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A third year course of organic chemistry

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OF

GENERAL ORGANIC CHEMISTRY

BY

Edward Immanuel

PROF. E. HJELT

HELSINGFORS

TRANSLATED FROM THE AUTHOR'S GERMAN EDITION
OF THE ORIGINAL WORK

By J. BISHOP TINGLE, Ph.D., F.C.S.

ASSISTANT IN THE LABORATORY OF THE HERIOT-WATT COLLEGE, EDINBURGH

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TRANSLATOR'S PREFACE

WITH REGARD to the object of this work there is little to add to Professor HJELT'S remarks; it is intended for those students who have already some general elementary knowledge of organic chemistry, and who wish to extend and *systematise* that knowledge. In Part I. the composition, constitution, and classification of organic compounds are discussed and explained as clearly and concisely as possible. Part II. is devoted to illustrating the connection between the constitution of organic compounds and their chief physical properties. Part III. deals with the chemical behaviour of organic compounds. The reactions described in this section are in all cases arranged according to the *results;* dehydration processes for instance being all classed together. Although such a division is somewhat novel, experience has shown that it materially assists students in obtaining a wide and thorough grasp of the subject. No pains have been spared in order to bring the work into harmony with the latest researches, though of course, from the very nature of the case, all controversial matter has been excluded. No similar work exists in English, and it is hoped that the present edition may obtain as favourable a reception as the foreign ones have done. The translator wishes to express his best thanks to Dr. ALEX. SMITH, of Edinburgh University, for his kind and valuable help in the revision of the proof sheets.

J. BISHOP TINGLE.

HERIOT-WATT COLLEGE, EDINBURGH,
February 1890.

PREFACE

MANY new compounds and reactions have been discovered during the past few years in the domain of organic chemistry. In systematic textbooks these must all be noticed even if they possess no important bearing upon the general and theoretical progress of the science. The enumeration and description of separate compounds, their preparation, composition, and properties, occupy a large amount of space in the ordinary textbooks. It naturally follows therefore, that in using such books, students are apt frequently to overlook much that is of general importance in their endeavour to remember particulars of the properties and reactions of single substances. The object of the present work is to give in a short and clear form the most important points of general and theoretical organic chemistry. The book is intended as a supplement to, rather than a substitute for, ordinary textbooks.

The description of the chemical behaviour of organic compounds is arranged according to the result of the reaction, and not according to the action of the reagent. Though difficulties are met with in such a classification, it is, in the author's opinion, the best.

The first and second editions of this work appeared in Swedish; the favourable reception they met with caused the publication of a German edition.

THE AUTHOR.

HELSINGFORS, *February* 1887.

CONTENTS

PART I

THE COMPOSITION OF ORGANIC COMPOUNDS

PART II

THE PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

PART III

GENERAL BEHAVIOUR OF ORGANIC COMPOUNDS

GENERAL ORGANIC CHEMISTRY

PART I

THE COMPOSITION OF ORGANIC COMPOUNDS

CHAPTER I

ELEMENTARY COMPOSITION

ALL so-called 'organic' bodies contain carbon as an essential constituent, they are carbon compounds. Carbon possesses the property, in a greater degree than any other element, of forming numerous compounds with other simple bodies. The number of known carbon compounds is already very great, and is increased daily by newly discovered and newly prepared substances, so that it really appears as if no limit could be assigned to its possible combinations. In these circumstances it becomes necessary to treat the compounds of carbon by themselves apart from those of the other elements. At the same time it was not to this practical reason that the first separation of inorganic from organic compounds was due. This division was made long before anything was known of the large number of the carbon compounds.

In the earlier periods of chemistry a distinction was made between mineral, vegetable, and animal bodies. This division was first put forward by Lemery (1675), and retained by Lavoisier, although he clearly recognised that the last two classes included bodies containing carbon.

In later times vegetable and animal substances were classed together under the name 'organic,' in contradistinction to inorganic or mineral substances. By the term 'organic compound' was understood all bodies in organic nature produced by vital processes, as well as any others which could be prepared from them by the action of chemical agents.

Inorganic substances were generally more stable and less complex in constitution, organic substances usually more complicated, and easily decomposed, especially by the action of high temperatures. Inorganic compounds could be easily prepared from their elements, but a similar synthesis of organic substances was not possible. A sharp division was believed to exist between these two groups of bodies, and it was thought that the compounds occurring in living nature were direct products of the 'vital principle,' and that, for the artificial preparation of an organic compound, a material produced under the influence of this special force was necessary. The view was strengthened that organic compounds in their production and reactions followed quite different and more complicated laws than those which had been discovered for inorganic substances.

The development of organic chemistry has gradually shown this conception to be untenable. The belief in the necessity of the 'vital principle' for the formation of organic compounds received the first blow in 1828 from Wöhler's synthesis of urea from simple substances which were regarded as inorganic (cyanic acid and ammonia). Notwithstanding this, Berzelius, in his text-book issued in 1849, defined organic chemistry as the chemistry of compounds formed under the influence of life. It was, however, soon perceived that organic compounds were subjected to the same chemical forces and followed the same laws as the inorganic, and that a sharp division between these groups of compounds did not exist. From the carbon of a mineral—witherite $BaCO_3$—Berthelot prepared a whole series of more or less complicated organic compounds. Many of the bodies which occur in the organisms of plants and animals have been prepared synthetically during late years. There are, however, many substances which cannot be produced apart from living organisms. These are more particularly the *organised* bodies, that is to say those possessed of a peculiar structure given to them by the living organism. Such bodies are the special material conductors of the vital functions, and include the simple constituents of cells, protoplasm, the cellulose of cell membranes, starch, &c. Substances endowed with vital properties may be called organic in the strict sense of the word, but they are not really definite chemical compounds, they are of physiological construction and consequently do not belong to the domain of organic chemistry. From a chemical standpoint they should be treated in botanical and zoological chemistry, sciences which could be much more truly termed 'organic chemistry' than that which at present bears the name.

The only property which organic compounds have in common is that they contain carbon as an essential constituent. Organic chemistry must consequently be defined as the chemistry of carbon compounds, and it is therefore only a special part of general chemistry. The simpler carbon compounds, such as carbon monoxide, and especially carbonic acid, salts of which occur generally throughout the mineral kingdom, are nevertheless termed inorganic. In order to escape classing these compounds as organic, L. Gmelin defined organic chemistry as the chemistry of carbon compounds containing more than one atom of carbon in the molecule. That this limitation is not correct is shown by the fact that methyl alcohol and its derivative formic acid would not be placed with organic compounds.[1]

It follows therefore that organic chemistry, in the widest sense of the term, embraces all compounds containing carbon and, as a matter of fact, carbon monoxide, carbon dioxide, carbon disulphide, &c., are very closely related to certain more complicated organic compounds. It is only on grounds of practical convenience that these important simply constituted bodies are discussed together with carbon itself in text-books of inorganic chemistry. Although the number of organic compounds is enormously great, the majority of them are

---

[1] This limitation appeared to be justified in Gmelin's time because carbonic acid and carbon disulphide were then written CO_2 and CS_2, but methyl alcohol $C_2H_4O_2$ and formic acid $C_2H_2O_4$ ($C = 6, O = 8$).

composed of very few elements. Besides carbon, the universal constituent, the majority of organic compounds contain hydrogen and oxygen—nitrogen is also frequently present. From this small number of elements many thousands of organic compounds have been built up. The four simple bodies already mentioned are the chief elements of organic compounds and of organised substances formed from them; to these must be added sulphur and phosphorus, which are often found in bodies produced in nature. By artificial means all elements without exception may be combined to form organic compounds. The hydrogen in such compounds can, for example, be easily replaced by halogens. The metals can not only form salts with organic acids, but many of them can also be combined with carbon in quite neutral bodies. In these compounds the halogen or metal is frequently masked—that is to say, it cannot be detected by its usual reagents. The halogens are often not precipitated from organic compounds by silver nitrate, nor mercury by hydrogen sulphide. They react only when the element has been liberated from the carbon by some means, or when the organic compound itself has been destroyed by heating or energetic oxidation.

In order to find the composition of an organic compound, it must be subjected to a complete elementary analysis. The quantity of each of its elements must be estimated. The ordinary methods employed are described in every text-book of organic chemistry. A simple empirical formula representing the composition of the compound can be easily calculated from the percentage numbers. Suppose, for example, the compound called 'butyric acid' gives, on analysis, the following percentage composition:—

$$\begin{array}{lr} C = & 54{\cdot}55 \\ H = & 9{\cdot}08 \\ O = & 36{\cdot}37 \\ \hline & 100{\cdot}00 \end{array}$$

In order to find the atomic proportions of the elements from these proportions by weight, the percentage numbers are divided by the atomic weights of the respective elements. The quotients represent the ratio of the elementary atoms contained in the compound.

$$\begin{array}{l} C = 54{\cdot}55 \div 12 = 4{\cdot}54 \\ H = 9{\cdot}08 \div 1 = 9{\cdot}08 \\ O = 36{\cdot}37 \div 16 = 2{\cdot}27 \end{array}$$

The atomic ratio is 4·54 : 9·08 : 2·27, or 2 : 4 : 1. The simplest possible formula for butyric acid is therefore C_2H_4O. It must not however be supposed that this formula represents the actual atomic composition, for we find the same atomic ratio in the formulæ $C_4H_8O_2$, $C_6H_{12}O_3$, &c. The chemical formula of a compound represents not only the simplest atomic ratios of the elementary components, but also the atomic composition of the molecule—that is to say, the real number of atoms in the molecule; in short, it is also a molecular formula.

On account of the excessively large number of carbon compounds, it is of particular importance to know the true molecular formula of each single substance. Which of the above formulæ to give to butyric acid can be known by determining the molecular weight of the compound, and there is no difficulty in doing that, as butyric acid can easily be gasified.

The specific gravity of butyric acid gas is 3·05. If this number be multiplied by 28·87 (= 2 × 14·435), the molecular weight 88 is obtained. This determination shows that butyric acid has the formula $C_4H_8O_2$, molecular weight 88, and not the simple formula C_2H_4O, molecular weight 44. If ordinary aldehyde be analysed, the atomic ratio C_2H_4O is also obtained. A determination of the vapour density of aldehyde shows that its molecular weight is 44, and that consequently the true formula is identical with the simplest. This method of determining the molecular weight by means of the vapour density can only be applied to bodies which can be heated above their boiling-points without decomposition. A process has however been discovered and recently worked out by means of which the molecular weight of substances can be found even when they do not admit of being gasified; it is called, after the name of the discoverer, the 'Raoult' method, and is based upon the fact that chemically similar compounds generally produce equal lowerings of the freezing-point of water or some other solvent. It has been calculated from experiment that if the molecular weight in grams of a substance were to be dissolved in water, under certain conditions of concentration, the freezing-point would be lowered on the average 19° C. With benzene as a solvent, the lowering of the freezing-point would be 49° C., with glacial acetic acid 39° C., always provided that the substance under examination has no chemical action on the solvent employed. The analysis of phenol leads to the formula C_6H_6O; 1 gr. of phenol dissolved in 100 gr. of water lowers the freezing-point 0·165°; the molecular weight of phenol must therefore be 94, and not 188 or 282, because $94 \times 0{\cdot}165 = 15{\cdot}5$.

It is however possible, by studying the reactions and compounds of a substance, to determine its molecular formula by purely chemical means. The problem is simplest in the case of acids or bases. The molecular formula of butyric acid can be determined chemically in the following manner. The silver salt of the acid is prepared and analysed. The percentage composition is found to be—

$$\begin{array}{lr} C = & 24{\cdot}62 \\ H = & 3{\cdot}59 \\ Ag = & 55{\cdot}38 \\ O = & 16{\cdot}41 \\ \hline & 100{\cdot}00 \end{array}$$

From these numbers the atomic ratio is calculated:—

$$\begin{array}{l} C \ = 2{\cdot}05 = 4 \\ H \ = 3{\cdot}59 = 7 \\ Ag = 0{\cdot}51 = 1 \\ O \ = 1{\cdot}02 = 2 \end{array}$$

The formula $C_4H_7AgO_2$ is consequently obtained. It is however known that butyric acid is monobasic, and that its silver salt is formed by replacing one atom of hydrogen by one of silver; the formula of the acid must therefore be $C_4H_8O_2$.

In order to determine the molecular formula of an organic base, a neutral salt of it is prepared and its molecular weight determined from the quantity of acid in the salt. For convenience the platinum double salt is usually chosen. The hydrochloric acid salts of organic bases give compounds with platinum chloride strictly analogous with ammonium platinum chloride $PtCl_4.2NH_4Cl$. By estimating the quantity of platinum in the salt the molecular formula of the base can be calculated.

In the case of indifferent substances which form compounds with neither acids nor bases, other reactions must be employed to determine the molecular weight. The simplest formula for acetic ether is C_2H_4O; if it be treated with potassium hydrate equal molecules of ethyl alcohol C_2H_6O and potassium acetate $C_2H_3O_2K$ are produced. The formula C_2H_4O must therefore be doubled, as there are 4 atoms of carbon in one molecule of alcohol and one of acetic acid. The decomposition of acetic ether is thus represented :—

$$C_4H_8O_2 + KOH = C_2H_6O + C_2H_3O_2K.$$

A study of the substitution products of an organic compound may also serve to fix its smallest possible molecular formula. From the analysis of benzene the atomic ratio of CH is obtained. If chlorine be allowed to act on benzene, a compound C_6H_5Cl is formed as the first substitution product. The smallest possible formula for benzene is consequently C_6H_6.

