).

Hydroxy Acids

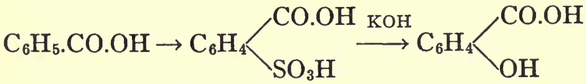
Hydroxy or phenol acids can be made by the introduction of hydroxyl groups into acids: 1. through nitro derivatives by reduction of the nitro to the amino groups followed by the diazo reaction:



$$\mathrm{C_6H_5.CO.OH} \rightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{NO_2}\end{matrix} \rightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{NH_2}\end{matrix} \rightarrow$$

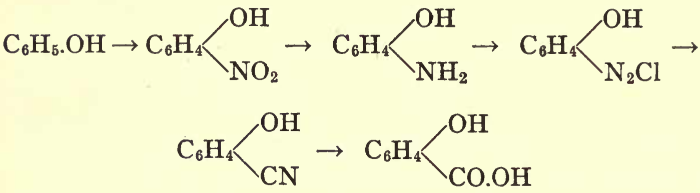
$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{N_2Cl}\end{matrix} \rightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{OH}\end{matrix}$$

2. or through the sulphonic acids by fusion with potassium hydroxide:



$$\mathrm{C_6H_5.CO.OH} \rightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{SO_3H}\end{matrix} \xrightarrow{\mathrm{KOH}} \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO.OH}\\\mathrm{OH}\end{matrix}$$

3. The carboxyl group can be introduced into phenols by way of the nitro derivatives. The nitro group is reduced to the amino group, the cyanogen group is substituted for this by Sandmeyer's reaction (p. 316), and the resulting nitrile is finally converted into the carboxyl group by hydrolysis:

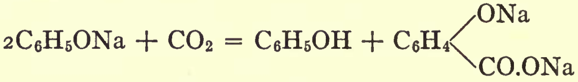


$$C_6H_5.OH \rightarrow C_6H_4\Big\langle\begin{array}{l}OH\\NO_2\end{array} \rightarrow C_6H_4\Big\langle\begin{array}{l}OH\\NH_2\end{array} \rightarrow C_6H_4\Big\langle\begin{array}{l}OH\\N_2Cl\end{array} \rightarrow$$

$$C_6H_4\Big\langle\begin{array}{l}OH\\CN\end{array} \rightarrow C_6H_4\Big\langle\begin{array}{l}OH\\CO.OH\end{array}$$

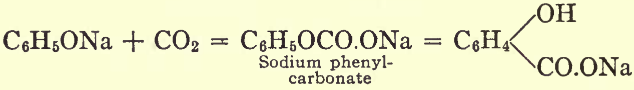
4. Homologues of phenol are converted into phenol acids by the oxidation of the side chains. The reaction is particularly successful when the phenols are first changed into their sulphuric acid or phosphoric acid esters.

5. An important method for making hydroxy acids is by Kolbe's synthesis. As originally carried out, an alkali phenolate is heated in a current of carbon dioxide with the result that half distils as phenol, and the rest is converted into the basic salt of the hydroxy acid:



$$2C_6H_5ONa + CO_2 = C_6H_5OH + C_6H_4\Big\langle\begin{array}{l}ONa\\CO.ONa\end{array}$$

But if the alkali phenolate is heated with carbon dioxide under pressure, it is completely transformed into the normal salt by intramolecular change, a phenylcarbonate being formed as an intermediate step:



$$C_6H_5ONa + CO_2 = \underset{\text{Sodium phenyl-carbonate}}{C_6H_5OCO.ONa} = C_6H_4\Big\langle\begin{array}{l}OH\\CO.ONa\end{array}$$

It is an interesting fact that the *ortho* compound results when sodium phenolate is used, while potassium phenolate at temperatures from 170° to 210° yields the salt of the *para* hydroxy acid. The formation of the meta compound by this method has not been observed.

Properties.—The hydroxy acids are colorless, crystalline substances, more soluble in water (influence of hydroxyl groups) than the acids from which they are derived. The hydrogen of the hydroxyl, as well as that of the carboxyl, is replaced by an alkali metal when the hydroxy acid is treated with an alkali hydroxide, but these salts are changed to mono-metal salts of the hydroxy acids by carbon dioxide; and by alkali carbonates only the hydrogen of the carboxyl group is replaced. They are converted into phenols by heating with lime,—the general reaction for replacing the carboxyl group with hydrogen:

$$C_6H_4(OH).CO.OH + CaO = C_6H_5OH + CaCO_3$$

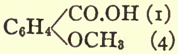
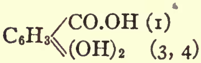
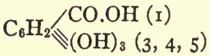
Effect of Position. The relative positions of the carboxyl and the hydroxyl groups have a striking influence on their activity as acids, as shown by the ionization constants (see also p. 408).

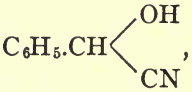
	$k \times 10^5$
Benzoic acid	6.6
o-Hydroxybenzoic acid	100.
m-Hydroxybenzoic acid	8.3
p-Hydroxybenzoic acid	2.8
2, 6-Dihydroxybenzoic acid	5000.

It is seen from these figures that the hydroxyl group in the meta position produces little effect, and in the para position decreases the acidity to less than one-half that of the simple acid. In the ortho position, however, the acidity is very greatly increased,—17 times by a single hydroxyl group, and 833 times when two stand in the ortho position to the carboxyl group. Similar influences are found in the case of other substitutes, and are most marked, as here, when they occupy the ortho position. Thus the constant for o-nitrobenzoic acid is 100 times that of benzoic acid, that for o-brombenzoic acid is 24 times, and that for o-methyl-benzoic acid (o-toluic) 2 times as large.

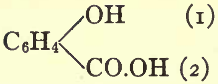
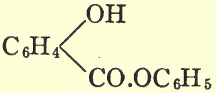
The ortho hydroxy acids differ from the meta and para compounds also, in that they alone give the violet coloration with ferric chloride which is characteristic of phenol, and are volatile with steam. Ortho and para hydroxy-acids are much more readily converted into phenols by heating alone or with concentrated hydrochloric acid than are the meta compounds, and the greater stability of the latter is indicated by other reactions.

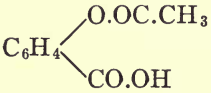
HYDROXY-ACIDS

Name	Formula	Melting point
Mandelic	$C_6H_5.CH.OH.CO.OH$	118°
Phenyl-lactic	$C_6H_5.CH_2.CH.OH.CO.OH$	98°
Salicylic acid	 $C_6H_4{<}\begin{matrix}CO.OH & (1)\\ OH & (2)\end{matrix}$	159°
Anisic	 $C_6H_4{<}\begin{matrix}CO.OH & (1)\\ OCH_3 & (4)\end{matrix}$	184°
Protocatechuic	 $C_6H_3{<}\begin{matrix}CO.OH & (1)\\ (OH)_2 & (3, 4)\end{matrix}$	199°
Gallic	 $C_6H_2{<}\begin{matrix}CO.OH & (1)\\ (OH)_3 & (3, 4, 5)\end{matrix}$	220°

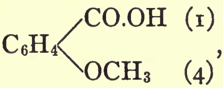
Mandelic acid, $C_6H_5.CH.OH.CO.OH$, *phenylglycollic acid*, is the simplest hydroxy-acid which has hydroxyl in a side chain. It was originally obtained from bitter almonds (German, *Bittermandel*). The amygdalin contained in the almonds breaks up, as we have seen, into benzaldehyde, hydrocyanic acid and glucose (p. 345). The mandelic acid is the result of the union of the aldehyde and acid, forming the cyanhydrin,  $C_6H_5.CH{<}\begin{matrix}OH\\ CN\end{matrix}$, followed by the hydrolysis of this substance, which is the nitrile of mandelic acid. It is usually prepared by this reaction, but starting with benzaldehyde already made. From the synthetic mandelic acid which is optically inactive, like all synthetic products, dextro and levo rotatory acids can be obtained by the methods employed in the case of other active compounds (p. 192).

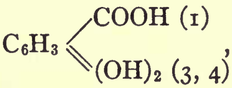
Mandelic acid resembles lactic acid—*methylglycollic acid*—in many respects, as might be expected from a comparison of their formulas.

Salicylic acid,  $C_6H_4\left\langle\begin{matrix}OH & (1)\\ CO.OH & (2)\end{matrix}\right.$, *o-oxybenzoic acid,* is the only important mono-hydroxybenzoic acid It occurs free in the buds of *spiræa ulmaria,* and in some other plants; and as methyl ester in oil of wintergreen and other ethereal oils. It was first obtained (1838) from salicylic aldehyde (p. 346) and was named from this. It was formerly prepared from oil of wintergreen, but is now made commercially from phenol by Kolbe's method (p. 362). It melts at 159° and on careful heating, sublimes without decomposition, but on sharp heating, partially decomposes into phenol and carbon dioxide. Heated for some time at 200°–220°, it is largely converted into *Salol,*  $C_6H_4\left\langle\begin{matrix}OH\\ CO.OC_6H_5\end{matrix}\right.$ its phenyl ester, a substance much used in medicine on account of its antiseptic properties. Salicylic acid itself is a powerful antiseptic, and as it has no odor, is often used in place of phenol as a disinfectant. It is also used as a preservative for foods, etc., and its salts and certain derivatives are employed in medicine. especially acetyl salicylic acid, known as "aspirin,"

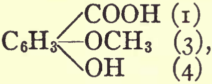
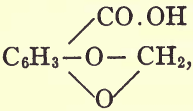


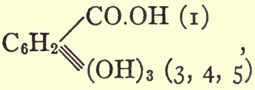
$$C_6H_4\left\langle\begin{matrix}O.OC.CH_3\\ CO.OH\end{matrix}\right.$$

Anisic acid,  $C_6H_4\left\langle\begin{matrix}CO.OH & (1)\\ OCH_3 & (4)\end{matrix}\right.$, *p-methoxybenzoic acid,* is obtained by oxidizing anethol (p-propenyl anisol) (p. 347), which is the chief constituent of anise oil. It has long been known, is readily obtained, and it and its derivatives have been much studied.

Protocatechuic acid,  $C_6H_3\left\langle\begin{matrix}COOH & (1)\\ (OH)_2 & (3,4)\end{matrix}\right.$, dioxybenzoic acid, is the most important of the six possible isomeric dihydroxy acids. It is obtained from many resins and some tannins, and other substances by fusion with potassium hydroxide. Protocatechuic acid belongs to a class of compounds which may be regarded as derivatives of catechol (p. 333) in which a third group stands in a position para to one hydroxyl, and meta to the other. Compounds with this grouping are found frequently in nature, as for instance, eugenol, safrol, and vanillin.

Protocatechuic acid solutions are colored bluish-green by ferric chloride, and the color changes to blue and finally to red on addition of dilute alkalies. It reduces ammoniacal silver nitrate, but does not reduce Fehling's solution.

The m-methyl ether of protocatechuic acid is vanillic acid,  $C_6H_3\left\langle\begin{matrix}COOH\ (1)\\ OCH_3\ \ (3)\\ OH\ \ \ \ (4)\end{matrix}\right.$, and can be obtained by oxidation of vanillin (p. 347) which is the corresponding aldehyde, and from other substances. The dimethyl ether is *veratric acid*, and the methylene ether,  $C_6H_3\left\langle\begin{matrix}CO.OH\\ -O-CH_2\\ O\end{matrix}\right.$, is *piperonylic acid*, both of which are obtained from vegetable substances.

Gallic acid,  $C_6H_2\left\langle\begin{matrix}CO.OH\ (1)\\ (OH)_3\ (3,4,5)\end{matrix}\right.$, is the only one of the trihydroxybenzoic acids which needs to be described. There are six possible acids of this formula, and three of them are known. Gallic acid occurs free in gall-nuts, tea, and in the astringent parts of the sumach and many other plants. It is readily obtained from tannins by boiling them with dilute acids, or by the action of moulds on their solutions. It crystallizes with one molecule of water in glistening needles, and loses its water at 120°. It has no definite melting point, decomposing at temperatures above 220° into pyrogallol (p. 335) and carbon dioxide. With ferric chloride its solutions give, according to the concentration, a bluish or greenish black color (or precipitate), and it reduces Fehling's solution and solutions of silver and gold salts.

It is employed in the preparation of pyrogallol, as a photographic developer, and in making certain dyes, such as "galloflavin" (by oxidation of its alkaline solutions in air), and of "anthracene brown."

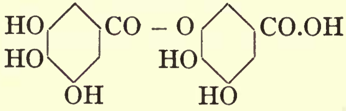
Tannic acids or **tannins,** are amorphous substances which occur widely distributed in the vegetable kingdom. The principal commercial sources are the bark of the oak and hemlock, sumach, gall-nuts, and a number of Indian and South American trees. Tannin is used for tanning leather, as a mordant in dyeing, in ink-making, and as the source of gallic acid and pyrogallol.

Some tannins yield gallic acid and glucose on hydrolysis and thus appear to be glucosides. These tannins give a blue black color with ferric chloride. Others are colored green by ferric chloride and give catechol when heated.

All tannins are astringent in taste, soluble in water and alcohol, and do not melt without decomposition. A characteristic property is that of forming insoluble compounds with gelatin or gelatin-forming tissues, and on this their use in leather-making depends.

Iron inks are usually made from ferrous sulphate and the tannin obtained from gall-nuts. In the older iron inks the nearly colorless solution was oxidized by the air with the formation of a finely divided and nearly black precipitate, which was held in suspension by the addition of gum. In the more modern iron inks the oxidation is prevented by the addition of acid, and the almost colorless solution is temporarily colored for writing, with a coal tar dye. The black color of the ink proper develops on the paper through atmospheric oxidation. Many inks are made of other materials and very commonly consist of solutions of coal tar dyes.

Gallotannic acid or **digallic acid,** occurs as a glucoside in gallnuts, forming about 70 per cent. of their weight. It is extracted by ether and alcohol. Its empirical formula is $C_{14}H_{10}O_9$, and its structure, as inferred from its synthetical formation from gallic acid by heating with phosphorus oxychloride is:



It is resolved into gallic acid by hydrolysis.

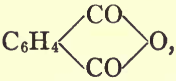
Polycarboxylic Acids

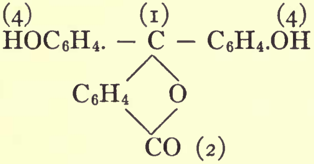
Aromatic acids with two, three, four, five, and six carboxyl groups are all known. Of these only those with two and six carboxyl groups are of particular interest.

Phthalic acids, $C_6H_4(CO.OH)_2$. Acids of this formula are the oxidation products of all benzene homologues with two side chains, and hence have been used as reference compounds in determinating the position of the side chains. Their name is derived from na*phthalene* from which the first one—the ortho acid—was obtained.

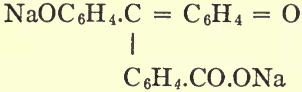
Orthophthalic acid, usually called simply *phthalic acid,* is the most important of the three isomers, being extensively manufactured for the preparation of phthaleïn dyes, and of anthranilic acid which serves as a step in making artificial indigo.

Its technical production is from naphthalene by oxidation with concentrated sulphuric acid and mercury sulphate at a temperature above 300°. o-Phthalic acid differs from its two isomers by its much greater solubility, and by the facts that it has no definite melting point, and gives, on heating, a crystalline sublimate of its anhydride. The meta acid—*isophthalic acid*—and the para acid —*terephthalic* acid—both sublime unchanged, the latter without melting. Another characteristic difference is shown by o-phthalic acid in the fluoresceïn reaction which its anhydride gives with resorcinol (p. 334). By chromic acid it is easily and completely oxidized; on heating with lime to 330°–350°, it yields benzoic acid; and benzene is formed when it is distilled with lime.

Phthalic anhydride,  sublimes from o-phthalic acid in beautiful long crystals. It melts at 128° and boils at 284.5°. When heated with phenol and concentrated sulphuric acid, phthalic anhydride gives *phenolphthaleïn.* This is only slightly soluble in water, but dissolves readily in alcohol. Its neutral or acid solutions are colorless, but in alkaline solutions it becomes intensely red. On this account and because it is sensitive even to weak acids, it is much employed as an indicator in titrating acids and bases. Its constitution appears to be:



In alkaline solution it is converted into a salt,



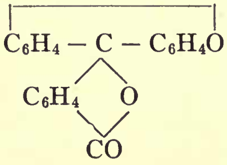
$$\mathrm{NaOC_6H_4.C = C_6H_4 = O} \quad | \quad \mathrm{C_6H_4.CO.ONa}$$

in which by molecular rearrangement a quinoid group,

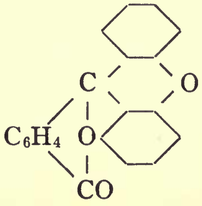
$$= C_6H_4 =$$

is present (*cf.* p. 352):

Fluoran is formed as a by-product in making phenolphthaleïn. Its structure is thus indicated,

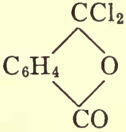
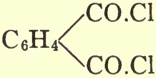
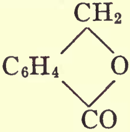


or



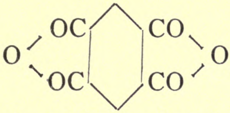
It is insoluble in alkalies.

Fluoresceïn is a dihydroxyl derivative of fluoran, formed by heating phthalic anhydride with resorcinol. Dilute alkaline solutions of it show a strong yellow green fluorescence, which is so intense that it can be recognized in the weakest solutions. A number of its halogen derivatives are useful dyes. Among them is **eosin** which is an alkali salt of tetrabromfluoresceïn. Its solutions are rose colored and show the same fluorescence as fluoresceïn. The corresponding iodine compound, *iodeosin*, is used as an indicator for acids and alkalies.

Phthalyl Chloride appears from its reactions to be  rather than the normal chloride . It is an oil which boils at 276°. Sodium amalgam and water change it to *phthalide*,  which is a lactone (p. 172).

Mellitic acid, $C_6(CO.OH)_6$, is found in the form of its hydrated aluminium salt in some lignite beds. This salt, which is called *honeystone* from its color, gives the name to the acid (*mel*, honey). The acid can be obtained from honeystone or made by oxidation of hexamethylbenzene, which can be synthesized from benzene or its methyl derivatives with methyl halide by the Friedel-Craft's reaction. It is also formed by the oxidation of carbon, in the form of graphite, by alkaline permanganate; from charcoal, by heating with sulphuric or nitric acid; and by the electrolytic oxidation of carbon anodes.

Mellitic acid is readily soluble in water and in alcohol, and crystallizes from solution in fine, silky crystals. It is quite stable, but on dry distillation yields *pyromellitic anhydride*,



, and like all acids has all its carboxyl groups replaced by hydrogen when distilled with lime. Through mellitic acid, therefore, the benzene ring can be built up from elementary carbon, and benzene itself obtained. Mellitic acid is readily converted by reducing agents in ammoniacal solution into hexahydromellitic acid, $C_6H_6.(CO.OH)_6$.

CHAPTER XXVIII

HYDROAROMATIC HYDROCARBONS AND THEIR DERIVATIVES

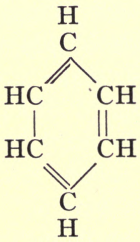
Terpenes and Camphors

When benzene vapor and hydrogen are passed over finely divided nickel at 180°–200°, *hexahydrobenzene,* C_6H_{12}, is obtained (Method of Sabatier and Sendersen). On treatment with bromine, this compound forms a substitution product, $C_6H_{11}Br$, and from this, *tetrahydrobenzene,* C_6H_{10}, is produced by digestion with alcoholic potassium hydroxide:

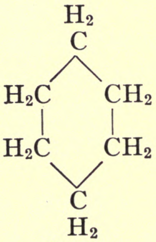
$$C_6H_{11}Br + KOH = C_6H_{10} + KBr + H_2O$$

Tetrahydrobenzene is an unsaturated compound and combines additively with bromine, yielding $C_6H_{10}Br_2$; and this dibromhexahydrobenzene, when treated with alcoholic potassium hydroxide gives *dihydrobenzene,* C_6H_8.

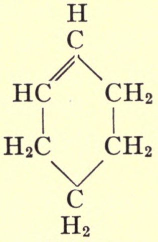
The structural relations of the three hydrobenzenes to benzene and to each other are represented by the following formulas,



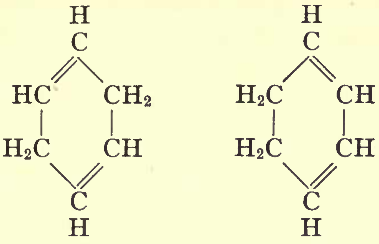
C_6H_6
Benzene



C_6H_{12}
Hexahydrobenzene



C_6H_{10}
Tetrahydrobenzene



C_6H_8 C_6H_8

Dihydrobenzene

As in the case of quinone (p. 350), the valence requirements in the hydrobenzene formulas are met by the change of one or more of the double linkages of the benzene ring to single bonds. Two formulas for dihydrobenzene are given, representing the two possible relative positions of the two double bonds. Two corresponding hydrocarbons are known.

It should be noticed that while hexahydrobenzene behaves as a saturated hydrocarbon, giving substitution products with halogens, the tetra and dihydrobenzenes are unsaturated, absorbing two and four atoms of chlorine and bromine respectively, and decolorizing permanganate. According to the formulas given above, the presence of one or two double linkages gives an unstable condition as in the olefines. In benzene, which, according to the Kekulé formula, has three double bonds, the condition is much more stable, though benzene does unite with chlorine in sunlight to form $C_6H_6Cl_6$, and with hydrogen to form C_6H_{12}, as we have just seen.

Other aromatic hydrocarbons are also hydrogenated to hexahydrobenzene derivatives by the method given for benzene; and a number of aromatic derivatives unite with hydrogen through the action of reducing agents. The reduction of benzoic acid to hexahydrobenzoic acid has been already given (p. 355), and the reduction of polycarboxylic acids is readily effected by sodium amalgam in aqueous solutions.