CHAPTER II

CONSTITUTION

AN empirical molecular formula for a compound is obtained by an elementary analysis together with a molecular weight determination. Experience has shown, however, that compounds having exactly the same molecular formula are not therefore necessarily identical, they may differ considerably in properties from one another. This can only be accounted for by supposing that the atoms in the molecules of the different compounds are differently bound together or differently grouped. The properties of compounds do not depend entirely on the nature and number of their atoms, as was formerly supposed—the manner of their relative arrangement in the molecule is of equal importance. The discovery of this inner grouping of the atoms of a compound, or of its *chemical constitution*, is one of the more weighty problems of chemical research.

This constitution is represented by graphic formulæ, which only serve to give a systematic plan of the relative atomic groupings of the compound as deduced from a study of its general relations and chemical reactions. Notwithstanding the apparent probability and agreement with facts of our present theory of chemical constitution, it is only really of a hypothetical nature, for our knowledge of the workings of affinity and of that force exerted by atoms which holds the molecules together is still very incomplete and faulty. Carbon is the chief element of organic compounds. The great number of these compounds and the peculiarities they show are dependent on the chemical nature of carbon, and certain of its peculiar properties. In considering this part of the subject four circumstances are of importance:—

(1) The property possessed by carbon of combining with elements of the most different nature.

(2) The power of carbon to combine with itself, together with the high valency of its atom.

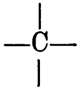
(3) The stability of the carbon bond.

(4) The behaviour of carbon towards hydrogen.

In the natural classification of the elements carbon occupies the central place in the first period. Li(7), Be(9), B(11), C(12), N(14), O(16), F(19). If the different valencies of these elements be compared with that of any other element, a regular increase or decrease is found from Li to F. The valency reaches its maximum or minimum at one or other of these elements at the ends of the period. From the position of carbon in the middle of the period it follows that the difference of valency in its case must be small, or in other words, that carbon possesses the property of combining with elements of the most different nature. Atoms can not only combine with dissimilar atoms but also with similar ones. Molecules of hydrogen and of chlorine, for example, are formed by the combination of two similar atoms H—H, Cl—Cl.

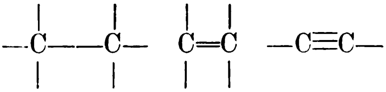
No more than two monovalent atoms can enter into direct combination with each other—their combining powers are thereby mutually satisfied. If however two atoms of a polyvalent element unite, they may do so in such a way that only a part of the valencies are used in order to join them together:—

$$-O-O-\,;\ -N=N-\,;\ =N-N=.$$

Carbon is a tetravalent element, each atom has four units of affinity 

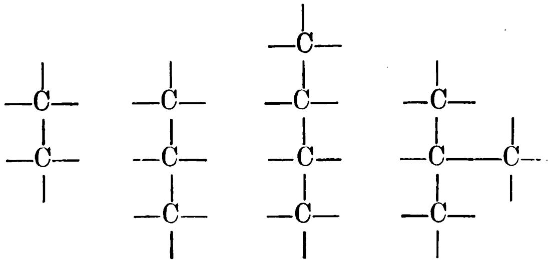
$-\overset{|}{\underset{|}{C}}-$

If two carbon atoms combine together without mutually satisfying all the valencies, three cases are possible, those namely in which one, two, or three valencies of one atom are saturated by a corresponding number of the other:—



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \qquad -C\equiv C-$$

In such groups of two atoms of carbon free affinities exist, by means of which the group is able to attach to itself more carbon atoms. The polyvalent elements have consequently the power of forming true atomic chains by the combination of a number of their atoms. The greater the valency of an element the more complicated are its combining ratios, and the greater possibility exists of its atoms forming numerous compounds with similar and dissimilar atoms. The atoms of carbon possess, in a much greater degree than those of any other element, the property of combining with similar atoms whereby a part of their valencies are saturated.

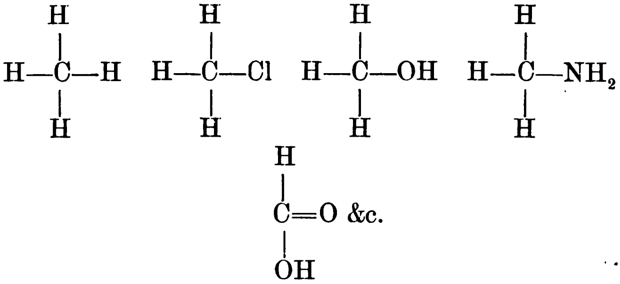


The free valencies in such carbon chains must of course be satisfied by other atoms, or in other words, carbon chains only exist in combination with other elements; they are therefore sometimes called carbon nuclei. A limit to the length of these chains is unknown. It must not however be understood that all imaginable or even theoretically possible chains of carbon atoms can actually exist; in many cases the contrary has been proved by direct experiment. The carbon bond shows great stability, and resistance to the action of forces, not only when it exists between carbon and some other element, but more especially when it is between carbon and carbon. It is for this reason that the number of atoms in an organic compound may be exceedingly great without the molecule decomposing. It follows also from the above that an enormously large quantity of energy may be accumulated in organic compounds. It is only occasionally that this energy is sufficient, either alone or in combination with a slight external force, to overcome the resistance of the carbon bond. (Atomic rearrangement accompanied by evolution of heat; explosion.)

All free valencies in a carbon group may be saturated with hydrogen. If the above carbon nuclei combine with hydrogen, the hydrocarbons C_2H_6, C_3H_8, C_4H_{10} are formed. An enormously large number of hydrocarbons exist; the other elements form as a rule only one or two hydrogen compounds. The number of hydrocarbons, like that of the carbon nuclei, is unlimited—each nucleus corresponds to a hydrocarbon. All other carbon compounds may be considered to be derived more or less directly from the hydrocarbons. They may be regarded as hydrocarbons in which hydrogen is replaced by other elements or radicles. Even the most complicated carbon compound may be theoretically derived from the corresponding hydrocarbon. It is in consequence of this that organic chemistry has been defined as the 'chemistry of the hydrocarbons and their derivatives.' The fact that organic compounds may be theoretically traced back to hydrocarbons makes the classification and systematisation of the enormous number of bodies included in organic chemistry very much easier than it otherwise would be.

The sum total of hydrogen or other atoms of uneven valency in a carbon compound must always be an even number. This so-called 'law of even numbers' (Kekulé) is a natural result of the tetravalency of carbon.

Carbon being a tetravalent element, one atom combines with four of hydrogen, forming marsh gas or methane CH_4. If hydrogen atoms in this compound be replaced by equivalent quantities of other elements or radicles, the following compounds may be formed:—CH_3Cl methyl-chloride; CH_3OH methyl alcohol; CH_3NH_2 methyl-amine; CH_2I_2 methylen iodide; CHOOH formic acid; CHN prussic acid; CO_2 carbon dioxide, &c. The way in which the atoms of these compounds are bound together in the molecule is much more plainly shown by the use of graphic formulæ:—[1]



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array} \quad \begin{array}{ccc} & H & \\ & | & \\ H- & C & -Cl \\ & | & \\ & H & \end{array} \quad \begin{array}{ccc} & H & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array} \quad \begin{array}{ccc} & H & \\ & | & \\ H- & C & -NH_2 \\ & | & \\ & H & \end{array}$$

$$\begin{array}{cc} H & \\ | & \\ C & =O \text{ \&c.} \\ | & \\ OH & \end{array}$$

These graphic formulæ must not be misunderstood. They do not profess to represent the actual grouping of the atoms, they only aim at giving a systematic picture of the comparative linking of the atoms, or of the relative constitution as this can be determined from the chemical behaviour of the compound; they are there-

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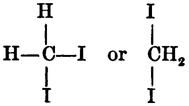
[1] These formulæ were introduced by Couper (1858); the atoms combined directly together are by them represented as being connected by strokes. The formulæ may be used in a more or less expanded form, as for example:—

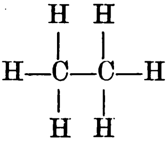


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -I \\ & | & \\ & I & \end{array} \quad \text{or} \quad \begin{array}{c} I \\ | \\ CH_2 \\ | \\ I \end{array}$$

fore often called *constitutional* or *structural* formulæ, though this latter term is not so correct. If two carbon atoms combine together in the simplest possible way, so that each atom binds the other to itself with one affinity, and the unit of valency be represented by f, the expression

$$2Cf_4 - f_2 = C_2f_6$$

is obtained, that is to say, the sum of the disposable valencies in this dicarbon group = 6; if all these be saturated with hydrogen the hydrocarbon ethane is formed :—

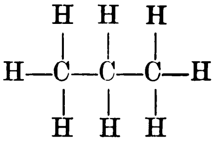


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

If three carbon atoms combine together in the simplest way, a tricarbon group with eight free valencies results :—

$$3Cf_4 - 2f_2 = C_3f_8$$

The corresponding hydrocarbon is propane C_3H_8 :—



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

If more carbon atoms join together in a similar manner two valencies will be used by each new atom, consequently each additional carbon atom raises the collective valency by two units. The group C_4 is 10-valent, C_5 12-valent, &c. The carbon group contains one bond less than the number of carbon atoms; if these be represented by n the number of free valencies will be $= 4n - (n-1)\,2 = 2n + 2$.

The general formula for the corresponding hydrogen compounds is C_nH_{2n+2}. The hydrocarbons which are derived from the above carbon nuclei are the following:—

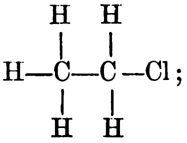
$$\begin{array}{l} CH_4 \\ C_2H_6 \\ C_3H_8 \\ C_4H_{10} \\ C_5H_{12} \text{ \&c.} \end{array}$$

Each is distinguished from the one immediately above or below by a difference of CH_2; such compounds are called *homologues.*

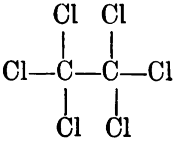
In these hydrocarbons, as in CH_4, the hydrogen can be replaced by other elements or radicles giving rise to compounds analogous to CH_3Cl, CH_3OH, &c. The free valencies of the carbon group $(2n + 2)$ may be saturated not only with hydrogen but with any other element which, if it be a polyvalent one, can bind other atoms to itself; for example:—

$$\begin{array}{ll} C_2H_5Cl & C_2Cl_6 \\ C_3H_7OH & C_3H_6(OH)_2 \end{array}$$

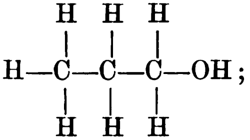
or expressed in graphic formulæ,



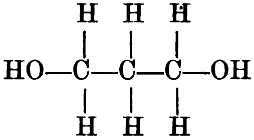
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & Cl; \\ & & | & & | & & \\ & & H & & H & & \end{array}$$



$$\begin{array}{ccccccc} & & Cl & & Cl & & \\ & & | & & | & & \\ Cl & — & C & — & C & — & Cl \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH;$$



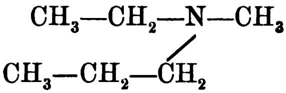
$$HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$$

Each of these carbon groups occurs in a large number of compounds.

Several carbon chains may be united to form one molecule by means of a polyvalent element.

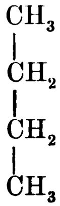
$CH_3—CH_2—O—CH_2—CH_3$;

Ethyl ether



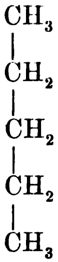
Methylethylpropylamine.

If the carbon atoms of a nucleus are joined together in a single straight chain, they are said to form *a simple or normal chain.*



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

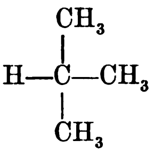
Normal butane



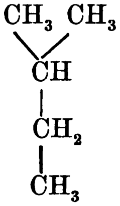
$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_2\\|\\CH_2\\|\\CH_3\end{array}$$

Normal pentane.

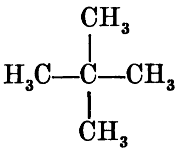
If one carbon atom is joined to more than two others *a side chain* is produced. The construction of the chain is thus *abnormal*; substances containing such a carbon chain are usually called *iso*-compounds.



Isobutane

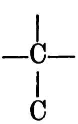


Isopentane

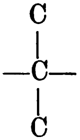


Tetramethylmethane.

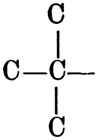
The carbon atoms in these chains are said to be primary, secondary, tertiary, or quaternary, according as they are connected with one, two, three, or four other carbon atoms.



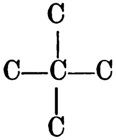
Primary C atom



Secondary C atom



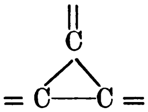
Tertiary C atom

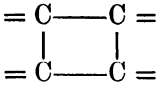


Quaternary C atom.

In normal carbon chains only primary or secondary carbon atoms are found, but in the iso-compounds at least one atom must be tertiary or quaternary.

All the above carbon chains are open; if the two end carbon atoms of such a chain unite together a *closed carbon chain* or *carbon ring* is formed.





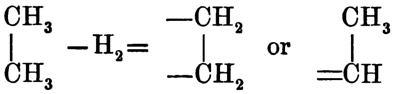
Two valencies are used in order to close the chain, the sum of the valencies of such a simple carbon ring is therefore $2n+2-2=2n$.

Closed chains consisting of three, four, five, and six atoms of carbon are known. The greater the number of carbon atoms linked together, the greater may be the differences in construction of the carbon nuclei. As regards closed rings, the number of them which can exist in compounds is relatively small.

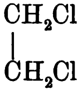
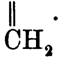
Saturated and unsaturated compounds.—Compounds containing open carbon chains, the carbon atoms of which are simply joined together, all free valencies being satisfied with other atoms, are called *saturated* compounds, because no more atoms can be attached to the carbon chain without first causing it to split. The maximum of free units of affinity in a carbon nucleus consisting of n carbon atoms is $2n+2$. The above-mentioned hydrocarbons of the composition C_nH_{2n+2} are therefore saturated compounds. Compounds are however known which contain less hydrogen, or its equivalent quantity of other atoms, than the corresponding saturated compounds. If for example ethane C_2H_6 lose two atoms of hydrogen, the compound called ethylene C_2H_4 is produced, and exists as free hydrocarbon. If two atoms of hydrogen be taken from this ethylene, the hydrocarbon acetylene C_2H_2 is formed. These compounds are called *unsaturated* because the carbon group contained in them does not use all its disposable valencies to attach other atoms.

As has already been shown, the group C_2 can combine with six atoms of hydrogen. The hydrocarbons C_2H_4 and C_2H_2 are therefore not fully saturated compounds;

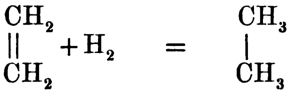
they are capable of combining with respectively two and four atoms of hydrogen, giving rise to the saturated hydrocarbon C_2H_6. The hydrocarbon C_2H_6 can lose two atoms of hydrogen in two different ways, thus:—



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_3}\end{array} - \mathrm{H_2} = \begin{array}{c}-\mathrm{CH_2}\\ |\\ -\mathrm{CH_2}\end{array} \text{ or } \begin{array}{c}\mathrm{CH_3}\\ |\\ =\mathrm{CH}\end{array}$$

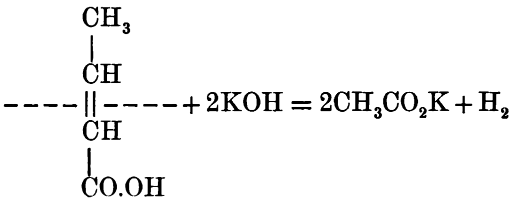
The hydrogen atoms may either be taken from both carbon atoms or only from one. That ethylene is not represented by the second of the above formulæ is shown by the fact that this hydrocarbon unites directly with two atoms of a halogen element, giving a compound in which the halogen atoms can be proved to be united to different carbon atoms  $\begin{array}{c}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2Cl}\end{array}$. The two unused valencies in ethylene must therefore belong to different carbon atoms. As according to the present theory carbon is regarded as a constant tetravalent element, and compounds which contain really uncombined valencies do not exist in the free state—at all events when those valencies belong to different carbon atoms—it has been supposed that the two unoccupied valencies in ethylene mutually satisfy each other  $\begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{array}$. This is expressed by saying that in ethylene the carbon atoms are linked by a *double bond.* In a precisely similar way the presence of a triple bond in acetylene is assumed  $\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array}$.

In almost all unsaturated organic compounds with open carbon chains the free valencies are in connection with *neighbouring* carbon atoms, *i.e.*, those directly linked together, and a double or triple bond is supposed to exist between these carbon atoms. If the unsaturated compound unite with atoms of other elements by direct addition, the double bond is converted into a simple one :—



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + H_2 = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$$

The existence of double bonds is quite hypothetical, although many circumstances appear to point to the truth of the theory. It must, however, be borne in mind that a 'double bond' does not imply a *firmer linking of the carbon atoms*, as might be expected; the attraction between doubly bound atoms is, on the contrary, *weaker than when they are simply linked.* That this is the case is proved by the fact that by the action of powerful reagents on unsaturated compounds the carbon chain is always broken exactly at the position of the double bond; for example, by fusing crotonic acid with potassium hydrate, acetic acid is produced :—



$$\begin{array}{c} CH_3 \\ | \\ CH \\ ----\|----- \\ CH \\ | \\ CO.OH \end{array} + 2KOH = 2CH_3CO_2K + H_2$$

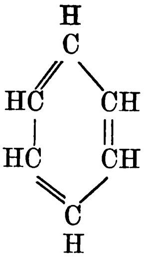
The molecule containing four carbon atoms is split up into two molecules of acetic acid $C_2H_4O_2$. A comparison of the optical and thermal relations, and of the specific volume of saturated and unsaturated compounds, also shows that a so-called double bond between two carbon atoms is looser and weaker than a simple one. (See the chapter on the physical properties of organic bodies.)

These facts are, however, not conclusive against the supposition of several bonds existing between carbon atoms in unsaturated compounds.

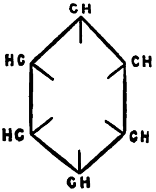
The real nature of the saturating power of atoms and of atomic linking is quite unknown, and consequently no definite representation of them can be made.

A large number of organic compounds exists, which contain a smaller number of atoms than corresponds with the highest possible valency of their carbon nuclei, but which differ in many respects from ordinary unsaturated compounds.

The most important are the so-called 'aromatic' compounds. In these compounds the existence of closed carbon chains is assumed; the simplest of these bodies is benzene C_6H_6, which contains eight atoms of hydrogen less than the corresponding saturated hydrocarbon hexane C_6H_{14}. These eight valencies are distributed amongst the carbon atoms; two are used by the closing of the chain, the other six are disposed of in the manner represented by one or other of the following two formulæ :—



Kekulé

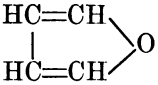


Von Baeyer.

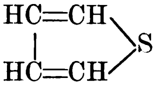
A closed chain of this nature, consisting of six atoms of carbon (benzene nucleus), is supposed to exist in all aromatic compounds (benzene derivatives). In the above formula of von Baeyer a peculiar kind of 'central' linking is assumed. As a matter of fact, benzene compounds are able to combine directly with six monovalent atoms (hydrogen or halogens), but they do so much less energetically than the ordinary unsaturated compounds.

The question of the constitution of benzene is one of the most interesting in the domain of organic chemistry. It cannot be fully treated here—the large number of necessary references to separate compounds and reactions would take up too much space. Opinions are divided as to which of the above formulæ best represents the behaviour of this compound; this much however is certain—each of the six carbon atoms in benzene is joined to one hydrogen atom, the carbon atoms being linked together in such a way that a ring is formed about which the hydrogen atoms are symmetrically disposed. The group of six carbon atoms which occurs in all aromatic compounds is called the *benzene* *nucleus*; it is exceedingly stable and can withstand the action of very powerful chemical agents.

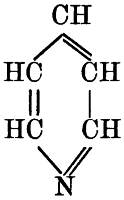
Besides carbon, other polyvalent elements, such as oxygen, nitrogen, or sulphur, may bring about the formation of a closed chain in an organic molecule:—



Furfuran



Thiophene



Pyridine.

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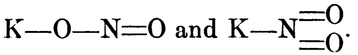
CHAPTER III

ISOMERISM

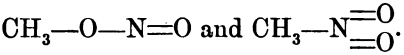
It was formerly taken for granted that bodies possessing the same qualitative and quantitative composition had also like chemical and physical properties, or in other words, that such substances were identical. By the researches of Liebig on fulminic acid and those of Wöhler on cyanic acid completed about seventy years ago, it was shown that these bodies have the same composition. In the year 1828 Wöhler converted ammonium cyanate into urea, and soon afterwards Berzelius found that racemic and tartaric acids have the same quantitative composition. These facts showed that the nature and properties of a compound were influenced by other circumstances as well as by the qualities and quantities of its constituents. Berzelius explained this by supposing that 'the simple atoms were differently arranged in the compound atom' (molecule). Bodies with the same composition which were not identical were termed *isomers*, and the property itself was called *isomerism*.

Very few cases of isomerism have been detected amongst inorganic substances, but many instances have been noted amongst organic compounds. The cause of this is to be found in that property of the carbon bond, which renders possible the arrangement of the atoms in many different ways. Of all isomeric compounds one must possess a greater degree of stability than the others; this peculiar property of the carbon bond is the reason why, in many cases, organic isomers exist separately and do not become converted into the compound having the greatest stability. Inorganic bodies behave differently; that peculiar resistance which hinders the transformation of one isomer into another is absent. It follows therefore that that compound is the most stable which is formed by the most different reactions. A compound of the formula KNO_2 could exist in two forms:—



$$K—O—N{=}O \text{ and } K—N\begin{smallmatrix}=O\\=O\end{smallmatrix}.$$

Only the first occurs, because it is the more stable. Of the corresponding organic compounds however two isomeric forms are known:—



$$CH_3—O—N{=}O \text{ and } CH_3—N\begin{smallmatrix}=O\\=O\end{smallmatrix}.$$

Methylnitrite Nitromethane.

Two substances having the compositions of hydrocyanic and cyanic acids are possible:—

$H—C{\equiv}N$ $H—N{\equiv}C$ (Hydrocyanic acid).
$N{\equiv}C—OH$ $O{=}C{=}NH$ (Cyanic acid).

In reality however only one hydrocyanic acid and one cyanic acid occurs, together with one series of metallic cyanides and cyanates; but two series of organic cyanides and cyanates are known:—

$CH_3—CN$ Methylcyanide (Acetonitrile)	$CH_3—NC$ Methylisocyanide (Methylcarbylamine)
$NC—OCH_3$ Methylcyanate	$OC{=}NCH_3$ Methylisocyanate.

The two iso-esters are certainly the more stable, but both series of compounds can be obtained in the free state. Free cyanic acid and its salts are transformed, immediately they are produced, into the more stable isomeric compounds OCNH and OCNM respectively.

In the widest sense, all compounds are isomeric that possess the same empirical formula and show the same percentage composition on analysis. Isomerism may be divided into *polymerism*, *metamerism*, *isomerism in the restricted sense*, and *geometrical isomerism.*

Polymerism.—Compounds possessing the same percentage composition but different molecular weights are called polymers; their molecular formulæ bear a simple arithmetical relation to one another. The following compounds may be cited as good examples of polymerism:—

Formic aldehyde	CH_2O	– – – –	CH_2
Acetic acid	$C_2H_4O_2$	Ethylene	C_2H_4
Lactic acid	$C_3H_6O_3$	Propylene	C_3H_6
Grape sugar	$C_6H_{12}O_6$	Butylene	C_4H_8
		Amylene	C_5H_{10}

A distinction must be made between *accidental* and *generic* polymerism.

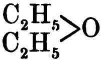
The first of the above series of polymeric compounds forms a good instance of accidental polymerism. Formic aldehyde, acetic acid, lactic acid, and grape sugar do not stand in any simple chemical relation to each other; the polymerism between them depends, so to speak, upon accident.

Many organic compounds are converted directly and easily into polymers owing to the union of several molecules of the substance to form a single molecule. By treating ordinary aldehyde C_2H_4O with a mineral acid, three molecules combine together to form one molecule of paraldehyde $C_6H_{12}O_3$; this latter body is decomposed on heating into ordinary aldehyde. Cyanic and cyanuric acids stand in a similar relation to each other: Cyanic acid, OCNH; cyanuric acid, $O_3C_3N_3H_3$.

In these cases, the higher molecular compounds are produced by direct combination of the simpler molecules. The above examples show the nature of generic polymerism.

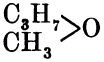
Metamerism.—Compounds are called *metamers* when they possess the same molecular formula but contain several carbon groups (radicles) linked together by a polyvalent element, usually oxygen, sulphur, or nitrogen. The radicles of the different compounds are of different sizes, but the sum of the atoms contained in them is the same. Metamerism occurs chiefly in the case of ethers, amines, and esters.[1]

The following metameric ethers have the formula $C_4H_{10}O$:—



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right>O$$

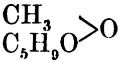
Ethyl ether



$$\left.\begin{matrix}C_3H_7\\CH_3\end{matrix}\right>O$$

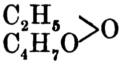
Propylmethyl ether.

Examples of metameric esters of the formula $C_6H_{12}O_2$:—



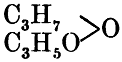
$$\left.\begin{matrix}CH_3\\C_5H_9O\end{matrix}\right>O$$

Methylvalerate



$$\left.\begin{matrix}C_2H_5\\C_4H_7O\end{matrix}\right>O$$

Ethylbutyrate



$$\left.\begin{matrix}C_3H_7\\C_3H_5O\end{matrix}\right>O$$

Propylpropionate.

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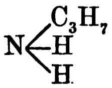
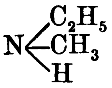
[1] The term ester is used to denote ethereal salts or compound ethers.

The following are instances of metameric amines of the formula C_3H_9N:—



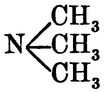
$$N\begin{array}{l}\diagup C_3H_7\\ - H\\ \diagdown H\end{array}$$

Propylamine



$$N\begin{array}{l}\diagup C_2H_5\\ - CH_3\\ \diagdown H\end{array}$$

Ethylmethylamine



$$N\begin{array}{l}\diagup CH_3\\ - CH_3\\ \diagdown CH_3\end{array}$$

Trimethylamine.