While the hydroaromatic compounds are thus related to the aromatic substances, and undoubtedly contain rings of six carbon atoms, they are also related to aliphatic compounds in their behavior, and by the fact that many of them can be made by synthesis from these compounds. From this point of view they are *cycloparaffins*—and hexahydrobenzene is also called *hexamethylene* or *cyclohexane* (*cf.* p. 258). A number of compounds belonging to this group occur naturally, and some of them are of considerable importance.

Properties.—Hexahydrobenzene and the homologous hydrocarbons are thin, volatile oils having an odor like that of "benzine." Toward chemical agents they act more like saturated paraffins than like aromatic hydrocarbons. Nitric and sulphuric acids leave them unchanged under conditions which lead to the formation of nitro and sulphonic-acid products with benzene and its homologues, and advantage is taken of this indifference in separating the hydroaromatic from the aromatic hydrocarbons. When boiled with strong nitric acid, however, cyclohexane is converted chiefly into normal adipic acid, $CO.OH.(CH_2)_4.CO.OH$, with rupture of the ring configuration; and homologues of cyclohexane containing methyl groups have been changed into nitro compounds of the corresponding aromatic hydrocarbons by the simultaneous oxidizing and nitrating action of nitric acid. With bromine in the presence of aluminium bromide, aromatic derivatives have been obtained, *e.g.*, tetrabromxylene, $C_6Br_4(CH_3)_2$, from dimethylcylohexane, $C_6H_{10}(CH_3)_2$. Chlorine substitution products are formed more readily than with the aromatic hydrocarbons.

Cyclohexane and **methylcyclohexane** are found in Russian petroleum. Cyclohexane has almost the same boiling point as benzene (80.2°). Both of the unsaturated hydrocarbons, dihydro- and tetrahydrobenzene, have been found in coal tar.

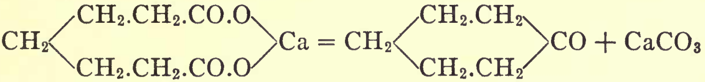
Of the hydroxyl derivatives of cyclohexane, **quercite,** $C_6H_7(OH)_5$ (*quercus,* oak) is found in acorns, and **inosite,** $(C_6H_6(OH)_6$

ἴς, ἰνός, muscle, is widely distributed in many leguminous plants), and in animal tissues. Both of these substances have a sweet taste and were formerly classed with the sugars. It will be noted that inosite has the same molecular formula as the hexoses.

Quercite is dextro-rotatory; inosite is optically inactive and cannot be resolved into active components. Methyl ethers of dextro and levo inosite are, however, found in certain plants, and from them the optically active inosites can be prepared.[1]

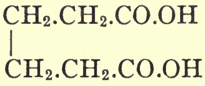
The constitution of these substances is shown by their reactions. They form penta and hexa acetyl compounds respectively with acetic anhydride, and the ring configuration is indicated by their transformation into benzene derivatives. Thus, by reduction with hydrogen iodide, they both yield phenol and benzene, and other products.

Ketocyclohexane or ketohexamethylene can be prepared from calcium pimelate by dry distillation:



Calcium pimelate Ketocyclomethylene

and this is oxidized by nitric acid to adipic acid,



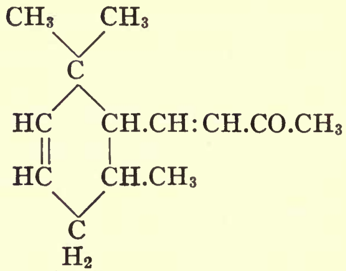
$$\begin{array}{l} CH_2.CH_2.CO.OH \\ | \\ CH_2.CH_2.CO.OH \end{array}$$

This is a good illustration of the relation of hydroaromatic compounds to aliphatic compounds.

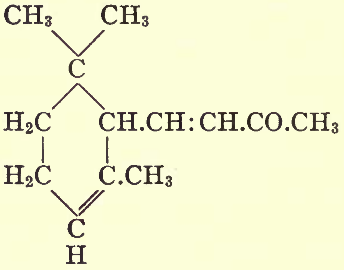
Irone, the odoriferous principle of violets, is a hydroaromatic ketone with the carbonyl group in a side chain. Its formula and that of the artificial oil of violets, **ionone,** which is made from geranial (citral) (p. 87), differ only in the position of the double bond in the ring:

---

[1] For the optical activity of inosite, see Stewart's "Stereo-Chemistry."



Irone



Ionone

The hydroaromatic acids resemble the saturated aliphatic acids having an equal number of carbon atoms. Thus, **hexahydrobenzoic acid,** $C_6H_{11}.CO.OH$, is like heptylic acid, $C_6H_{13}.CO.OH$ in its odor and other characteristics. It melts at 29°, boils at 235°, and is converted into benzoic acid by heating with anhydrous copper sulphate to 290°.

Quinic acid, $C_6H_7(OH)_4.CO.OH$, a tetrahydroxyl acid which is a derivative of cyclohexane, occurs in cinchona bark and in many other plants, and is obtained as a by-product in the manufacture of quinine. Its relation to the aromatic compounds is shown by the following facts: When melted with potassium hydroxide it gives protocatechuic acid (p. 364); hydrogen iodide reduces it to benzoic acid; on dry distillation, it yields phenol, quinol, benzoic acid and salicylic aldehyde. Quinic acid melts at 161.6° and its solutions are levo-rotatory.

Hydromellitic acid, $C_6H_6(CO.OH)_6$, is of interest as being the compound whose discovery led Baeyer to his fruitful investigations of the hydroaromatic compounds. It is formed by the reduction of an ammoniacal solution of mellitic acid with sodium amalgam.

The Terpenes

Terpenes are hydrocarbons which occur in many plants, and they are often the chief constituents of the essential oils obtained by distilling flowers, fruits, parts of plants, or exuded balsams and oleo-resins with steam (*cf.* p. 160). By fractional distillation of the oils a more or less complete separation of the hydrocarbons from other constituents can be effected; but as it is often difficult to separate the individual terpenes in this way, purification is sometimes accomplished by converting the terpenes into compounds which can be freed from impurities by crystallization, and from which the terpenes can then be recovered.

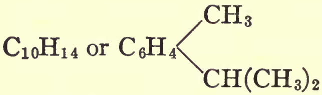
Pinene, $C_{10}H_{16}$, is much the most important of all the many terpenes from a practical point of view. It is the chief constituent of turpentine oil. Turpentine is an oleo-resin which exudes from many coniferous trees. It consists chiefly of a solution of resin (colophony) in pinene. On distillation with steam, turpentine oil comes over and the resin is left behind. This well-known oil, often called "turpentine," has a characteristic and pungent odor, which is pleasant when the oil is freshly distilled; but on exposure to the air the odor becomes unpleasant, and the oil gradually grows viscid and finally resinous from absorption of oxygen. Like some other substances which oxidize spontaneously (*cf.* p. 345) the turpentine oil under these conditions acquires strong oxidizing properties, and its value in paints and varnishes depends largely on its behavior as an oxygen-carrier to the drying oils which are used. Besides its employment in painting, it is used as an excellent solvent for fats, resins, and caoutchouc. It also dissolves sulphur, phosphorus and iodine.

By fractional distillation of turpentine oil, pinene is obtained nearly pure. Pinene from French turpentine oil is levo-rotatory; from American and most other oils, dextro-rotatory. An optically inactive form can also be obtained from an addition product which is formed with nitrosyl chloride.

Pinene is an unsaturated hydrocarbon, and is shown by its addition products with chlorine or bromine to have one double linkage. It also absorbs dry hydrogen chloride with the production of pinene hydrochloride, $C_{10}H_{17}Cl$, which forms a white crystalline mass, melting at 131°, and is called "artificial camphor" as it resembles camphor in appearance and odor.

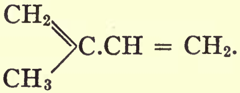
Pinene burns with a very smoky flame, and its energetic reaction with chlorine is shown by the common lecture experiment of bringing a strip of turpentine-soaked paper into this gas.

The evidence for the constitution of pinene and the other terpenes is much too intricate for discussion here. Most of the terpenes can be converted into cymene,



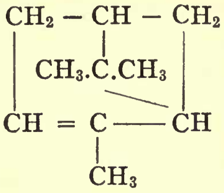
$$C_{10}H_{14} \text{ or } C_6H_4\begin{matrix} \diagup CH_3 \\ \diagdown CH(CH_3)_2 \end{matrix}$$

by withdrawal of two atoms of hydrogen through heating with sulphuric acid or iodine. These terpenes are therefore hydroaromatic compounds. Other terpenes are apparently open-chain compounds of the olefine series. Isoprene, C_5H_8 (p. 50), which is obtained as a distillation product from caoutchouc and some of the terpenes, is considered to be a "hemiterpene" of this kind with the formula,



$$\begin{matrix} CH_2 \diagdown \\ CH_3 \diagup \end{matrix} C.CH = CH_2.$$

The structure of pinene as shown in the following formula is dicyclic—a ring within the aromatic ring.



Pinene

Artificial Rubber.—The fact that isoprene can be converted into rubber has been mentioned (p. 50). The transformation, which is one of polymerization or condensation, may be brought about by contact with hydrochloric acid or certain other reagents. A small amount of metallic sodium produces the change in a few hours or a few days, according to the temperature. Methods for obtaining isoprene cheaply and in sufficient quantity for the industrial manufacture of artificial rubber have not yet been found.

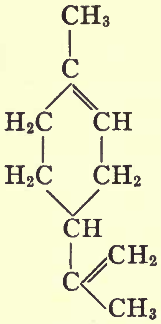
Another possible source for a commercial synthesis of rubber is *butadiene*, CH_2: $CH.CH$:CH_2, which is condensed by sodium to a product which, though not identical with natural rubber, seems to be superior to it in some respects. Butadiene is prepared from normal butyl alcohol which, in turn, may be obtained from gelatinized starch by the action of a special ferment—acetone being formed at the same time.

Camphene, $C_{10}H_{16}$, which is the only known solid terpene, is also an unsaturated compound whose exact constitution is not yet known, though probably of the same type as that of pinene. It is found in two optically active forms in French and American turpentine and in other vegetable oils. It melts at 48–50°, boils at 160°, and is oxidized to camphor by chromic acid.

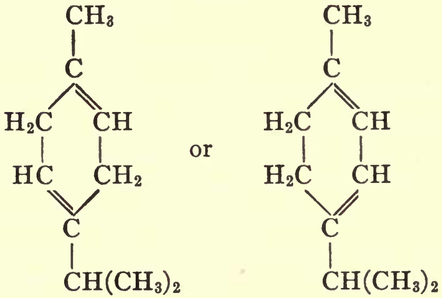
In another group of terpenes the members combine with four atoms of bromine or two molecules of a hydrogen halide, and are therefore represented with two double bonds.

Limonene is a representative of this group. Dextro-limonene is found in considerable quantity in orange-peel oil and in caraway oil; the levo form occurs in pine-needle oil, and the racemic form is obtained together with isoprene in distilling caoutchouc. Many other oils also contain these hydrocarbons.

The formula for limonene is given below with that of **terpinene,** which is a constituent of cardamon oil.