If metameric compounds be treated with substances which can destroy the bond between the carbon groups and the connecting element, entirely different products are obtained. The above esters, of the formula $C_6H_{12}O_2$, are decomposed by the action of potassium hydrate according to the following equations:—

$$C_5H_9O.OCH_3 + KOH = C_5H_9OOK + CH_3OH$$

Methyl valerate — Potassium valerate — Methyl alcohol

$$C_4H_7O.OC_2H_5 + KOH = C_4H_7OOK + C_2H_5OH$$

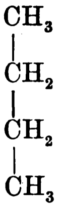
Ethyl butyrate — Potassium butyrate — Ethyl alcohol

$$C_3H_5O.OC_3H_7 + KOH = C_3H_5OOK + C_3H_7OH$$

Propyl propionate — Potassium propionate — Propyl alcohol.

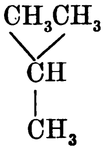
Isomerism in the restricted sense.—Two or more compounds the molecules of which contain the same number of atoms not divided into carbon nuclei of different sizes, as in metameric substances, are called true isomers or *isomers in the restricted sense.* The carbon nuclei of these compounds are of the same size, but the carbon atoms of which the nuclei are composed are differently grouped, or the elements linked to the nuclei are differently disposed. The term *nucleus isomerism* is applied to bodies of the first class, whilst bodies of the second are called *isomerides of position.*

Nucleus isomerism proceeds from the carbon chain itself, as the following examples clearly show :—

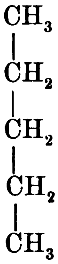


$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

Normal butane

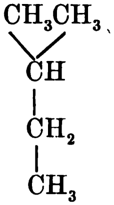


Isobutane

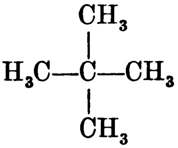


$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

Normal pentane



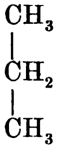
Isopentane



$$H_3C-\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{C}}-CH_3$$

Tetramethylmethane.

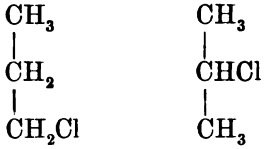
The expression *isomerism of position* is used to denote isomeric bodies with similar carbon nuclei in which one or more of the atoms linked to the carbon atoms have different situations in the molecule. For example, if an atom of hydrogen in the hydrocarbon propane be replaced by chlorine the substitution may occur in two different places in the molecule, in other words, the molecule of this hydrocarbon possesses two chemical positions.



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

The chlorine may be attached either to one of the end (primary) carbon atoms, or to the intermediate (secondary) one.

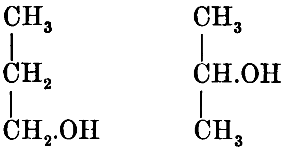
Two compounds of the formula C_3H_7Cl exist:—



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2Cl \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CHCl \\ | \\ CH_3 \end{array}$$

Primary Secondary
propylchloride.

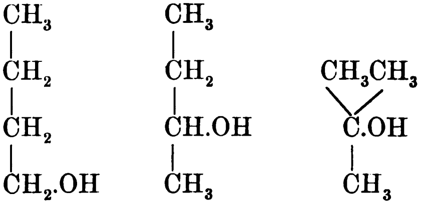
These two chlorides correspond to two alcohols (hydroxyl compounds):—



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

Primary Secondary
propylalcohol.

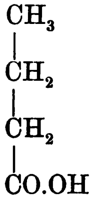
The alcohols are divided into *primary*, *secondary*, or *tertiary*, according to the position of the *hydroxyl* group. The following further examples may be given:—



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

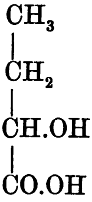
Primary Secondary Tertiary
butyl alcohol.

If one atom of hydrogen be replaced in normal butyric acid, the substituting element may take three different positions in the molecule. Three oxybutyric acids are known; their constitution is shown by the following formulæ:—



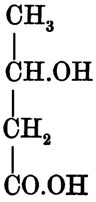
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Normal butyric acid



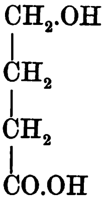
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

α-



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

β-

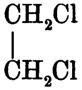


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

γ-

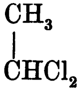
Oxybutyric acid.

If in ethane two hydrogen atoms be replaced by chlorine two isomeric chlorides are obtained, because the entering elements may link themselves either to the same or to different carbon atoms.



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

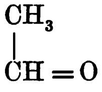
Ethylenechloride



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

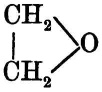
Ethylidinechloride.

If two atoms of hydrogen in similar hydrocarbons be replaced by a divalent element, such as for example oxygen, the substitution may also take place in two ways:—



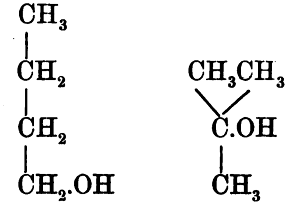
$$\begin{array}{l} CH_3 \\ | \\ CH = O \end{array}$$

Aldehyde



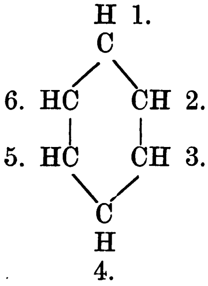
Ethylene oxide.

The above compounds are examples of isomerism of position, which can only occur if the atoms or radicles linked to the carbon atoms are not all alike. Both isomerism of position and nucleus isomerism may occur simultaneously between two compounds, as in the following bodies :—



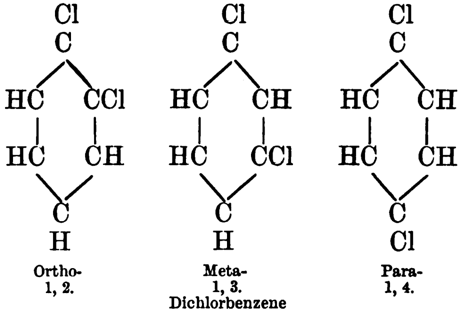
Normal primary Tertiary
butyl alcohol.

A peculiar isomerism of position which may be termed *relative isomerism of position* occurs in the aromatic compounds. The fundamental type of these compounds is benzene C_6H_6, and it has already been shown that they contain a closed carbon nucleus consisting of six carbon atoms arranged in the form of a ring. If in benzene any one atom of hydrogen be replaced by another element the same product is always obtained, because all the hydrogen atoms have a similar position in the molecule, but if several hydrogen atoms be replaced the substitution may take place in different ways. If the carbon atoms be numbered it is easily



seen that two hydrogen atoms may be substituted in three different ways—viz., in the positions 1 and 2, 1 and 3, or 1 and 4 (1, 6 = 1, 2 ; 1, 5 = 1, 3).

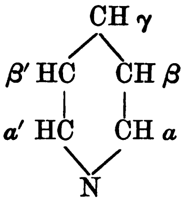
In agreement with this, three dichlorbenzenes are known; their isomerism is shown by the following formulæ:—



Dichlorbenzene

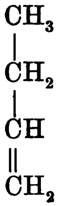
All aromatic compounds with the general formula $C_6H_4X_2$ occur in three series ; they are distinguished as *ortho-*, *meta-*, or *para-compounds*. The isomerism of these compounds depends on the *different relative positions* of the two atoms of the element introduced—the previous position of either of them in the molecule is without effect, because the constitution of the benzene nucleus is completely symmetrical; the result is therefore the same, no matter whether the two atoms introduced be alike or not. The case is however different if three atoms of hydrogen in benzene be replaced by other elements or groups. Compounds of the formula $C_6H_3X_3$ occur in three forms (1, 2, 3 ; 1, 2, 4 ; 1, 3, 5), but those of the formulæ $C_6H_3X_2Y$ and C_6H_3XYZ occur in six and ten forms respectively.

Compounds whose atoms are linked in rings, but whose constitution is not perfectly symmetrical, show a different isomeric relation. By the introduction of one element into pyridine a triple isomerism is produced, since it may enter any one of the three chemically different positions *α*, *β*, *γ* (*α*′ = *α*, *β*′ = *β*) :—



If two atoms of hydrogen be replaced, six isomeric compounds are obtained if the substituting elements be alike, if they be unlike ten are formed.

A species of isomerism which stands as it were between nucleus and position isomerism, has been observed in certain unsaturated compounds: the double bond may occupy different positions in the carbon nucleus, as for example :—



$CH_3-CH_2-CH=CH_2$

Butylene

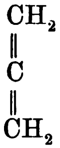
$CH_3-CH=CH-CH_3$

Isobutylene.

Doubly unsaturated compounds may have two carbon atoms trebly linked, or one may be connected to two others by two double bonds :—

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

Allylene



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

Isoallylene.

The isomerism which occurs where an element shows a variable valency must be classed as a special kind; the isomerism of the two series of organic cyanides is usually considered to be of this nature:—

$CH_3—C\equiv N$ Methylcyanide (Acetonitrile)

$CH_3.N\equiv C$* Methylisocyanide (Methylcarbylamine).

The number of possible isomerides increases rapidly as the number of atoms contained in compounds becomes greater. Hydrocarbons of the formula C_nH_{2n+2} can naturally only differ by means of nucleus isomerism. The hydrocarbon C_4H_{10} of this series occurs in 2 isomeric forms, that of the formula C_6H_{14} in 5, whilst of the compounds $C_{12}H_{26}$ and $C_{13}H_{28}$ the number of possible isomerides is 355 and 802 respectively. If the atoms linked to the carbon be different, isomerism of position comes into play, the number of possible isomerides being thereby enormously increased.

Nucleus isomerism only	Number of compounds	Nucleus and position isomerism	Number of compounds
C_3H_8	1	$C_3H_7.OH$	2
C_4H_{10}	2	$C_4H_9.OH$	4
C_5H_{12}	3	$C_5H_{11}.OH$	8
C_6H_{14}	5	$C_6H_{13}.OH$	16

---

* Some chemists consider the nitrogen to be trivalent in both cases, but assume that the carbon in the cyanide groups of the isocyanides only acts with two valencies.

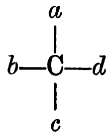
The smaller the difference which causes isomerism between two bodies the more closely they resemble each other in properties. The probability of the present view of the constitution of organic compounds is greatly strengthened by the fact that the number and nature of known isomerides is in entire agreement with the conclusions to which a study of atom-linking leads.

Geometrical isomerism (physical isomerism, alloisomerism).—Many cases of isomerism are known which cannot be explained by any difference in constitution; no doubt this is often due to the fact that the constitution of these substances has not yet been correctly determined. Numerous cases have, however, been observed in which the molecules show certain differences in their properties, whilst it is very probable, in some instances certain, that the manner in which the elementary atoms are linked is the same. These differences are often very slight chemically, but they appear much more plainly if the action of the substances upon the plane of polarisation of a ray of light be examined. In some cases considerable chemical differences are apparent. Bodies belonging to the first class are termed *physical isomers*.

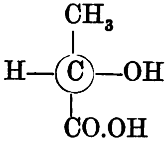
Two lactic acids are known with the same chemical constitution: one of them occurs in flesh, and turns the plane of polarisation of a ray of light to the right; the other is formed by the fermentation of sugar, and is entirely without optical action. Natural and synthetical malic acids show the same differences.

A similar relation exists between the dextro- and lævo-rotatory tartaric acids. Their optical properties are different—the one turns the plane of polarisation to the right, the other to the left. They also possess different crystalline forms: the crystals of the one show certain hemihedral faces developed to the right, whilst corresponding faces on the crystals of the other are seen to the left; the one set of crystals appears therefore as the reflected image of the other. Optically inactive racemic acid, which is isomeric with tartaric acid, may be split up into dextro- and lævo-components.

Many physically isomeric compounds may be easily changed, the one into the other modification, and this conversion may be regarded as particularly characteristic of physical isomerides, since it only occurs exceptionally in the case of chemical isomerides. The differences between physically isomeric compounds which occur in the solid form can be traced in many instances to differences in the arrangement of the molecules. Isomeric compounds which show optical differences often continue to show them when they are in a fluid state or in solution; the cause of the isomerism is therefore probably to be found in the molecule. Le Bel and Van 't Hoff have pointed out that all compounds observed to show physical isomerism in their optical behaviour possess one or more asymmetric carbon atoms, *i.e.*, carbon atoms linked to four different atoms or atomic groups.

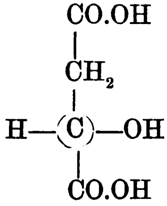


$$\begin{array}{c} a \\ | \\ b\text{—}C\text{—}d \\ | \\ c \end{array}$$



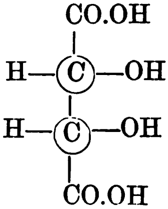
$$\begin{array}{c} CH_3 \\ | \\ H\text{—}\textcircled{C}\text{—}OH \\ | \\ CO.OH \end{array}$$

Ethidene lactic acid



$$\begin{array}{c} CO.OH \\ | \\ CH_2 \\ | \\ H\text{—}\textcircled{C}\text{—}OH \\ | \\ CO.OH \end{array}$$

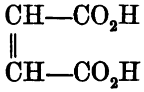
Malic acid



$$\begin{array}{c} CO.OH \\ | \\ H\text{—}\textcircled{C}\text{—}OH \\ | \\ H\text{—}\textcircled{C}\text{—}OH \\ | \\ CO.OH \end{array}$$

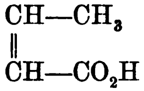
Tartaric acid.