Limonene



Terpinene

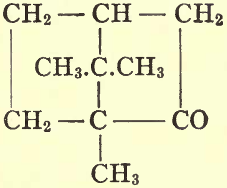
Camphors

Camphors are solid crystalline substances which are found associated with terpenes, and in many essential oils. They have characteristic odors, sublime easily, and are volatile with steam.

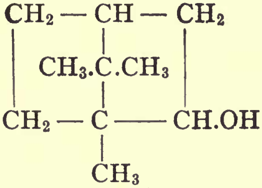
Camphor, *common or Japan camphor,* $C_{10}H_{16}O$, is obtained by distilling the wood or leaves of the camphor tree with steam. The camphor from this source is dextro-rotatory. A levo-rotatory form is found in the oils from certain plants. Both optically active forms and a racemic form can be obtained by oxidation of the corresponding borneols with nitric acid, or camphenes with chromic acid.

The common d-camphor melts at 178.7°. Its uses in medicine (spirits of camphor) and in making celluloid are well known.

Camphor is a saturated compound. When distilled with phosphorus pentoxide, camphor yields pure cymene. By reduction it is converted into borneol. It forms an oxime with hydroxylamine, and its oxygen atom can be replaced by two chlorine atoms, —reactions which are characteristic of the carbonyl group. The structure which has been established for camphor is that of a saturated ketone. This is shown by its formula which is given below together with that of borneol:



Camphor



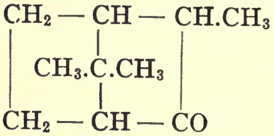
Borneol

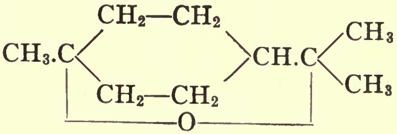
Camphor can be made from turpentine oil by the following steps: The hydrogen chloride addition product which pinene forms (artificial camphor) is converted by alkalies into camphene; camphene unites with hydrogen chloride to form a compound which is changed by glacial acetic acid into *isoborneol acetate*, $C_{10}H_{17}O.OC.CH_3$; this on saponification yields borneol, which is oxidized by nitric or chromic acid to camphor. This is only one of several methods by which camphene hydrochloride from turpentine oil has been converted into camphor. The product is identical with natural camphor in every respect except that of optical activity. The production of artificial camphor was stimulated by the Russo-Japanese war, and a good deal of the artificial product is now sold.

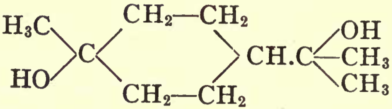
Borneol, $C_{10}H_{18}O$, is a secondary alcohol, as the formula (above) shows. It is obtained from certain trees of Borneo and Sumatra, and is found in rosemary and some other oils. It is formed by reduction of camphor in alcoholic solution by sodium; but some *isoborneol* is produced at the same time. Borneol has a camphor-like odor. It melts at 203°–204°, boils at 212°, and is converted into camphor by oxidation. Isoborneol is extremely volatile, is more soluble than borneol, and melts at 212°.

Fenchone, $C_{10}H_{18}O$, which occurs in fennel oil, is nearly related to camphor. It probably contains the CO group in a different position. It melts at 5–6°.

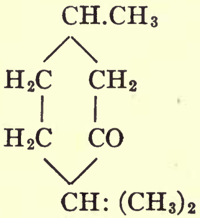
Cineol or **Eucalyptol** is another liquid camphor which is found especially in oil of eucalyptus. It boils at 177°. Eucalyptol can be made from terpine hydrate, a dihydric alcohol, $C_{10}H_{18}(OH)_2.H_2O$, which is readily obtained from turpentine oil by treatment with dilute acids.

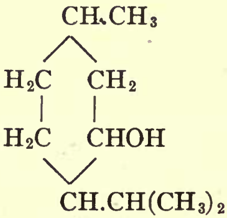

Fenchone


Cineol


Terpine

Menthone $C_{10}H_{18}O$, and **Menthol**, $C_{10}H_{20}O$, are substances contained in peppermint oil, menthol being the chief constituent, and crystallizing out of the oil when it is cooled. Menthol can also be made from *pulegone*, $C_{10}H_{16}O$, an unsaturated ketone which is the chief constituent of oil of pennyroyal, by reduction with sodium in alcoholic solution. Menthol has a strong peppermint odor, and a pleasant cooling taste. It is used as a remedy for neuralgic headache, etc. It melts at 43°. Chemically it stands in the same relation to menthone that borneol does to camphor, one being a saturated ketone and the other a secondary alcohol.


Menthone


Menthol

CHAPTER XXIX

NAPHTHALENE AND ANTHRACENE

From the higher boiling fractions of coal tar a number of solid hydrocarbons are obtained which have larger molecular weights than benzene and a smaller proportion of hydrogen. Of these naphthalene and anthracene are much the most important.

Naphthalene

Naphthalene, $C_{10}H_8$, crystallizes from the fractional distillate of coal tar which comes over between 170° and 230° and is known as "carbolic oil" or "middle oil." Naphthalene is present in coal tar in larger amounts (5–10 per cent.) than any other constituent, and forms an inexpensive source for the preparation of valuable azo dyes. After being freed by pressure from most of the oils which cling to it, it is purified by treatment with concentrated sulphuric acid, followed by distillation with steam or by sublimation.

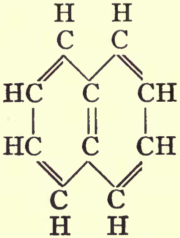
Properties.—Naphthalene crystallizes in white lustrous plates, melts at 80° and boils at 218°. It sublimes very readily, volatilizing slowly at ordinary temperatures, and has a characteristic odor which is well-known from its wide use in the form of "moth-balls" for protecting woolens and furs from moths. It is insoluble in water, but dissolves freely in various organic solvents. It is one of the principal illuminating constituents of coal gas, and occasionally causes stoppages in the gas mains by crystallizing out of the gas in cold weather.

Naphthalene is produced when the vapors of many organic compounds are passed through a red-hot tube (which explains its presence in coal tar) and it is present in the products of the dry distillation of wood.

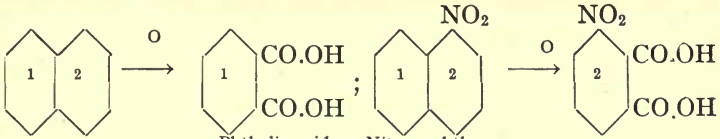
Chlorine, bromine, and nitric acid act on naphthalene with the production of substitution products; and other groups such as the hydroxyl and amino groups can be introduced by methods used in making benzene derivatives. Chlorine and bromine also form addition products with naphthalene. But while naphthalene and its derivatives are, in general behavior, like other aromatic compounds, there are certain differences which appear in a readier activity of the naphthalene derivatives as compared with those of benzene.

The hydrogen addition products—hydronaphthalenes—and their derivatives, on the other hand, are, in several cases, wholly aromatic or benzene-like in their reactions.

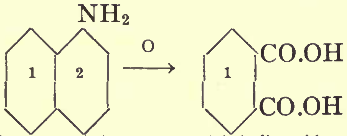
Structure.—Naphthalene is represented by the formula,



The evidence for this formula is as follows: 1. From the products of oxidation: By active oxidizing agents, naphthalene is converted into phthalic acid (p. 368); this indicates that it contains a benzene ring, and that naphthalene is an ortho di-derivative of benzene. When nitronaphthalene is oxidized, nitrophthalic acid (1, 2, 3) is formed; but if the nitronaphthalene is reduced to aminonaphthalene and this is oxidized, unsubstituted phthalic acid is the product, the amino group being in the part that is oxidized:



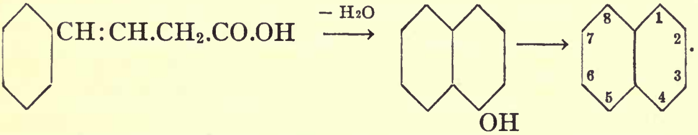
Naphthalene
Phthalic acid
Nitronaphthalene
Nitrophthalic acid



Aminonaphthalene
Phthalic acid

The same difference in behavior toward oxidation is observed in other nitro and amino derivatives. The nitro compounds are stable, while the amino compounds are readily attacked. From this we may conclude that naphthalene consists of two benzene molecules which are coalesced with the dropping out of four hydrogen atoms, as shown in the formula.

2. Syntheses of naphthalene can also be made which lead to the same conclusion as to its structure. One of these is the following. Phenylisocrotonic acid, which can be made by heating benzaldehyde with sodium succinate and acetic anhydride (Perkin's reaction p. 357) is converted by continued boiling into α-naphthol, from which naphthalene is readily obtained:



Phenylisocrotonic acid
α-Naphthol
Naphthalene

Substitution products are obtained in greater numbers than with benzene, and the number of isomers is in accordance with the possibilities which the naphthalene formula indicates. In the above formula where the hydrogen-bearing carbon atoms are numbered, it is seen that the positions 1, 4, 5, and 8 are alike, and different from 2, 3, 6, and 7, all of which, again, bear the same relation to the molecule. A compound of this formula should, therefore, yield two and only two monosubstitution products, and this is found to be the case with naphthalene. These compounds are distinguished as α-derivatives when replacement is at 1, 4, 5, or 8, and β-derivatives when in any of the other positions.

When further replacements of hydrogen are made the isomeric possibilities are: For two or six like substituents, 10 isomers; for three or five, 14; and for four, 22. Two unlike atoms or groups may give 14 isomers, and the total possible number of derivatives by direct replacement of hydrogen has been calculated to be 10,766,600.

While only a very few of the polysubstitution products have been made, in no case have more derivatives been obtained than is predicted by the theory, and in the case of dichlor substitutions, all ten have been made. The positions of substituents may be determined by oxidation into benzene derivatives of known positions, as in the case of nitronaphthalene above.

Chlorine and bromine act on boiling naphthalene with the formation of α-derivatives. β-halogen derivatives are obtained indirectly from amino or sulphonic derivatives by methods of replacement used for the derivatives of benzene. From one to four chlorine atoms can be introduced by the action of chlorine alone, and in the presence of a chlorine "carrier" (p. 284) the number may be increased to eight, with replacement of all the hydrogen atoms.

Concentrated sulphuric acid at a temperature not above 80° gives chiefly α-naphthalene sulphonic acid; at higher temperatures (160°) the β-sulphonic acid is the sole product, since the α-acid passes by intramolecular rearrangement into the β-acid when heated to the higher temperature with sulphuric acid. By more energetic sulphonation two sulphonic groups are introduced, the chief products being the 2, 7, and the 2, 6 compounds, both of them di-β-derivatives. At higher temperatures and on prolonged heating, the proportion of the 2, 6 sulphonic acid is greater.

Nitric acid under usual conditions of nitration produces only α-mono- and α-dinitro derivatives. On further nitration trinitro- and tetranitronaphthalenes in many isomeric forms are obtained. A mixture of nitronaphthalenes is used in making certain explosives, but their chief importance is the preparation of naphthylamines.

The formation of *other derivatives* is accomplished by the methods used for making benzene derivatives.

Naphthols, the hydroxyl derivatives of naphthalene, are of importance in the dye-stuff industry, since they combine readily with all diazo compounds to form azo-derivatives. The hydroxyl group of the naphthols is replaced more easily than that of phenol; they give ethyl-naphthyl ethers, $C_2H_5.O.C_{10}H_7$, when heated with alcohol and hydrochloric acid to 150°; and when heated with zinc chloride at 200°, naphthol forms naphthyl ether, $(C_{10}H_7)_2O$, (reactions not given by phenol). The naphthols also differ from phenol by having much higher melting points and being difficultly soluble in water.

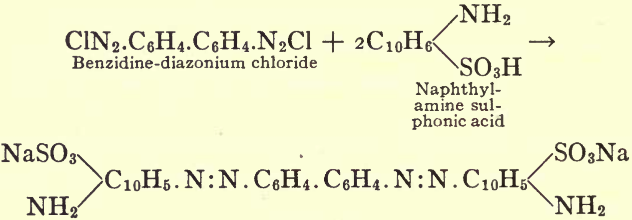
The naphthols occur in coal tar, but in very small quantities, and are usually made from naphthalene sulphonic acids by melting with alkalies.

α-Naphthol, $C_{10}H_7.OH$, melts at 94° and boils at 278°–280°. *β-naphthol* melts at 122° and boils at 285°–286°. Bleaching powder gives a dark violet color with α-naphthol in aqueous solution, and a pale yellow with β-naphthol. Ferric chloride oxidizes both to *dinaphthols,* $HO.C_{10}H_6.C_{10}H_6.OH$.

Dinitro-α-naphthol (2, 4) is obtained by the action of dilute nitric acid on α-naphthol-disulphonic acid (2, 4), which effects the replacement of the sulphonic acid groups by nitro groups. The sodium salt is known as "Martius' yellow" which is a direct dye for wool and silk.

Naphthylamines, $C_{10}H_7.NH_2$, can be obtained from the nitronaphthalenes by reduction, but are often prepared from the naphthols by heating with ammonium chloride and caustic soda or with zinc chloride and ammonia (*cf.* p. 303). This reaction is used especially for β-naphthylamine, as the β-nitronaphthalene is not formed by direct nitration, and, in fact, is itself most readily made from β-naphthylamine by the diazo reaction; while β-naphthol is easily obtained from naphthalene sulphonic acid.

The naphthylamines are well-crystallizing substances which can be distilled without decomposition. Their melting points are, for the α-amine, 50°, for the β-amine, 112°. The α-amine has a most disagreeable odor, while the other is almost odorless. They are of importance as sources (with benzidine, p-diamino-diphenyl) of the *Congo dyes* which are substantive dyes for cotton. Congo-red is made by treating diazotized benzidine with naphthylamine-sulphonic acid, and converting the product into a sodium salt:



$$ClN_2.C_6H_4.C_6H_4.N_2Cl + 2C_{10}H_6\left\langle\begin{matrix}NH_2\\SO_3H\end{matrix}\right. \rightarrow$$

Benzidine-diazonium chloride

Naphthylamine sulphonic acid

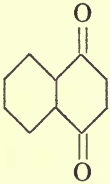
$$\left.\begin{matrix}NaSO_3\\NH_2\end{matrix}\right\rangle C_{10}H_5.N:N.C_6H_4.C_6H_4.N:N.C_{10}H_5\left\langle\begin{matrix}SO_3Na\\NH_2\end{matrix}\right.$$

Congo-red

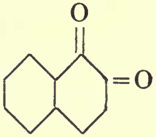
The acid of this salt is blue. *Benzopurpurin* is made in the same general way, and differs from Congo-red by having a methyl group replaced in each of the benzene radicals.

α-Naphthoquinone, $C_{10}H_6O_2$ (1, 4) is formed as the result of direct oxidation of naphthalene by chromic acid in glacial acetic acid, and is also a product of the oxidation of many α-derivatives. It melts at 125° and resembles benzoquinone in its yellow color, odor and other properties, and is reduced to 1, 4-dihydroxynaphthalene by sulphurous acid, but the reduction does not occur as readily as that of benzoquinone.

β-Naphthoquinone, $C_{10}H_6O_2$ (1, 2), forms from its ether solution red crystals which are not volatile, and decompose at 115°–120° without melting. By sulphurous acid it is reduced to 1, 2-dihydroxynaphthalene. Some derivatives of the naphthoquinones are dyes.



α-Naphthoquinone



β-Naphthoquinone

Anthracene

Anthracene $C_{14}H_{10}$, is obtained from "anthracene oil" which is the highest boiling fraction in the distillation of coal tar. Its amount in coal tar is only 0.25 to 0.45 per cent., but it is an important substance as it serves as the basis for making the valuable dye "alizarin" or "turkey red."

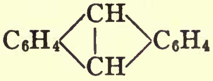
It forms white crystals which, when quite pure, have a violet fluorescence. It melts at 216° and boils at 351°. It dissolves with difficulty in many of the usual organic solvents, and is most easily soluble in benzene and toluene.

It was discovered in coal tar in 1832 and first called "paranaphthalene," and later, anthracene, from its occurrence in anthracite coal tar. In 1868 Graebe and Liebermann found that alizarin, the dye extracted from madder, was converted into anthracene by distillation with zinc dust; and, in the next year, they synthesized alizarin from anthracene through anthraquinone.

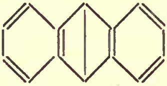
The structure of anthracene is established by several synthetical methods of formation. The first of these to be carried out was by heating benzylchloride with water at 190°:

$$\underset{\text{Benzychloride}}{2C_6H_5.CH_2Cl} \longrightarrow \underset{\text{Anthracene}}{C_{14}H_{10}} + 2HCl + H_2$$

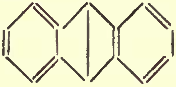
This indicates that there are two benzene rings in anthracene connected with two additional carbon atoms, as in



$C_6H_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_4$

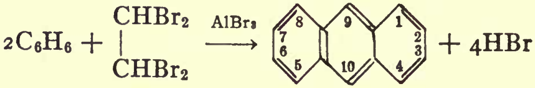


or



1 2

Another synthesis which leads to the same conclusion is from benzene and acetylene tetrabromide by the Friedel-Craft's method:

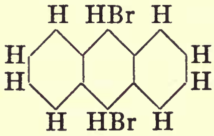


$2C_6H_6 + \begin{matrix}CHBr_2\\|\\CHBr_2\end{matrix} \xrightarrow{AlBr_3}$ + 4HBr

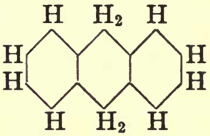
3

It is evident that, in the Kekulé formulation, the middle ring in anthracene cannot have the constitution of a true benzene ring. The double bonds in the two outer benzene rings may have different positions as shown in the above formulas, and the valence requirement in the middle ring can be met by one (or possibly two) cross bonds as is indicated, or as in formula 3. In fact, anthracene is an unsaturated compound, readily uniting with two bromine or two hydrogen atoms with the formation of

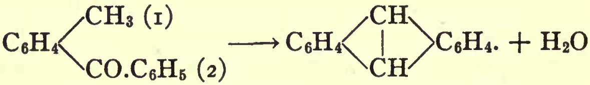
$C_{14}H_{10}Br_2$,



and $C_{14}H_{12}$, or



The ortho position of the linking carbon atoms is proved by the synthesis of anthracene from o-tolylphenylketone when heated with zinc dust:

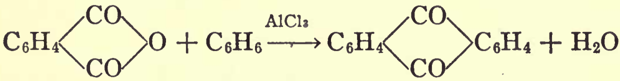


$C_6H_4\left<\begin{matrix}CH_3\ (1)\\CO.C_6H_5\ (2)\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_4. + H_2O$

The constitution of anthracene indicates that the number of substitution products should be still greater than those of naphthalene. There should be, for instance, three monosubstitution products, there being three groups of positions, in which the members of each group are relatively the same, but differ from those of the other groups. These groups are, α: 1, 4, 5, 8; β: 2, 3, 6, 7; γ: 9, 10.

The halogens act on anthracene in much the same way as on naphthalene. Concentrated sulphuric acid usually gives at once disulphonic acids. Nitric acid, however, first oxidizes anthracene to anthraquinone, and then converts this into nitro-derivatives when the acid is strong enough, or heated.

Anthraquinone, $C_{14}H_8O_2$, is very important as the source of alizarine. It is a product of the oxidation of anthracene and of many derivatives of anthracene. It is conveniently prepared by the method used for making naphthoquinone—the oxidation by chromic acid of the hydrocarbon in glacial acetic acid. It forms yellow crystals which melt at 284° and sublime in yellow needles, and boils at 382°. It is not as volatile with steam as other quinones are, lacks their pungent odor, is not reduced by sulphurous acid, and differs from them in some other respects, having rather the character of a diketone than of a quinone. Such a structure is indicated by its synthesis from phthalic anhydride and phenol when heated with sulphuric acid, or from phthalic anhydride and benzene in the presence of aluminium chloride:

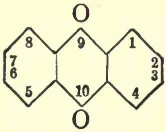


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + C_6H_6 \xrightarrow{AlCl_3} C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_4 + H_2O$$

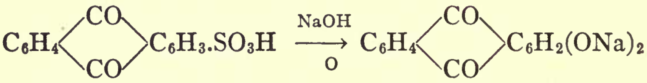
Phthalic anhydride

Anthraquinone

Anthraquinone resists oxidation to an extraordinary degree. From anthraquinone only two mono-substitution products can be obtained, and it is easily seen that this exhausts the possibilities in the formula:



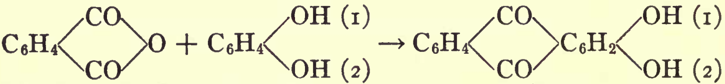
Alizarin, $C_{14}H_6O_2(OH)_2$, (1, 2) was formerly obtained from its glucoside which occurs in madder-root, but is now almost wholly prepared from anthracene. Anthraquinone is first made and then converted into monosulphonic acid by heating with fuming sulphuric acid containing 50 per cent. of sulphur trioxide. The sodium salt of this sulphonic acid is then heated in a closed vessel with sodium hydroxide and potassium chlorate. In this operation the sulphonic acid group is replaced by hydroxyl, and a second hydroxyl group formed. On acidifying the product of the fusion with hydrochloric acid, alizarin is precipitated:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3.SO_3H \xrightarrow[O]{NaOH} C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(ONa)_2$$

Anthraquinone sulphonic acid — Sodium salt of alizarin

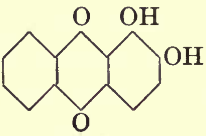
By another synthesis of alizarin from phthalic anhydride and catechol by heating with sulphuric acid, it is shown that the hydroxyl groups are in the ortho position to each other:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_4\left\langle\begin{matrix}OH\ (1)\\OH\ (2)\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2\left\langle\begin{matrix}OH\ (1)\\OH\ (2)\end{matrix}\right.$$

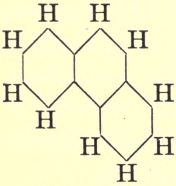
Phthalic anhydride — Catechol — Alizarin

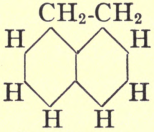
and by a study of the nitration products the formula is proved to be:

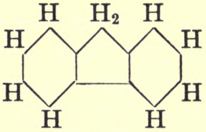


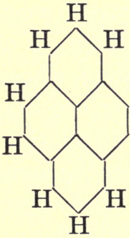
Alizarin is only slightly soluble in water. From organic solvents it forms reddish-yellow crystals which melt at 289–290°, and sublime in orange-colored needles. Its alkali salts are soluble, and give colored precipitates with the salts of most other metals. It is an adjective dye and gives fast colors with mordanted wool, silk, and cotton, forming "lakes" of different colors with the oxides of the metals whose salts are employed as mordants. When ferric salts are used, the color is violet-black; with chromium, claret; with aluminium or tin, red, etc.