Unsaturated compounds are also known, the inner constitution of which must be represented by the same graphic formulæ, although they differ altogether in properties from each other. Fumaric and maleic acids



$$\begin{array}{l} \mathrm{CH{-}CO_2H} \\ \| \\ \mathrm{CH{-}CO_2H} \end{array}$$

and crotonic and iso-crotonic acids



$$\begin{array}{l} \mathrm{CH{-}CH_3} \\ \| \\ \mathrm{CH{-}CO_2H} \end{array}$$

are examples of such compounds. The isomeric relations of these substances are explained by the existence of differences in the way in which the atoms are linked in the molecule, which differences are not shown by ordinary formulæ. As molecules are built up of atoms and occupy space, it is easy to imagine that whilst the constituent atoms of two molecules may be linked in the same way, the manner of their arrangement in the molecule may be different. It may now be regarded as certain that physical isomerism and alloisomerism are caused by differences of the position of atoms in the molecule. This has been called *geometrical isomerism*, and the theory itself is chiefly due to Van 't Hoff and J. Wislicenus.

As the four affinities of a carbon atom are alike in every respect, it follows as a simple mathematical possibility that four atoms may attach themselves to the carbon atom in the directions of the summits of a regular tetrahedron, the centre of which is occupied by the carbon atom. If four, or three, or two of the elements which are united to the carbon atom be alike, only one form of arrangement in space is possible. Compounds of the types $C\,a_4$, Ca_2b_2, or $C\,a_2b\,c$ cannot occur in geometrical isomeric forms. So soon however as all the four atoms, or groups, which are linked to the carbon are different, two combinations exist, as shown in the figures.

The two combinations cannot be superposed by turning; the one is as it were the reflected image of the other. Compounds containing an *asymmetric* carbon atom, *i.e.* one with the grouping $C\,a\,b\,c\,d$, may occur in geometrical isomeric forms. As a matter of fact, all compounds which have the same constitution, but different optical properties contain at least one asymmetric carbon atom.

FIG. 1.

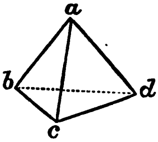
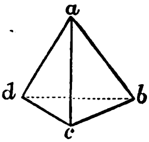
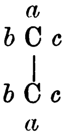


FIG. 2.



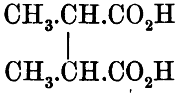
If two or more asymmetric carbon atoms be contained in a compound, the number of possible groupings in space becomes greater; four forms of tartaric acid are known.

All compounds which are constituted according to the formula



$$\begin{array}{c} a \\ b\,\mathrm{C}\,c \\ | \\ b\,\mathrm{C}\,c \\ a \end{array}$$

show geometrical isomerism, and it is noteworthy that the differences between isomeric compounds are much greater than those between compounds containing only one asymmetric carbon atom. These latter are really only 'optically isomeric.' All symmetrically substituted succinic acids, such as



$$\begin{array}{c} CH_3.CH.CO_2H \\ | \\ CH_3.CH.CO_2H \end{array}$$

are known in two forms which are termed para- and anti-acids, and which show considerable differences in melting point, solubility, and certain chemical properties, but the one form may be converted into the other.

The isomerism of the above-mentioned unsaturated compounds may be explained by this theory of arrangement in space. Two doubly linked carbon atoms would be represented by a figure consisting of two tetrahedra with one edge in common. Two arrangements are possible of substances of the type C *a b* = C *a b*. Fumaric and maleic, crotonic and isocrotonic, citraconic and mesaconic acids are examples of such compounds.

Fig. 1.

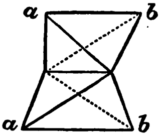
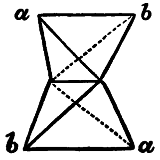


Fig. 2.



This dicarbon system is stable—the one carbon atom cannot be rotated without the second going with it. The one compound is not immediately converted into the other, but both exist as separate and distinct substances. It can be proved that fumaric acid is constituted like fig. 2 and maleic acid like fig. 1. It is not possible here to give a systematic account of the principles upon which the discovery of geometrical isomerism is based.

The investigation of the isomeric relations of bodies forms one of the most important problems in the domain of organic chemistry, because by this means a glimpse of the internal arrangements of the molecules is obtained; this problem is intimately connected with the general determination of the constitution of compounds. In such researches a knowledge of the actual number of atoms in the molecule as well as of their valency is absolutely necessary.

The chemical methods used for determining the constitution are partly of an analytical, partly of a synthetical nature: by means of the first, attempts are made to split the substance into simpler compounds of known constitution; whilst the second class of methods is employed to build up the substance from such compounds. Important conclusions with regard to the constitution of bodies may frequently be drawn by analogy from their general chemical behaviour as well as from their physical properties.

CHAPTER IV

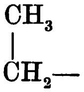
ORGANIC RADICLES

It has been observed that single groups of linked atoms remain unaltered by many reactions to which organic compounds may be subjected, and that they pass from one compound into another without any change in their structure; such atomic groups or molecular residues are called *radicles.*

The group C_2H_5 remains unaffected by many of the reactions of ordinary alcohol; it is therefore looked upon as the radicle of alcohol, which is itself regarded as the hydrate of this radicle, that is to say, as a compound of the radicle with hydroxyl OH, $C_2H_5—OH$:—

$$C_2H_5.OH + HCl = C_2H_5Cl + H_2O.$$
$$C_2H_5.OH + HNO_3 = C_2H_5.NO_3 + H_2O.$$

The radicle C_2H_5 is called ethyl and contains one atom of hydrogen less than the saturated hydrocarbon C_2H_6. One valency is disposable, it is therefore a monovalent radicle—



$$\begin{array}{l} CH_3 \\ | \\ CH_2— \end{array}$$

The same applies to the radicles C_3H_7 propyl, C_4H_9 butyl; they also contain one atom of hydrogen less than the saturated hydrocarbons C_3H_8 and C_4H_{10}. Monovalent radicles can only combine with one atom of a monovalent element, and can only replace one atom of hydrogen in a compound.

The radicles C_2H_4 and C_3H_6 are divalent because they contain two atoms of hydrogen less than the corresponding hydrocarbon.

$$C_2H_6 - 2H = \overset{II}{C}_2H_4\,;\; C_3H_8 - 2H = \overset{II}{C}_3H_6.$$

Such radicles can combine with two atoms of hydrogen or chlorine, and can replace two atoms of hydrogen in a compound. The radicle C_3H_5 is trivalent, the radicle C_4H_6 is tetravalent, &c.

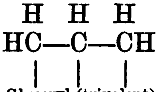
$$C_3H_8 - 3H = \overset{III}{C}_3H_5\,;\; C_4H_{10} - 4H = \overset{IV}{C}_6H_6.$$

The valency of such radicles, composed of hydrogen and carbon only, is determined from the composition of the saturated hydrocarbons (C_n) containing the same quantity of carbon. The difference between the number of hydrogen atoms in the hydrocarbon and in the radicle gives the valency of the radicle.

	Hydrocarbon	CH_4 Methane	C_2H_6 Ethane	C_3H_8 Propane	C_4H_{10} Butane
Radicles	Monovalent	CH_3 Methyl	C_2H_5 Ethyl	C_3H_7 Propyl	C_4H_9 Butyl
	Divalent	CH_2 Methylene	C_2H_4 Ethylene	C_3H_6 Propylene	C_4H_8 Butylene
	Trivalent	CH Methenyl	C_2H_3 Vinyl	C_3H_5 Glyceryl	C_4H_7 Crotyl
	Tetravalent	C Carbon atom	C_2H_2 Acetylene (Ethine)	C_3H_4 Allylene (Propine)	C_4H_6 Crotonylene (Butine).

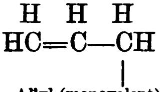
It should not be forgotten that a radicle does not necessarily bring into activity all its disposable valencies;

a double bond may be formed between neighbouring carbon atoms with free valencies, whereby the valency of the radicle will of course be decreased; for example, the trivalent radicle glyceryl can also occur in a monovalent form:—



$$\overset{\text{H}}{\underset{|}{\text{HC}}}-\overset{\text{H}}{\underset{|}{\text{C}}}-\overset{\text{H}}{\underset{|}{\text{CH}}}$$

Glyceryl (trivalent)

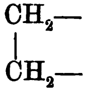


$$\overset{\text{H}}{\text{HC}}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{|}{\text{CH}}}$$

Allyl (monovalent).

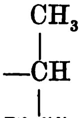
The doubly linked valencies of allyl may easily be satisfied by other elements, as is always the case with unsaturated compounds. The allyl compounds thus become converted into glyceryl compounds, except when hydrogen be taken up. The result of the law of even numbers of atoms is that every radicle consisting of hydrogen and carbon contains an uneven number of hydrogen atoms if its valency be represented by an uneven number, and *vice versâ*. Radicles of similar composition may show both nucleus isomerism and isomerism of position.

Radicle C_2H_4 :



$$\begin{array}{l} CH_2- \\ | \\ CH_2- \end{array}$$

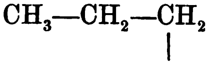
Ethylene



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

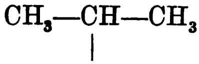
Ethylidine
(Ethidene).

Radicle C_3H_7:



$$CH_3-CH_2-\underset{|}{CH_2}$$

Primary



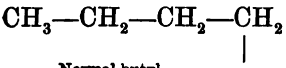
$$CH_3-\underset{|}{CH}-CH_3$$

Secondary

Propyl.

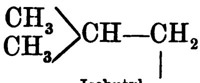
Radicle

C_4H_9 :



$$CH_3-CH_2-CH_2-\underset{|}{CH_2}$$

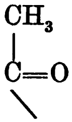
Normal butyl

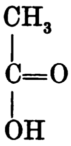


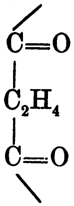
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-\underset{|}{CH_2}$$

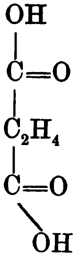
Isobutyl.

Radicles may contain other elements besides hydrogen and carbon. The organic acids may be regarded as hydrates of radicles containing oxygen. Acetic acid $C_2H_4O_2$ can be looked upon as a compound of the monovalent radicle C_2H_3O (acetyl) and OH, and succinic acid as the hydrate of the divalent radicle $C_4H_4O_2$ (succinyl).


Acetyl


Acetic acid


Succinyl


Succinic acid.

These radicles are also of course found in the simple derivatives of the acids, as for example :—

$C_2H_3O.Cl$ Acetylchloride

$C_4H_4O_2.O$ Succinic anhydride

The first organic radicle containing oxygen which was observed to exist was benzoyl; it occurs in benzoic acid, benzaldehyde, and in other compounds (Liebig and Wöhler, 1832).

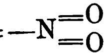
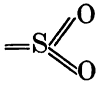
The radicles containing only carbon and hydrogen are called alcohol-, aldehyde-, or ketone radicles, after their oxygen compounds. They possess a slight positive or basic character, which is most marked in the alcohol radicles rich in hydrogen, and in general they resemble the metals.

The less hydrogen a radicle contains, the less positive is its character. This is clearly seen by comparing together corresponding compounds of the phenyl radicle C_6H_5, and of the hexyl radicle C_6H_{13}.

Radicles containing oxygen are called acid radicle if their hydroxyl compounds are acids; they possess a negative or acid character, and correspond completely with the inorganic acid radicles

$$N\overset{\text{I}}{O}_2,\ S\overset{\text{II}}{O}_2,\ \&c.$$

The following simple inorganic radicles occur in a number of organic compounds in combination with organic radicles:—

Hydroxyl, or the water molecule residue	$-OH$
Nitro group	$-NO_2 =$  $-N{=O \atop =O}$
Nitroso group	$-NO$
Amido group, or the ammonia molecule residue	$-NH_2$
Imido group	$=NH$
Sulphuryl, or the sulpho group	$=SO_2 =$ 
Thionyl group	$=SO$
Cyanogen	$-C\equiv N$ or $C\equiv N-$

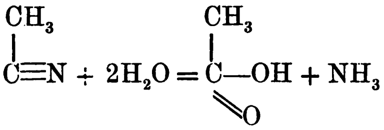
The atomic groups or molecular residues which are called radicles remain unaffected by certain reactions and behave in many respects like elements; they must not however be thought to be linked together in any special way, because as a rule they may easily be split up. If ethyl alcohol be heated with sulphuric acid ethylene is formed; the radicle C_2H_5 loses one atom of hydrogen:—

$$C_2H_5.OH = H_2O + C_2H_4.$$

Acetic acid is decomposed into carbon dioxide and methane by heating with an alkaline hydrate:—

$$CH_3 \vdots CO.OH = CH_4 + CO_2.$$

The radicles are only hypothetical residues; whether this or that group of atoms be considered to be the radicle of a compound depends upon the reaction to which most importance is given. The trivalent radicle $CH_3.C\equiv$ could be considered to exist in acetic acid, because it comes into prominence in some reactions, as for example in the following:—

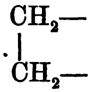


$$\begin{array}{l} CH_3 \\ | \\ C\equiv N \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ C-OH \\ \;\; \searrow\!\!\searrow O \end{array} + NH_3$$

as however in most of the reactions of acetic acid the acetyl group CH_3CO- remains unchanged, it is usual to regard this as the radicle.

The adoption of the theory of radicles in organic compounds is due entirely to practical reasons; a clear general view of the composition of substances and of their mutual relations is obtained by its means, and rational formulæ gain greatly in brevity and simplicity.

Alcohol radicles of even valency can exist as free hydrocarbons if the free bonds belong to adjacent carbon atoms.



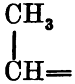
$$\begin{array}{l} CH_2- \\ | \\ CH_2- \end{array}$$

Ethylene
(radicle)

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$$

Ethylene
(hydrocarbon).