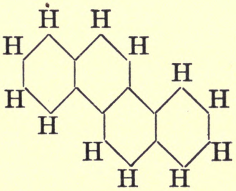
The formulas only of some of the other "condensed ring" hydrocarbons which are found in anthracite coal tar are given here. *Fluorene* was named from the violet fluorescence it shows.


Phenanthrene
$C_{14}H_{10}$


Acenaphthene
$C_{12}H_{10}$


Fluorene
$C_{13}H_{10}$


Pyrene
$C_{16}H_{10}$


Chrysene
$C_{18}H_{12}$

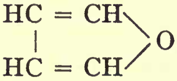
Is this "Pyrene" of 7-e?

CHAPTER XXX

HETEROCYCLIC COMPOUNDS

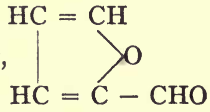
In the chapter on the cycloparaffins reference was made to the existence of compounds which contain a ring formation composed of different elements, and some illustrations were given of such compounds. Other heterocyclic compounds have been met with in our study of the aromatic substances—chiefly compounds in which the heterogeneous rings are united with the benzene nucleus—such as acid anhydrides, imides, etc. In compounds of this kind the ring is usually broken readily by various reactions, and does not show the persistent integrity and property of forming derivatives by replacement which distinguish the isocyclic compounds which we have studied in the aromatic group.

There are, however, a number of compounds obtained from natural sources, and others which have been made in the laboratory, which have these properties, and are proved to contain ring-nuclei of carbon and oxygen, carbon and sulphur, or carbon and nitrogen. The natural compounds of this group, whose structure has been definitely established, are mostly obtained from coal tar, or from the oil which results from the dry distillation of bones, and which was formerly used in medicine under the name of "Dippel's oil." A few of these compounds will be briefly described. It will be noticed that in all of them there are either five or six atoms in the ring-nucleus—the conditions for greatest stability according to v. Baeyer's strain theory (p. 259).

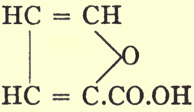
Furan or **Furfuran,** C_4H_4O, boiling at 32°, is present in pine-wood tar. A substance which has the composition $C_5H_4O_2$ and the properties of an aromatic aldehyde, was discovered in 1849 in the products of the dry distillation of bran (*furfur*). This aldehyde, whose formula may therefore be written $C_4H_3O.CHO$, is readily oxidized to pyromucic acid, $C_4H_3O.CO.OH$; and furan was first obtained by the distillation of barium pyromucate. The formula assigned to furan is  This is based on the synthesis of furan derivatives, and is supported by the resemblance in properties between some of these derivatives and corresponding aromatic compounds. The oxygen atom of furan can be shown to be neither hydroxyl or carboxyl oxygen.

The most important derivatives are the two compounds which have been mentioned;

furfuraldehyde,



and *pyromucic acid*,

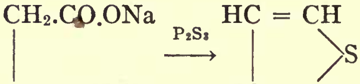


The aldehyde is formed when pentoses (p. 201) are boiled with dilute sulphuric or hydrochloric acid. It gives an intense red dye when treated with aniline and hydrochloric acid, and hence its formation, as shown by this test, is a convenient means for recognizing pentoses. It resembles benzaldehyde in its reactions —thus with alcoholic potash it yields pyromucic acid (salt) and *furfuryl alcohol*, $C_4H_3O.CH_2OH$. As its name indicates, pyromucic acid was originally obtained by dry distillation of mucic acid (p. 206).

Thiophene, C_4H_4S, gives a blue color with isatin (an oxidation product of indigo) and sulphuric acid (indophenine reaction). This reaction was thought to be characteristic of benzene, and the failure of the test in some benzene which had been made from benzoic acid led to the discovery of thiophene in commercial benzene by V. Meyer (1883). Thiophene is present in coal-tar benzene to the amount of about 0.5 per cent. It can be separated from benzene by the fact that its sulphonic acid is formed more readily than that of benzene. By heating with water under pressure thiophene is regenerated from its sulphonic acid. Methyl derivatives of thiophene are found in coal-tar toluene, xylenes, etc.

Thiophene is a colorless liquid boiling at 84°, and cannot be separated from benzene by distillation. It is somewhat heavier than water and has no characteristic odor. Its aromatic character, as shown by its reactions, is pronounced.

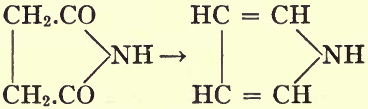
Thiophene has been synthesized by heating sodium succinate with phosphorus trisulphide:



Sodium succinate Thiophene

Its structure as given in the above formula is inferred from this and other syntheses, and is seen to be of the same type as that of furan, with sulphur in place of oxygen.

Pyrrol, C_4H_5N, is a colorless oil which has an odor resembling that of chloroform, and which boils at 131°. It is found in coal tar and bone oil. Its name is from its property of giving a bright red (*πυρρός*) color to a pine shaving moistened with hydrochloric acid. It can be synthesized by distilling succinimide with zinc dust:

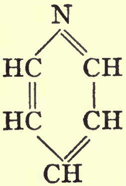


Succinimide Pyrrol

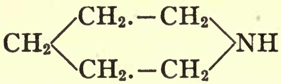
This and other syntheses, and its reactions have led to the establishment of the structure shown above, which makes it a secondary amine. It is, however, only a weak base, dissolving slowly in dilute acids in the cold, and it is changed by strong acids to a resin. As a consequence, no sulphonic acids can be obtained, and nitro derivatives only by an indirect method.

Pyrrol shows more striking analogies to the phenols than to the aromatic hydrocarbons. The imide (NH) hydrogen, like the phenol hydroxyl hydrogen, can be replaced by potassium forming potassium pyrrol, $C_4H_4{:}NK$, and the hydrogen atoms of the CH groups are replaced by halogens with great readiness. It also couples directly with diazonium salts giving azo dyes. Homologous pyrrols occur in bone oil, and can be made by passing vapors of pyrrol and alcohols over zinc dust. Pyrrol derivatives are very widely distributed in nature. The pyrrol ring is found to be present in certain alkaloids, and hæmoglobin (the red coloring matter of the blood) and chlorophyll are to be considered as derivatives of methyl-propyl pyrrol.

Pyridine, C_5H_5N, a liquid of very disagreeable odor, boiling at 115°, can be obtained from the "light oil" distillate from coal tar, and also from bone oil. Syntheses of pyridine and its reactions indicate that it may be regarded as benzene with one CH group replaced by a nitrogen atom



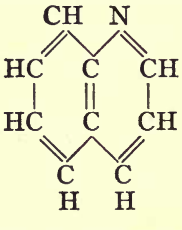
It is a very stable compound, behaving very much like benzene, but it cannot be nitrated, and gives sulphonic and halogen derivatives with greater difficulty than benzene. It is, however, easily reduced by sodium and alcohol, and adds six hydrogen atoms to form *piperidine,*



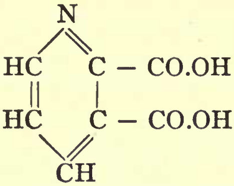
a liquid of pepper-like odor, boiling at 106°, which is also obtained from pepper. Pyridine is a tertiary amine as its formula shows. Its basic properties are stronger than those of pyrrol, and about the same as aniline, its solutions being weakly alkaline, and fairly stable salts being formed.

Homologues of pyridine occur with it, and can also be synthesized. The side chains of these homologues are oxidized to carboxyl groups, as in the case of toluene, etc. One of them is called *nicotinic acid* because it is also a product of the oxidation of the alkaloid nicotine. Pyridine and its homologues, the pyridine bases, are found to occur in the products of distillation of almost all kinds of nitrogenous substances; and among the naturally occurring members of the pyridine group are several important alkaloids.

Quinoline, C_9H_7N, which occurs in coal tar and bone oil, is a liquid boiling at 239°. It has been synthesized by methods which establish its structure as a condensation of benzene with pyridine:



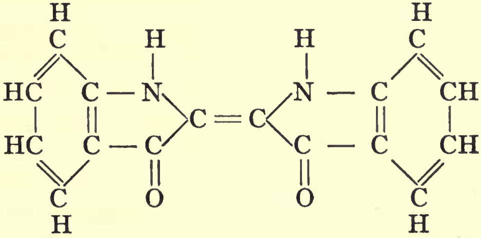
Its name is from its discovery as a product of the distillation of quinine. Quinoline is a tertiary base which forms crystalline and very soluble salts with one equivalent of acids. It forms derivatives like other aromatic compounds. It has a penetrating odor and a strong antiseptic action. When oxidized by potassium permanganate the benzene ring breaks down with the production of carboxyl groups and the formation of *quinolinic acid*:



This when heated is decomposed into nicotinic acid and when distilled with lime gives pyridine. Quinoline adds hydrogen atoms easily, which go almost exclusively into the pyridine ring.

An isomer of quinoline, called **isoquinoline,** also occurs in coal tar. It melts at 21° and boils at 237°. The nitrogen atom in isoquinoline is not directly united to the benzene nucleus as in quinoline, but occupies what in naphthalene is called the β-position. Isoquinoline is more basic than quinoline, and absorbs carbon dioxide from the air.

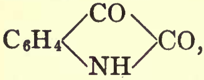
Indigo, $C_{16}H_{10}N_2O$, is a compound containing two heterocyclic groups, as shown in the following formula which is seen to contain two pyrrol rings:

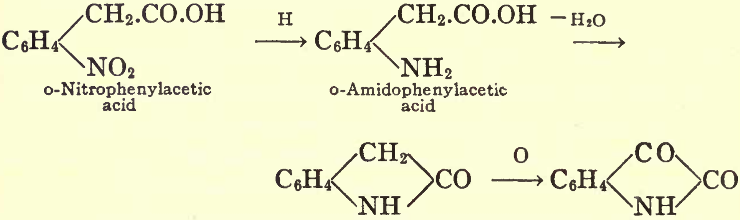


The history of the elucidation of the structure of indigo is very interesting.[1] The following is a brief summary. In 1826 aniline was obtained from indigo by dry distillation. In 1841, anthranilic acid (p. 360) was found to be a product of its oxidation. Later, it was found that when indigo was oxidized by nitric acid *isatin*

---

[1] See Sidgwick's "Organic Chemistry of Nitrogen."

was produced, whose constitution was afterward established as  $C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO$, and which was synthesized from o-nitrophenylacetic acid through *oxindol:*



$$C_6H_4\left\langle\begin{matrix}CH_2.CO.OH\\NO_2\end{matrix}\right. \xrightarrow{H} C_6H_4\left\langle\begin{matrix}CH_2.CO.OH\\NH_2\end{matrix}\right. \xrightarrow{-H_2O} C_6H_4\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle CO \xrightarrow{O} C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO$$

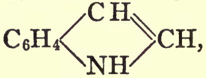
o-Nitrophenylacetic acid

o-Amidophenylacetic acid

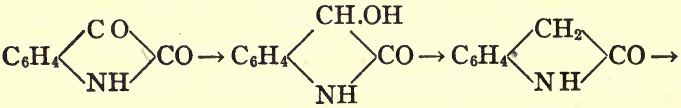
Oxindol

Isatin

In 1870 indigo was made from isatin by treatment with phosphorus pentachloride, followed by reduction. This was the first true synthesis of indigo. Its structure, however, was not yet established.