The isomeric radicle ethylidene or ethidine

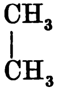


$$\begin{matrix}CH_3\\ |\\ CH=\end{matrix}$$

cannot exist in a free state. Two free monovalent radicles frequently join together, forming a saturated compound :—

$$\begin{matrix}CN\\ |\\ CN\end{matrix}$$

Free cyanogen
(Dicyanogen)



$$\begin{matrix}CH_3\\ |\\ CH_3\end{matrix}$$

Dimethyl
(Ethane).

Organic compounds, like inorganic ones, can be traced back to certain simple compounds, so-called *types*; they may be regarded as hydrogen H_2, water H_2O, ammonia NH_3, &c., in which the hydrogen is partially or wholly replaced by organic radicles.

$$\text{Type}\ \left.\begin{matrix}H\\H\end{matrix}\right\}\qquad \left.\begin{matrix}CH_3\\H\end{matrix}\right\}\qquad \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$$

Methane Aldehyde.

$$\text{Type}\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\qquad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O\qquad \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Ethyl alcohol Ethyl ether Acetic acid.

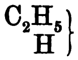
$$\text{Type}\ \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2\qquad \left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$$

Glycol.

$$\text{Type}\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\qquad \left.\begin{matrix}C_3H_7\\H\\H\end{matrix}\right\}N\qquad \left.\begin{matrix}C_2H_5\\CH_3\\H\end{matrix}\right\}N\qquad \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$$

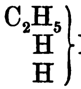
Propylamine Ethylmethylamine Trimethylamine.

On the other hand these compounds, especially those of the types H_2O and NH_3, may be regarded as substituted hydrocarbons; there exists of course no fundamental difference between the formulæ



$$\left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O, \text{ and } C_2H_5.OH$$

for alcohol, and



$$\left.\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right\}N, \text{ and } C_2H_5.NH_2$$

for ethylamine; both show that the radicle C_2H_5 is linked to the groups OH and NH_2 respectively; the difference is simply that in the one case water and ammonia have been taken as the starting points, and in the other the hydrocarbon.

The hydroxyl hydrogen of an organic compound is frequently called the *typical* hydrogen; this simply means that if the compound were referred back to water, this hydrogen would belong to the type itself.

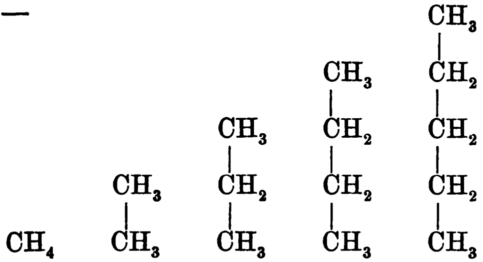
CHAPTER V

HOMOLOGOUS SERIES

COMPOUNDS are said to be homologues when they may be derived from each other by the substitution of methyl CH_3 for one atom of hydrogen; for each H replaced a CH_3 enters; the empirical formulæ of homologous compounds differ from each other therefore by $n(CH_3-H)=n(CH_2)$. One homologous series,[1] that, viz., of the saturated hydrocarbons, has already been mentioned :—

$$\begin{array}{l} CH_4 \\ C_2H_6 \\ C_3H_8 \\ C_4H_{10} \\ C_5H_{12}, \text{\&c.} \end{array}$$

The difference between each two members of the series is CH_2, as the following graphic representation shows :—



$$\begin{array}{ccccc} &&&& CH_3 \\ &&&& | \\ &&& CH_3 & CH_2 \\ &&& | & | \\ && CH_3 & CH_2 & CH_2 \\ && | & | & | \\ & CH_3 & CH_2 & CH_2 & CH_2 \\ & | & | & | & | \\ CH_4 & CH_3 & CH_3 & CH_3 & CH_3 \end{array}$$

---

[1] Schiel first called attention to the existence of these groups and called them 'progressive series.' Gerhardt gave them the name 'homologous series.'

A general formula can be given to the different compounds of a homologous series; for the above hydrocarbons this is C_nH_{2n+2}. Other series of homologous hydrocarbons are the following:—

$$\begin{array}{ll}
C_2H_4 & C_2H_2 \\
C_3H_6 & C_3H_4 \\
C_4H_8 & C_4H_6 \\
| & | \\
C_nH_{2n} & C_nH_{2n-2}
\end{array}$$

Not only the hydrocarbons, but all other organic compounds may be arranged in homologous series; for example, very many organic compounds are known which form the series having the following general formulæ:—

Alcohols	$C_nH_{2n+2}.O$	$= C_nH_{2n+1}.OH$
,,	$C_nH_{2n+2}.O_2$	$= C_nH_{2n}(OH)_2$
Acids	$C_nH_{2n}O_2$	$= C_nH_{2n+1}.CO_2H$
,,	$C_nH_{2n-2}.O_4$	$= C_nH_{2n}(CO_2H)_2$
Nitriles	$C_nH_{2n-1}N$	
Aldehydes	$C_nH_{2n}O$	
Hydrosulphides (Thioalcohols)	$C_nH_{2n+2}S$	

No limit (maximum value for *n*) to the homologous series is known.

Homologous series are characteristic of carbon compounds; nothing at all corresponding to them occurs in the compounds of other elements.

All compounds with the same general formula are not homologous, they must also be chemically similar substances. The difference between the empirical formula of acetic acid $C_2H_4O_2$, and that of methyl acetate $C_3H_6O_2$, is CH_2, but they are not therefore homologous; they belong to different classes of compounds—the first is an acid, the second an ester:—

$$\underset{\text{Acetic acid}}{CH_3.CO_2H} \qquad \underset{\text{Methyl acetate.}}{CH_3.CO_2CH_3}$$

Propionic acid $C_3H_6O_2 = CH_3.CH_2.CO_2H$ is however really homologous with acetic acid.

A general agreement in chemical properties is characteristic of homologous compounds. If the reactions and compounds of one substance belonging to such a series have been investigated the general behaviour of the other members will be known. The nearer two compounds stand in the series the more closely they agree in properties; the further apart they are the more they differ from one another. If homologous substances be subjected to like reactions homologous compounds will be formed. For example:—

$$\begin{aligned} CH_3.OH + HCl &= CH_3Cl + H_2O \\ C_2H_5.OH + HCl &= C_2H_5Cl + H_2O \\ C_3H_7.OH + HCl &= C_3H_7Cl + H_2O \end{aligned}$$

The general formula for the reaction is

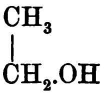
$$C_nH_{2n+1}.OH + HCl = C_nH_{2n+1}Cl + H_2O$$

$$\begin{aligned} CH_3Cl + KSH &= CH_3.SH + KCl \\ C_2H_5Cl + KSH &= C_2H_5.SH + KCl \\ C_3H_7Cl + KSH &= C_3H_7.SH + KCl \end{aligned}$$

The general formula for the reaction is

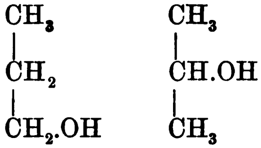
$$C_nH_{2n+1}Cl + KSH = C_nH_{2n+1}.SH + KCl$$

Organic compounds may be more or less homologous. The more alike the constitution of two homologous compounds is, the more closely do their chemical properties agree, and the more completely homologous they therefore are. The monad alcohols of the formula $C_nH_{2n+1}.OH$ form a homologous series, but all the compounds belonging to it are not homologous in the same degree. Two propyl-alcohols are known: one of these, the primary, shows much more likeness to ethyl alcohol than the other, the secondary.



$$\begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array}$$

Ethyl alcohol



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

Primary Secondary
propyl alcohol.

Ethyl alcohol is more truly homologous with primary propyl alcohol than with secondary because the position of the hydroxyl is alike in the first two but is different in the last one.

The same series can be divided into several classes, as for instance alcohols of the general formula $C_nH_{2n+1}OH$:—

	1	2	3	4
$CH_3.OH$	Methyl alcohol	—	—	—
$C_2H_5.OH$	Ethyl alcohol	—	—	—
$C_3H_7.OH$	Primary	Secondary	—	—
	propyl alcohol,			

	1	2	3	4
$C_4H_9.OH$	Normal primary	Secondary	Primary iso-	Tertiary
	butyl alcohol.			
$C_5H_{11}.OH$	Normal primary	Normal secondary (2)	Primary iso- (2)	Tertiary
	amyl alcohol.			

In the widest sense all these alcohols are homologous, but in the restricted sense only those belonging to the same class.

In the above only those compounds have been termed homologous whose formulæ differ by CH_2. Compounds belonging to the aromatic series are also homologous when their formulæ show a difference of C_6H_4 or C_4H_2, and their chemical properties correspond.[1]

Benzene . .	C_6H_6	Difference C_6H_4
Diphenyl . .	$C_{12}H_{10}$	
Diphenyl benzene	$C_{18}H_{14}$	
Triphenyl benzene	$C_{24}H_{18}$	

Benzene . .	C_6H_6	Difference C_4H_2
Naphthalene .	$C_{10}H_8$	
Phenanthrene .	$C_{14}H_{10}$	
Chrysene . .	$C_{18}H_{12}$	
Picene . .	$C_{22}H_{14}$	

Compounds such as $CH_3.OH$, $CH_3.Cl$, $CH_3.SH$, or $C_2H_5.OH$, $C_2H_5.Cl$, $C_2H_5.SH$, which contain the same

---

[1] G. Schultz (*Chemie des Steinkohlentheers*, 1882) called these compounds *aromatic homologues*.

radicle and can be easily derived from one another, form what is called a *heterologous* series.

The homologous and heterologous series form the groundwork of the system of organic chemistry. Each organic compound can be classed in a homologous and a heterologous series, so that as soon as the constitution of a substance is known its place in the system is determined. Many gaps still occur in the homologous series; the filling of them is, however, only a question of time. The missing members may in general be obtained by the methods ordinarily used for preparing the other compounds in the series; but the greater the number of known bodies, the less interest attaches to the filling of the gaps, because the properties of the new compounds are only repetitions, with unimportant modifications, of those of the substances already known.

CHAPTER VI

NOMENCLATURE AND DIVISION

THE naming of organic compounds has not been carried out according to any one uniform system. An attempt is made however to indicate as far as possible the constitution of a compound by its name, which therefore shows its inner composition and its general behaviour towards other substances. Bodies whose constitution has not yet been determined must be characterised by trivial names. This is particularly the case with the majority of the substances occurring in nature, such as the carbohydrates, the alkaloids, &c. These bear a name usually derived from that of the plant from which they were first prepared, as, for instance, the names mannitan, inulin, aniline, coniine, &c. Numerous compounds have retained their popular names even after their constitution has been ascertained, because in many cases these have been found to be simpler and more convenient than the rational ones.

The terms acetic acid, aniline, mercaptan, are generally used instead of the scientific names methyl carboxylic acid, amido-benzene, ethyl hydrosulphide. The rational terminology is much simplified owing to the fact that certain groups of atoms, *i.e.*, radicles, are recognised as occurring in organic compounds. According to Hofmann's system, which is the one in general use, at all events for compounds with open carbon chains, radicles which have the same general formula, and bear the same relation to saturated hydrocarbons, are distinguished by names derived in a similar manner from the corresponding hydrocarbon.

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_nH_{2n+2}
Methane	Ethane	Propane	Butane	Pentane.	(-ane)
CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}	C_nH_{2n+1}
Methyl	Ethyl	Propyl	Butyl	Pentyl.	(-yl)
CH_2	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_nH_{2n}
Methene	Ethylene	Propylene	Butylene	Pentylene.	(-ylene)
CH	C_2H_3	C_3H_5	C_4H_7	C_5H_9	C_nH_{2n-1}
Methenyl	Ethenyl	Propenyl	Butenyl	Pentenyl.	(-enyl)
	C_2H_2	C_3H_4	C_4H_6	C_5H_8	C_nH_{2n-2}
	Ethine	Propine	Butine	Pentine.	(-ine)

The above terms occur in the names of compounds containing these radicles, as for example, methyl alcohol, diethyl ether, &c.

The names of the radicles of acids are usually formed by adding -oyl or -yl to the stem of the name of the acid; thus, for instance, acetyl, succinyl, and benzoyl are the radicles of acetic, succinic, and benzoic acids respectively. The names of aromatic hydrocarbons generally end in -ene, as benzene, anthracene, toluene. The hydroxyl compounds of the hydrocarbons end in -ol, alcohol, phenol. Basic compounds end in -ine, as for example, amine, sulphine, hydrazine. In the case of sulphur compounds the prefix sulph- or thio- is used according to whether the sulphur is singly or doubly linked to a carbon atom.

Names are often derived from substitution processes. The compound C_2H_5Cl is called ethyl chloride because the presence in it of the radicle ethyl C_2H_5 is assumed, but it may also be looked upon as ethane in which one atom of hydrogen is replaced by chlorine, and it therefore also bears the name monochlorethane. If acetic acid be treated with chlorine, compounds are obtained which are named according to the number of hydrogen atoms replaced.

Monochloracetic acid	$CH_2Cl—CO_2H$
Dichloracetic acid	$CHCl_2—CO_2H$
Trichloracetic acid	$CCl_3—CO_2H$

The compound $C_6H_5.NH_2$ (aniline) may be called either phenylamine, in order to exhibit the radicle C_6H_5, or amido-benzene, so as to show its relation to benzene. In acids with open carbon chains substituting groups or elements are distinguished by the letters α, β, γ, &c., according to whether they are linked to the first, second, or third carbon atom counting from the carboxyl group.