The heterocyclic hydrogen compound of which isatin is a derivative is *indol,*  $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH$, which is obtained from indigo or oxindol on distillation with zinc dust, and can be synthesized in several ways. It may be regarded as the mother substance of indigo and its derivatives. It is a crystalline solid, melting at 52° and boiling at 245°. The presence of the pyrrol ring in indol is evident in its formula. It resembles pyrrol in many respects and gives the pyrrol reaction with a pine shaving.

It was shown that isatin could be reduced by successive steps to indol without the production of indigo:

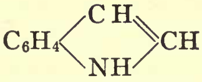


$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO \rightarrow C_6H_4\left\langle\begin{matrix}CH.OH\\NH\end{matrix}\right\rangle CO \rightarrow C_6H_4\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle CO \rightarrow$$

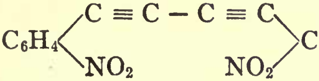
Isatin

Dioxindol

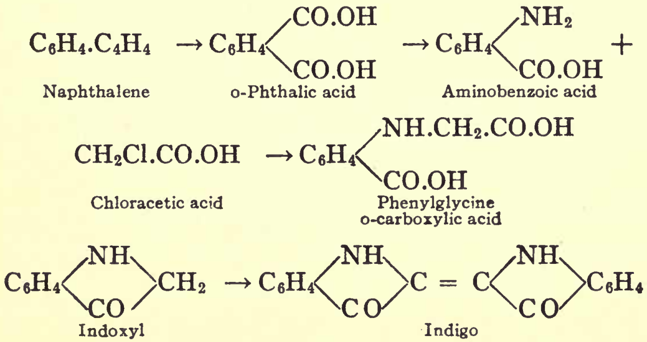
Oxindol



Indol

In these ways the relation of indigo to indol was determined and its structure was finally established by a synthesis by Baeyer; in 1882 of o-dinitro-diphenyl-diacetylene,  which on reduction yields indigo.

Many other syntheses of indigo have been effected since its structure became known, but only after twenty years of continuous research was a process found by which synthetic indigo could be manufactured at a price which could compete with the natural product. There are now several rival processes in the field, of which the most successful at present is that of Heumann. This is, in brief, as follows: Naphthalene is oxidized to o-phthalic acid by heating with fuming sulphuric acid (made by the contact process); phthalic acid is converted into aminobenzoic acid (anthranilic acid, p. 360); this is then condensed with chloracetic acid to phenyl-glycine-o-carboxylic acid, which on fusion with potash gives indoxyl. When the mass containing indoxyl is treated with water and exposed to the air, oxidation to indigo takes place. The more important steps are:



The commercial success of the process depends largely upon (1) the cheapness of naphthalene, which is produced from coal tar in great excess of the demand, and (2) on the comparatively inexpensive production of fuming sulphuric acid, for oxidation of the naphthalene, by the contact process, and the fact that the sulphur dioxide which results from the oxidation is readily reoxidized by this same process.

Another synthesis that runs on simpler lines and gives a good yield of indigo is now worked in England. The starting point here is aniline, which is treated with chloracetic acid with the production of phenylglycine, $C_6H_5NH.CH_2.CO.OH$. This when heated with sodium amide, or sodium in the presence of ammonia, is dehydrated with the formation of indoxyl which gives indigo on oxidation by a current of air.

Natural indigo occurs as *indican* (probably a glucoside of indoxyl) in the indigo plant. It is obtained by immersing the leaves in water and stirring to promote atmospheric oxidation. An enzyme present in the leaves breaks up the indican into glucose and indoxyl, and the latter is oxidized to indigo.

Indigo is a dark blue substance, insoluble in most ordinary solvents, but dissolving in aniline, melted paraffin, etc., and crystallizes from these solutions. It forms a dark red vapor when heated, and under diminished pressure can be sublimed without decomposition. In dyeing it is either converted into a soluble disulphonic acid, or it is reduced to the leuco-base, indigo white (probably a di-indoxyl), by glucose in alkaline solution. In the former case it dyes directly; in the latter, the indigo white deposited on the fibres is oxidized to indigo on exposure to the air.

CHAPTER XXXI

ALKALOIDS—PROTEINS

The alkaloids are organic bases which occur in plants. Most of them have a powerful physiological action and many are extremely poisonous. They were long considered to be substituted ammonias or ammonium bases. But while this is true of some of them, such as muscarine and amanitine, which occur in toad-stools, most of the important alkaloids are now known to be heterocyclic compounds which contain at least one nitrogen atom in their nucleus, and may therefore be regarded as derivatives of pyrrol, pyridine, quinoline, or iso-quinoline. Some of them have been synthesized.

Most of the alkaloids are crystalline solids, only a few, such as nicotine and coniïne, are liquids. They have a bitter taste, are mostly insoluble in water, but dissolve in alcohol, and to some extent in ether. They have an alkaline reaction, dissolve in acids forming salts which are often well-crystallizing compounds.

Most of the alkaloids are precipitated from their acid solutions by certain "general alkaloid reagents": tannic, picric, molybdic, phosphomolybdic, and phosphotungstic acids, potassium mercuric iodide, etc. These precipitates are decomposed by alkalies with liberation of the alkaloids. Many of the alkaloids are optically active and almost all of them are levo rotatory. The alkaloids are often identified by color reactions.

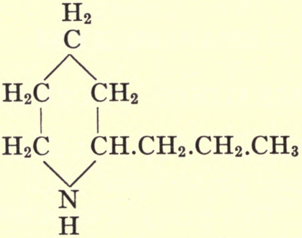
A few of the important alkaloids are here briefly described.

Coniïne, C_8H_7N, occurs in hemlock,[1] and was the first alkaloid

---

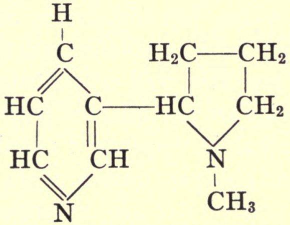
[1] The European poison hemlock, not the American hemlock, which is a species of pine.

to be synthesized. Its structural formula shows the pyridine ring, and that it is more directly a derivative of piperidine (p. 396), being *α*-propylpiperidine,



It is one of the few dextro rotatory alkaloids. Coniïne is a colorless liquid boiling at 167°.

Nicotine, $C_{10}H_{14}N_2$, is also a liquid alkaloid, obtained from tobacco. It boils at 247°. On oxidation with permanganate it yields nicotinic acid (p. 397), and therefore contains the pyridine ring. The pyrrol nucleus is also present, the formula for nicotine being,



It is exceedingly poisonous, but when tobacco is burned most of the nicotine is volatilized or destroyed.

Nicotine from tobacco is levo rotatory, but both optical forms have been obtained from the synthetical product. The two forms produce somewhat different physiological effects.

Atropine, $C_{17}H_{23}NO_3$, like all alkaloids which contain oxygen, is a solid. It melts at 115°. It is the principal alkaloid of belladonna or deadly nightshade, and is the most important alkaloid of the nightshade family. Its use by oculists to dilate the pupil of the eye is well known. The complicated structure of atropine has been determined.

Cocaïne, $C_{17}H_{21}NO_4$, from coca-leaves, is much used as a local anesthetic. It is related in structure to atropine. When heated with hydrochloric acid it gives benzoic acid, methyl alcohol, and *ecgonine*, a carboxylic acid of tropine, a substance which is obtained from atropine by hydrolysis.

Morphine, $C_{17}H_{19}NO_3$, is the chief alkaloid of opium, which is the dried juice of the seed capsules of a variety of poppy.

Strychnine, $C_{21}H_{22}N_2O_2$, and **brucine,** $C_{23}H_{26}N_2O_4$, are obtained from the *Strychnos nux vomica*.

Quinine, $C_{20}H_{24}N_2O_2$, is the most important of the twenty-four alkaloids which have been obtained from "Peruvian bark." Quinine melts at 177°. Its structure is evidently very complicated and has not been definitely established. It is known to contain the quinoline ring. Dilute solutions of its salts show a fine blue fluorescence. It is usually employed in medicine in the form of its soluble sulphate.

Proteins

Among the organic substances present in animals and plants, the compounds called proteins (*πρωτεῖον*, pre-eminent) are of very great importance. In animals by far the larger part of the tissue solids is generally protein, and protein-containing foods are absolutely essential for their nourishment.

Proteins, like the fats and carbohydrates, are found only in living matter or as products of living matter. The proteins in living matter are such a mixture of different kinds, and they are in general so unstable, that the extraction of individual, pure proteins is usually very difficult. In a few instances proteins that are apparently pure have been separated from animal tissues. Plants, unlike animals, store proteins as a reserve in their seeds, and these proteins are very stable. From seeds and nuts, therefore, proteins may be obtained with comparative ease by extraction with water, alcohol, or a solution of salt.

The composition of the proteins varies considerably. They all contain carbon, hydrogen, nitrogen, and oxygen, usually sulphur, and sometimes also phosphorus and iron. Typical proteins consist of carbon, about 52 per cent.; hydrogen, 7 per cent.; nitrogen, 15 per cent.; oxygen, 23 per cent.; sulphur, 0.5 per cent.; phosphorus, 0.3–5 per cent.

Many proteins are colloids, and advantage is taken of this property in separating them from salts and other crystalloids by diffusion through membranes. Many of them occur naturally in crystalline form in seeds and nuts, and have been crystallized in the laboratory. Their solutions are optically active and most of them are levo-rotatory. They all have a more or less amphoteric character. In aqueous solution they are coagulated by boiling or on the addition of strong alcohol or inorganic acids. Insoluble compounds are formed with solutions of salts of most of the heavy metals, and also with weak acids such as tannic, picric, and phosphotungstic acids.

We owe our present knowledge of these exceedingly complex substances largely to the work of Kossel and of Emil Fischer. It has been found that the final products of the hydrolysis of proteins are *amino acids* (p. 252), of which glycine or aminoacetic acid is the simplest representative. Intermediate compounds called *polypeptides* are formed which are condensation products of various amino acids, such as glycylglycine, $NH_2CH_2CO.NH.CH_2.CO.OH$, from two molecules of glycine.

From these facts and from other considerations the conclusion was drawn that the proteins are largely made up of α-amino acids linked through their amino and carboxyl groups, the number and kind of these amino acids being variable in different proteins.