$CH_3.CH_2.CHBr.CO_2H$	α-brombutyric acid.
$CH_3.CHBr.CH_2.CO_2H$	β-brombutyric acid.
$CH_2Br.CH_2.CH_2.CO_2H$	γ-brombutyric acid.

Compounds with closed carbon chains have their substitution positions indicated by numbers, one position being called 1, and the others 2, 3, 4, &c., in regular order; sometimes the letters of the Greek alphabet are used for this purpose as in the case of pyridine or naphthaline.

Von Baeyer has suggested that compounds with open carbon chains should have the terminal carbon atom distinguished by ω, and the following ones with α, β, γ.

$C_6H_5.CH_2.CH_2.CH_2Br$	ω-brompropyl benzene.
$C_6H_5.CH_2.CHBr.CH_3$	α-brompropyl benzene.
$C_6H_5.CHBr.CH_2.CH_3$	β-brompropyl benzene.

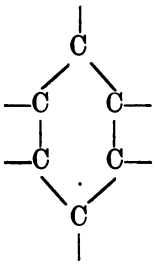
The terms ortho-, meta-, and para- are frequently abbreviated to o-, m-, p-. The benzene nucleus is sometimes represented by B, and the pyridine nucleus by Py.

Organic compounds are divided into two classes, viz., *fatty* and *aromatic* bodies. The division is founded on a difference in the linking of the atoms, and a consequent difference in the general chemical behaviour of the substances. The fatty compounds are so called from a number of bodies belonging to the group which have long been known, and which occur in vegetable and animal fats. The old name has been generally retained, although only a small number of bodies in this group are really fats; it is more rational to term them methane derivatives, because they can all be theoretically derived from the simple hydrocarbon methane. In these compounds the carbon atoms are so linked together that *open chains* are formed.

The fatty bodies are divided into *saturated* and *unsaturated* compounds, according to whether all the available valencies of the carbon chain are satisfied or not. A systematic division on this principle cannot however be very easily strictly enforced.

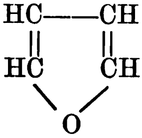
If the division of the methane derivatives into subdivisions were consistently carried out, it would be necessary to start from the different hydrocarbons, and give in series the compounds which are formed from them by the replacement of one, two, three, &c., atoms of hydrogen. Such a system would be too artificial, because many generically similar bodies would be widely separated. The generic principle must be introduced into the systematic arrangement and classification of organic compounds, particularly of the fatty bodies, but it should not form the sole ground of such classification.

The *aromatic compounds* are so called because many of those first known were resins, ethereal oils, balsams, &c. Like the fatty compounds they have retained their old name although most of them do not possess the properties included in the term 'aromatic;' a better name for these substances would be that of benzene derivatives, or benzenoids, because they may all be derived from the hydrocarbon benzene C_6H_6. Aromatic compounds contain at least six atoms of carbon in the molecule, which are so arranged as to form a *closed chain or ring* (Benzene nucleus) :—

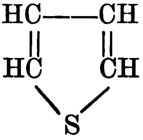


This carbon chain is very stable. The aromatic compounds are richer in carbon than the fatty bodies, the carbon in them is more condensed, they are consequently harder to burn than the fatty compounds, and during their combustion deposit carbon in considerable quantity. Compared with the fatty bodies the aromatic compounds show many chemical peculiarities, due partly to their higher percentage of carbon, and partly to the stability of the atomic linking.

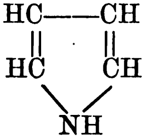
The furfuran, thiophene, and pyrrol compounds form a special class; their atoms are linked as shown below:—



Furfuran

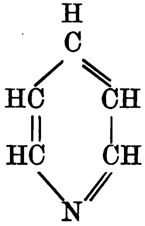


Thiophene



Pyrrol.

The *pyridine*, quinoline, and acridine derivatives form a separate series of carbon compounds; they contain a closed chain consisting of *five carbon atoms and one nitrogen atom*:—



Pyridine.

The compounds belonging to some of these groups, especially the thiophene derivatives, behave exactly like benzene derivatives; they may therefore be classed as 'aromatic' compounds, using the word in its widest sense.

It is of course quite obvious that a compound may be related in composition to two or more of the chief groups of organic substances.

The constitution of a number of bodies occurring in organic nature is at present unknown, and the compounds themselves cannot therefore be arranged in the system of organic chemistry; they are usually classed together under the term *bodies of unknown constitution.* The number of such compounds is continually decreasing, as the substances are gradually subjected to chemical investigation and research. They form different groups such as alkaloids, bitters, glucosides, &c.

PART II

THE PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS

CHAPTER VII

INTRODUCTORY REMARKS. CRYSTALLINE FORM. SOLUBILITY

CERTAIN physical properties such as crystalline form, specific gravity, melting and boiling points, are important characteristics of organic compounds. A comparative study of the physical properties of these compounds possesses much interest of a general nature, for it is by such means that we determine the relations between external properties and internal composition and constitution, and in how far the former are dependent upon the latter. After the determination of the relations between composition and properties, the further question arises, *why* a certain internal constitution causes certain definite properties. Comparative researches of the above nature have only been possible during late years, when a large number of organic compounds have been prepared and accurately investigated, so that it has been possible to obtain a glimpse into their inner constitution. Little had been previously done in this direction, though isolated rules had been deduced by a comparison of allied and isomeric compounds. Most of the properties which are now to be considered are of a *constitutional* kind, that is to say they are more or less dependent not only upon the nature and number of the elementary atoms, but also upon their arrangement in the molecule, *i.e.*, upon the constitution of the compound.

CRYSTALLINE FORM.

Isomorphism frequently occurs between homologous compounds or similar substitution products. According to Groth's researches, a definite alteration in crystalline form is produced in aromatic compounds when hydrogen is replaced by some other element or radicle. He lays down the following rules:—

(1) If hydrogen be replaced by OH, or NO_2, two axes (a and b) remain unaffected; only the third (c) undergoes an alteration, which increases with each additional NO_2 group.

(2) The substitution of halogens for hydrogen causes the crystalline form to change to one less regular. This phenomenon is called *morphotropism.* Nothing more is known of the relation between the internal composition and crystalline form of organic compounds. Researches on this subject would be full of interest both chemically and crystallographically.

SOLUBILITY.

Organic compounds containing only carbon and hydrogen are either only slightly soluble or insoluble in *water*; those containing oxygen are more soluble, and as a rule, the solubility increases in proportion to the quantity of oxygen. In the homologous series of the fatty group solubility in water decreases with increasing molecular weights. Compounds rich in carbon, such as the aromatic bodies, are in general more insoluble than those containing less carbon.

Most organic substances are soluble in *alcohol*, many of them also in *ether*. The solubility in ether decreases with the quantity of oxygen present, especially if the oxygen be in the form of hydroxyl as in the alcohols. Many organic compounds dissolve readily in *carbon disulphide*, *chloroform*, *benzene*, and other liquids. According to Raoult's experiments the temperatures at which the aqueous, benzene, and acetic acid solutions of organic compounds freeze, bear definite relations to the molecular weights of the substances dissolved. A like number of molecules dissolved in a similar quantity of water exerts almost the same influence in lowering the freezing point. See also page 7.

CHAPTER VIII

SPECIFIC GRAVITY. SPECIFIC VOLUME

Specific gravity is one of the most important physical characteristics of liquids; it has therefore been determined for the majority of organic compounds which are liquid at ordinary temperatures. In order to obtain directly comparable values the determinations are usually made at a temperature of 20 degs., the density of water at 4 degs. being taken as the unit.

In the homologous series of the fatty group, the specific gravity decreases as the quantity of carbon in the compounds becomes greater:—

		Specific gravity
Acetic acid .	. $C_2H_4O_2$	1·063
Propionic acid	. $C_3H_6O_2$	0·991
Butyric acid	. $C_4H_8O_2$	0·958

The same holds for the homologous benzene hydrocarbons:—

		Specific gravity
Benzene .	. C_6H_6	0·8995
Toluene .	. C_7H_8	0·8841
Xylene .	. C_8H_{10}	0·8770
Cymene .	. $C_{10}H_{14}$	0·8732

Researches comparing *specific or molecular volumes*, *i.e.*, the quotient of the molecular weight and specific gravity of organic compounds, have led to interesting results.

All liquids do not expand to the same degree when raised through the same interval of temperature; in order therefore to obtain comparable numbers from the specific volumes, it is necessary to make these determinations when the thermal condition of the compounds is the same, that is to say, at the temperature at which a change of state occurs. Kopp proposed that the determinations should be made at a temperature as near to the boiling point as possible. Such determinations are very difficult to make in the case of bodies with high boiling points; the specific gravities of such substances are therefore determined at a lower temperature, and by means of the dilatometer the coefficient of expansion is also measured. Specific volume determinations have been chiefly carried out by Kopp, Buff, Ramsay, Thorpe, R. Schiff, and Brühl. Isomeric saturated compounds have almost, but not quite, the same specific volumes. This property is of course only slightly affected by differences in constitution.

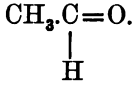
In homologous series the molecular volume increases by about 22 for each additional CH_2 :—

		Mol. wt.	Mol. vol.	Difference
Formic acid	CH_2O_2	46	41·4	
				22·3
Acetic acid	$C_2H_4O_2$	60	63·7	
				21·7
Propionic acid	$C_3H_6O_2$	74	85·4	
				21·7
Butyric acid	$C_4H_8O_2$	88	107·1	
				23·6
Valeric acid	$C_5H_{10}O_2$	92	130·7	

The difference is not so constant in all homologous series as in the above.

Compounds containing the same quantity of oxygen but with a difference of $C_n + (H_2)_n$ possess the same specific volume. One atom of carbon causes therefore the same alteration as two atoms of hydrogen, but the difference in the molecular volume for CH_2 equals 22, therefore the difference for one C atom = 11 and for $H_2 = 11$, or for one atom of hydrogen 5·5. These numbers, 11 and 5·5, are regarded as the atomic volumes of carbon and hydrogen. In a similar way the atomic volumes of oxygen, sulphur, nitrogen, chlorine, bromine, and iodine have been determined, but the numbers cannot be regarded as absolutely correct. It should be particularly noted that the above *polyvalent* elements show a *different specific volume according to the manner in which they are linked to the carbon atom.* The specific volume (atomic volume) for *singly* linked *oxygen* equals 7·8, and for *doubly* linked 12·2. Sulphur and nitrogen behave in a similar manner. This property renders it possible, by an estimation of the specific volume, to determine how the oxygen, nitrogen, or sulphur in a compound is linked to the carbon.

For example, it is required to determine whether aldehyde should be represented by the formula $C_2H_3.OH$ or



$$\begin{array}{l} CH_3.C{=}O. \\ \quad\;\;\,| \\ \quad\;\;\,H \end{array}$$

According to the first formula the specific volume would be $(2 \times 11) + (4 \times 5{\cdot}5) + 7{\cdot}8 = 51{\cdot}8$; according to the second $(2 \times 11) + (4 \times 5{\cdot}5) + 12{\cdot}2 = 56{\cdot}2$. The molecular volume of aldehyde calculated from the specific gravity is found to be 56·4; the constitution therefore corresponds to the second of the above formulæ.

Carbon itself does not always possess the same specific volume; it varies according to the way in which it is linked to other carbon atoms. The atomic volume of *singly* linked carbon is 11, but according to R. Schiff every *double* bond causes an increase of 4 units in the volume. Isomeric saturated and unsaturated compounds possess therefore different specific volumes. This clearly shows that the so-called double bonds are *not more intimate linkings of carbon atoms, but are on the contrary weaker* than the single ones. It may be mentioned that the benzene derivatives do not show such a high specific volume as would be expected from the presence of the three double bonds assumed in Kekulé's formula.

CHAPTER IX

MELTING POINT

EVERY solid compound capable of being melted, melts when pure at a definite temperature; the slightest impurity may however lower the melting point considerably. Kolbe (1860) believed that he had obtained an acid isomeric with benzoic acid which he called salylic acid. Beilstein however showed that Kolbe's acid was only ordinary benzoic acid containing a trace of chlorobenzoic acid, but so small was the quantity of chlorobenzoic acid present that it could scarcely be detected by analysis.

A mixture of two substances frequently melts at a lower temperature than either of its components. A mixture of equal parts of stearic acid (M.P. 69·2°) and palmitic acid (M.P. 62°) melts at 59°. A mixture of equal parts of metaoxybenzoic acid (M.P. 200°) and paraoxybenzoic acid (M.P. 210°) melts at 143–152°. These phenomena agree with those observed in the case of many alloys.

In homologous series the melting point usually increases with the molecular weight, though occasionally the opposite of this occurs. It has been observed, curiously enough, that in certain homologous series of compounds of normal structure, the melting point alternately rises and falls; the compounds containing an uneven number of carbon atoms possessing the lowest melting point.