This view is confirmed by the synthesis of more than one hundred complex polypeptides that have the properties of natural proteins after their modification by contact with reagents. One of the most complex of these synthesized substances contained eighteen amino acid groups and had a molecular weight of 1213.

The classification of the proteins adopted by the American Society of Biological Chemists is as follows.

I. *Simple Proteins.* Albumins, Globulins, Glutelins, Prolamins, Albuminoids, Histones, Protamins.

II. *Conjugated Proteins.* Nucleoproteins, Glycoproteins, Phosphoproteins, Hæmoglobins, Lecithoproteins.

III. *Derived Proteins.* Primary derivatives: Proteans, Metaproteins, Coagulated Proteins. Secondary derivatives: Proteoses, Peptones, Peptides.

The simple proteins and the conjugated proteins are all substances that are supposed to exist in the tissues and juices of animals and vegetables. The conjugated proteins consist of one or more molecules of albumin associated with some other substance of a different nature, such as sugar. They do not always contain sulphur, but phosphorus is a constituent of many of them. Several, such as hæmoglobin, the red coloring matter of blood, contain iron.

The derived proteins represent the first stages in the process of decomposition that the proteins, simple or conjugate, undergo in contact with almost any reagent. The solubility is affected by the simple operation of diffusion; and contact with acids, alkalies, or metallic salts causes incipient hydrolysis.

While the exact steps that lead to the formation of the natural proteins are obscure, it is probable that they are produced by the condensation of decomposition products of the carbohydrates with ammonia.

A few examples of the variety that proteins offer may be of interest. White of egg and serum albumin are illustrations of the *albumins*, which are the best known of the proteins; to the *albu-*

minoids belong: collagen, the chief constituent of connective tissue, bone, and cartilage, which yields gelatin or glue by partial hydrolysis; elastin in the elastic tissue of ligaments and walls of arteries; and keratin which contains sulphur—up to 5 per cent., and is the principal constituent of epidermis, hair, feathers, and horny tissues. An example of *a phosphoprotein* is casein, chief nitrogeneous constituent of milk, which is coagulated by rennet.

The molecular weights of the proteins are not accurately known, but they are certainly very large. Osborne has calculated the molecular weights in a number of instances from the percentage of sulphur present, on the assumption that there are two or more atoms of sulphur in the molecule. This assumption is based on the fact that cystine, whose molecule is known to contain two atoms of sulphur, is a constituent of many of these proteins. The following is an illustration of the method of calculation. A globin has the percentage composition: C = 54.98, H = 7.20, N = 16.89, O = 20.51, S = 0.42. If there are two atoms of sulphur in the molecule, weighing 64, the weights in atomic weight units of each of the other elements is readily calculated, and the sum is the molecular weight. From these figures an empirical formula may be obtained. In the case of this globin the figures for the molecular weight are 15,274, and the formula is:

$$C_{700}H_{1098}N_{184}O_{196}S_2.$$

Similar figures are obtained for other proteins by this and other methods.

Specific Rotations of Some Optically Active Substances

The angle through which plane polarized light is rotated by solutions of optically active substances depends on the concentration, the length of solution through which the light passes, the wave-length of the light, and the temperature, as well as on the nature of the substance. The *Specific Rotation* is the rotation produced with yellow (sodium) light in passing through one decimeter of a solution that has one gram of substance in each cubic centimeter, at 20°C.

In the following formula $[a]$ is the specific rotation, a the observed angle of rotation, l the length of the solution in decimeters, v the volume in cubic centimeters, and w the weight of substance in the solution. D indicates that the measurement is made with sodium light.

$$[a]_D = \frac{av}{lw}$$

In the case of liquid substances examined without a solvent, the formula becomes $[a]_D = \frac{a}{ld}$ in which d is the density.

		$[a]_D$			$[a]_D$
Arabinose	$C_5H_{10}O_5$	+105.0	Sucrose	$C_{12}H_{22}O_{11}$	+66.5
Xylose	$C_5H_{10}O_5$	+19.0	Lactose	$C_{12}H_{22}O_{11}$	+52.5
Rhamnose	$C_5(CH_3)H_9O_5$	+9.0	Maltose	$C_{12}H_{22}O_{11}$	+138.0
Glucose	$C_6H_{12}O_6$	+52.7	Raffinose	$C_{18}H_{32}O_{16}$	+104.0
Fructose	$C_6H_{12}O_6$	−93.8	Tartaric acid		+15.61
Invertose	$C_6H_{12}O_6$	−19.6	Saccharin		+88.7
Galactose	$C_6H_{12}O_6$	+81.0	Quinine sulphate		−213.7
Mannose	$C_6H_{12}O_6$	+14.0	Nicotine		−77.0
Sorbose	$C_6H_{12}O_6$	−42.0	Camphor (in alcohol)		+56.15
			Oil of turpentine		+36.0

Ionization Constants of Some Organic Acids and Bases

Monobasic Acids		$k \times 10_5$
Formic	$HCO.OH$	21.4
Acetic	$CH_3.CO.OH$	1.85
Glycollic	$CH_2OH.CO.OH$	15.0
Glyoxylic	$CHO.CO.OH$	50.0
Chloracetic	$CH_2Cl.CO.OH$	155.0
Dichloracetic	$CHCl_2.CO.OH$	5,000.0
Trichloracetic	$CCl_3.CO.OH$	30,000.0

Propionic	$CH_3.CH_2.CO.OH$	1.4
Lactic	$CH_3.CHOH.CO.OH$	13.8
β-Hydroxypropionic	$CH_2OH.CH_2.CO.OH$	3.1
Glyceric	$CH_2OH.CHOH.CO.OH$	23.0
α-Chlorpropionic	$CH_3.CHCl.CO.OH$	147.0
β-Chlorpropionic	$CH_3Cl.CH_2.CO.OH$	8.5
Butyric	$CH_3.CH_2.CH_2.CO.OH$	1.5
γ-Oxybutyric	$CH_2OH.CH_2.CH_2.CO.OH$	1.9
α-Chlorbutyric	$CH_3.CH_2.CHCl.CO.OH$	139.0
β-Chlorbutyric	$CH_3.CHCl.CH_2.CO.OH$	8.94
γ-Chlorbutyric	$CH_2.Cl.CH_2.CH_2.CO.OH$	3.0
Fumaric	$CO.OH.CH{:}CH.CO.OH$	100.0
Maleïc	$CO.OH.CH{:}CH.CO.OH$	1,500.0
Valeric	$CH_3.CH_2.CH_2.CH_2.CO.OH$	1.6
Benzoic	$C_6H_5.CO.OH$	6.6
o-Oxybenzoic	$C_6H_4(CO.OH)(OH)$ 1, 2	100.0
m-Oxybenzoic	$C_6H_4(CO.OH)(OH)$ 1, 3	8.3
p-Oxybenzoic	$C_6H_4(CO.OH)(OH)$ 1, 4	2.8
Dioxybenzoic	$C_6H_3.(CO.OH)(OH)_2$ 1, 2, 3	110.0
Dioxybenzoic	$C_6H_3.(CO.OH)(OH)_2$ 1, 2, 4	51.0
Dioxybenzoic	$C_6H_3.(CO.OH)(OH)_2$ 1, 2, 6	5,000.0
Dioxybenzoic	$C_6H_3.(CO.OH)(OH)_2$ 1, 3, 4	3.3
o-Nitrobenzoic	$C_6H_4.(CO.OH)NO_2$ 1, 2	650.0
m-Nitrobenzoic	$C_6H_4.(CO.OH)NO_2$ 1, 3	36.0
o-Chlorbenzoic	$C_6H_4.(CO.OH)Cl$ 1, 2	132.0
m-Chlorbenzoic	$C_6H_4.(CO.OH)Cl$ 1, 3	15.5
p-Chlorbenzoic	$C_6H_4.(CO.OH)Cl$ 1, 4	130.0
Cinnamic	$C_6H_5.CH{:}CH.CO.OH$	3.68
Sulphanilic	$NH_2.C_6H_4.SO_3H$	62.0
Anthranilic	$C_6H_4.(CO.OH)NH_2$ 1, 2	1.0

Dibasic Acids

Carbonic	$CO(OH)_2$	0.03
Oxalic	$(CO.OH)_2$	3,800.0
Malonic	$CH_2(CO.OH)_2$	163.0
Tartronic	$CHOH(CO.OH)_2$	500.0
Succinic	$CO.OH.CH_2.CH_2.CO.OH$	6.6
Malic	$CO.OH.CHOH.CH_2.CO.OH$	40.0
Tartaric	$CO.OH(CHOH)_2CO.OH$	110.0
o-Phthalic	$C_6H_4(CO.OH)_2$ 1, 2	120.0
m-Phthalic	$C_6H_4(CO.OH)_2$ 1, 3	29.0

p-Phthalic	$C_6H_4(CO.OH)_2$ 1, 4	15.0
Phenylacetic	$C_6H_5.CH_2.CO.OH$	5.3
Phenol	C_6H_5OH	0.000013
o-Nitrophenol	$C_6H_4(OH)NO_2$ 1, 2	0.006800
m-Nitrophenol	$C_6H_4(OH)NO_2$ 1, 3	0.000530
Dinitrophenol	$C_6H_3(OH)(NO_2)_2$ 1, 2, 4	8.0
Dinitrophenol	$C_6H_3(OH)(NO_2)_2$ 1, 2, 6	17.4
Dinitrophenol	$C_6H_3(OH)(NO_2)_2$ 1, 3, 6	0.7
Picric acid	$C_6H_2(OH)(NO_2)_3$	16,000.0
Bases		
Methylamine	CH_3NH_2	50.0
Dimethylamine	$(CH_3)_2NH$	74.0
Trimethylamine	$(CH_3)_3N$	7.4
Glycine	$CH_2NH_2.CO.OH$	0.000018
Aniline	$C_6H_5NH_2$	0.000046
Benzylamine	$C_6H_5.CH_2NH_2$	2.4
Diazoniumhydroxide	$C_6H_5N_2OH$	123.0

Ammonia	1.8
Boric acid	0.00006
Phosphoric acid	900.0
Sulphuric acid	45,000.0

Books for Reference and Collateral Reading

MEYER UND JACOBSON, Lehrbuch der Organischen Chemie.

ROSCOE AND SCHLORLEMMER, Organic Chemistry.

COHEN, J. B., Organic Chemistry for Advanced Students.

THORPE, T. E., Dictionary of Applied Chemistry.

MARTIN, GEOFFREY, Industrial and Manufacturing Chemistry; Organic.

SIDGWICK, N. V., Organic Chemistry of Nitrogen.

STEWART, A. W., Recent Advances in Organic Chemistry.

STEWART, A. W., Stereochemistry.

KEANE, C. A., Modern Organic Chemistry. (Stereochemistry and Sugars.)

THOMSEN, JULIUS, (Translated by Katharine A. Burke) Thermochemistry.

CAIN AND THORPE, Synthetic Dyestuffs.

FOWLER, G. J., Introduction to Bacteriological and Enzyme Chemistry.

CONHEIM, OTTO, Enzymes.

PLIMMER, R. H. A., Chemical Constitution of the Proteins.

MATHEWS, A. P., Physiological Chemistry.

INDEX

Where more than one reference is given, the most important is in heavy type.