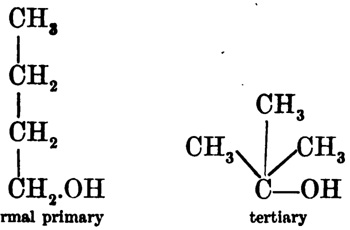
Normal acids of the formula $C_nH_{2n}O_2$:—

	M.P.		M.P.
CH_2O_2	2°	$C_2H_4O_2$	+ 17°
$C_3H_6O_2$ under	− 21°	$C_4H_8O_2$	0°
$C_5H_{10}O_2$,,	− 16°	$C_6H_{12}O_2$	− 2°
$C_7H_{14}O_2$	−10·5°	$C_8H_{16}O_2$	+ 16°
$C_9H_{18}O_2$	+ 12°	$C_{10}H_{20}O_2$	+ 30°
$C_{11}H_{22}O_2$	+ 28°	$C_{12}H_{24}O_2$	+43·6°
$C_{15}H_{30}O_2$	+ 51°	$C_{16}H_{32}O_2$	+ 62°
$C_{17}H_{34}O_2$	+59·9°	$C_{18}H_{36}O_2$	+69·2°

Normal acids of the formula $C_nH_{2n-2}O_4$:—

	M.P.		M.P.
$C_3H_4O_4$	132°	$C_4H_6O_4$	180°
$C_5H_8O_4$	97°	$C_6H_{10}O_4$	148°
$C_7H_{12}O_4$	103°	$C_8H_{14}O_4$	140°
$C_9H_{16}O_4$	106°	$C_{10}H_{18}O_4$	127°
$C_{11}H_{20}O_4$	108°		

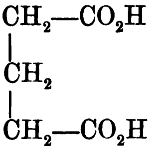
The derivatives of these acids show the same relations. The group methyl (CH_3) causes a rise in the melting point.



Normal primary (liquid)

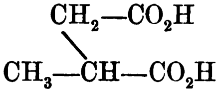
tertiary (M.P. 25°).

butyl alcohol.

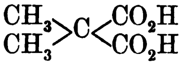


$$\begin{array}{l} CH_2-CO_2H \\ | \\ CH_2 \\ | \\ CH_2-CO_2H \end{array}$$

Glutaric acid
(M.P. 97°)



Pyrotartaric acid
(M.P. 112°)



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}{>}C{<}\begin{matrix} CO_2H \\ CO_2H \end{matrix}$$

Dimethylmalonic acid
(M.P. 170°).

If the hydrogen of a hydroxyl group be replaced by an alkyle radicle, as for example when an acid is converted into an ester, or an alcohol into an ether, the melting point of the compound is lowered, provided that the quantity of carbon in the radicle introduced is not proportionately very much greater than that contained in the hydroxyl compound:—

$C_4H_4O_2(OH)_2$ Succinic acid (M.P. 180°)

$C_4H_4O_2(OCH_3)_2$ Methyl succinate (M.P. 20°)

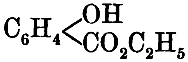
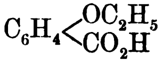
$C_4H_4O_2(OC_2H_5)_2$ Ethyl succinate (liquid)

$C_{16}H_{33}.OH$ Cetyl alcohol (M.P. 55°)

$C_{16}H_{33}.OC_2H_5$ Cetylethyl ether (M.P. 20°).

The formation of esters causes a greater lowering of the melting point than the formation of ethers, as is seen by a comparison of ether acids with isomeric oxyacid esters:—

		M.P.
Salicylic acid . .	$C_6H_4{<}\begin{matrix} OH \\ CO_2H \end{matrix}$	156°
Methylsalicylate . .	$C_6H_4{<}\begin{matrix} OH \\ CO_2CH_3 \end{matrix}$	Liquid
Orthomethoxybenzoic acid	$C_6H_4{<}\begin{matrix} OCH_3 \\ CO_2H \end{matrix}$	98·5°
Metaoxybenzoic acid .	$C_6H_4{<}\begin{matrix} OH \\ CO_2H \end{matrix}$	200°

Ethylmetaoxybenzoate	 $C_6H_4<\begin{matrix}OH\\CO_2C_2H_5\end{matrix}$	72°
Metaethoxybenzoic acid	 $C_6H_4<\begin{matrix}OC_2H_5\\CO_2H\end{matrix}$	137°

The para compounds of the aromatic series usually melt at higher temperatures than the isomeric ortho- and meta- compounds. Of the three cresols $C_7H_7.OH$, the meta- compound is liquid, the ortho- compound melts at 31°, and paracresol melts at 36°. Ortho- and meta- xylene are liquid, whilst paraxylenemelts at 15°.

It is also worthy of note that if the hydrogen in benzene be replaced by chlorine or bromine, the melting point of the compounds formed alternately rises and falls :—

	M.P.		M.P.
C_6H_6	+3°	C_6H_6	+3°
C_6H_5Cl	−40°	C_6H_5Br	Liquid
$C_6H_4Cl_2$ (Para)	+56°	$C_6H_4Br_2$ (Para)	+89°
$C_6H_3Cl_3$ (Unsymmetrical)	+17°	$C_6H_3Br_3$ (Unsymmetrical)	+44°
$C_6H_2Cl_4$ (Symmetrical)	138°	$C_6H_2Br_4$ (Symmetrical)	139°
C_6HCl_5	86°	C_6HBr_5	about 240°
C_6Cl_6	226°	C_6Br_6	above 310°

Similar results have been observed when the hydrogen in acetic acid is replaced by halogens :—

	M.P.		M.P.
$C_2H_4O_2$	17°		
$C_2H_3ClO_2$	62°	$C_2H_3BrO_2$	about 100°
$C_2H_2Cl_2O_2$	under 0°	$C_2H_2Br_2O_2$	45°–50°
$C_2HCl_3O_2$	52°	$C_2HBr_3O_2$	135°

The melting points of other groups of compounds show an analogous regularity, but no general law expressing the relation between the melting point and the constitution of compounds is known.

CHAPTER X

BOILING POINTS

THE boiling point is an important characteristic of substances volatile without decomposition. In general, a constant boiling point is a sure sign of the chemical purity of a compound.

In the case of a homogeneous mixture of liquids whose boiling points lie near each other, simple distillation is insufficient to effect a separation; the boiling point is never constant, and the various substances go over together at intermediate temperatures. The method usually adopted is to collect separately all that comes over between each 5° or 10°, and then subject these portions to a fresh distillation. After a number of such fractional distillations have been performed, larger quantities of the liquids collect at the respective boiling points of the compounds in the mixture.

The following example[1] serves to show how inadequate simple distillation is in effecting the separation of *two* liquids, whose boiling points are not particularly near to each other.

Two hundred gr. of a mixture of equal parts of ethyl alcohol (B.P. 78·3 degs.) and amyl alcohol (B.P. 132 degs.) were distilled, and the distillates for each 10° kept separate.

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[1] Roscoe and Schorlemmer, *Treatise of Chemistry*, Vol. 3. Pt. 1, P. 148.

Temperature °C.	80–90	90–100	100–110	110–120	120–130	130–131	131–132
Weight of distillate in grms.	47	45	25	14	18	11	36
Ethyl alcohol % .	88·1	82·0	61·5	52·1	14·4	4·5	0·2
Amyl alcohol % .	11·9	18·0	38·5	47·9	85·6	95·5	99·8
	100·0	100·0	100·0	100·0	100·0	100·0	100·0

The separation of a mixture of several different liquids by distillation would be, of course, much more difficult. The hydrocarbons possess the lowest boiling points of all compounds with a like carbon nucleus. Hydrogen increases the volatility; the more hydrogen a substance contains the lower is its boiling point.

		B.P.
Isopentane .	. C_5H_{12}	30°
Isoamylene .	. C_5H_{10}	35
Butyric acid .	. $C_4H_8O_2$	162
Crotonic acid	. $C_4H_6O_2$	180–182

Oxygen acts in the opposite way to hydrogen—it renders a compound less volatile. The boiling point is raised as a rule 40 degs., by the oxidation of an alcohol group $-CH_2OH$ to a carboxyl group $-CO.OH$.

If two substances unite together, with simultaneous formation of water, the boiling point of the resulting compound is equal to the sum of the boiling points of the components minus 100–120 degs. (*Berthelot*).

Acetic acid boils at .	118°
Ethyl alcohol „ .	78·5°
Sum . .	196·5°
Acetic ether boils at . .	77°
Difference .	119·5°

Ethyl alcohol boils at .	78·5°
Ethyl alcohol „ .	78·5°
Sum . .	157°
Ethyl ether boils at . .	35°
Difference .	122°

The replacement of an atom of hydrogen by a halogen usually causes a considerable rise in the boiling point; a chlorine atom effects an increase of about 40 degs.

In homologous series the boiling point rises with increasing molecular weights; this increase is often about 20 degs. for homologous compounds whose atoms are linked together in a strictly analogous manner.

Normal primary alcohols of the formula $C_nH_{2n+2}O$:—

	B.P. °C.	Difference
C_2H_6O	78·4	19
C_3H_8O	97·4	19·5
$C_4H_{10}O$	116·9	21·1
$C_5H_{12}O$	138	20
$C_6H_{14}O$	158	18
$C_7H_{16}O$	176	16
$C_8H_{18}O$	192	

Normal acids of the formula $C_nH_{2n}O_2$:—

	B.P.	Difference
$C_2H_4O_2$	118·1°	22·6
$C_3H_6O_2$	140·7	21·6
$C_4H_8O_2$	162·3	22·7
$C_5H_{10}O_2$	185	20
$C_6H_{12}O_2$	205	19
$C_7H_{14}O_2$	224	13
$C_8H_{16}O_2$	237	

Goldstein has given a general formula for calculating the boiling points of the normal hydrocarbons of the formula C_nH_{2n+2}, for every CH_2 the boiling point increases by $19 + \frac{380}{n(n+1)}$; for example :—

	Observed B.P. °C.	Calculated B.P. °C.
C_4H_{10}	1	1
C_5H_{12}	39	39
C_6H_{14}	70	70·6
C_7H_{16}	98·4	98·6
C_8H_{18}	124	122·4

From the above examples it is seen that the difference is not a constant number, but that it decreases with increasing molecular weight.

It is only natural that the rising of the boiling points should be limited; if, for instance, the boiling points of the fatty acid series increased 19 degs. for each member, from formic acid to the acid $C_{30}H_{60}O_2$, the calculated boiling point of this latter compound would be 100° + (29 × 19°) = 651°, a temperature at which all organic compounds are decomposed. Many organic compounds with particularly high molecular weights decompose before they volatilise; they cannot therefore be distilled at ordinary pressures, many of them may however be distilled in a vacuum. The volatility of an organic compound depends not only on the nature and quantity of its constituent elements, but also on the atomic linking.

Isomeric compounds of similar constitution show in general the same volatility, but considerable differences are often observed in the boiling points of isomeric compounds with different constitutions :—

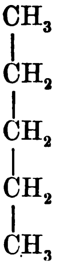
		B.P. °C.	Difference °C.
Methyl acetate .	$C_3H_6O_2$	56	1
Ethyl formate .	$C_3H_6O_2$	55	85
Propionic acid .	$C_3H_6O_2$	140	

A hydroxyl compound usually possesses a higher boiling point than a compound containing no hydroxyl; for example, the ethers and esters are more volatile than the isomeric alcohols and acids :—

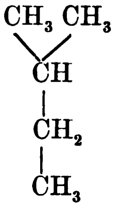
		B.P. °C.
Alcohol . .	$CH_3CH_2.OH$	78·4
Dimethyl ether .	$CH_3.O.CH_3$	—20
Butyric acid .	$CH_3.CH_2.CH_2.CO.OH$	162
Ethyl acetate .	$CH_3.CO.O.CH_2.CH_3$	74

The compounds termed aldehydes and ketones, which contain oxygen but no hydroxyl, are comparatively easily volatile; the lactones on the other hand, the oxygen of which is also not in the form of hydroxyl, have a higher boiling point than the isomeric unsaturated acids.

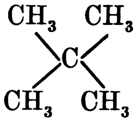
Compounds containing tertiary or quaternary linked carbon atoms, have lower boiling points than their isomers with normal carbon chains. The boiling point sinks as the number of side chains increases. The introduction of the methyl group into compounds produces an effect on the boiling point exactly opposite to that produced on the melting point.



Normal pentane
(B.P. 39°)



Isopentane
(B.P. 30°)

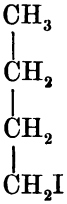


Tetramethylmethane
(B.P. 9·5°).

Boiling points of acids of the formula $C_5H_{10}O_2$:—

Normal valeric acid	184°
Isovaleric acid	175°
Trimethylacetic acid	161°

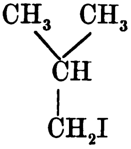
With regard to the influence of isomerism of position, the secondary and tertiary compounds of the monosubstituted hydrocarbons, boil at lower temperatures than the primary compounds:—



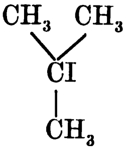
Primary
(B.P. 129°)

Secondary
(B.P. 117°-118)

Normal butyl iodide



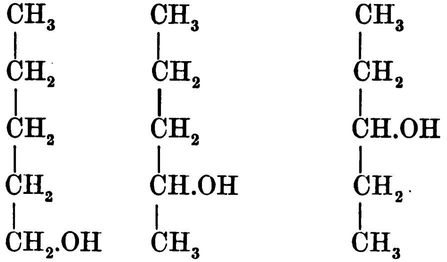
Primary
(B.P. 120·5°)



Tertiary
(B.P. 99°)

Isobutyl iodide.

Isomeric compounds containing oxygen, and having like carbon nuclei, have a lower boiling point the nearer the oxygen is to the middle of the carbon chain. Primary alcohols almost always boil 19° higher than isomeric secondary alcohols:—



$$CH_3-CH_2-CH_2-CH_2-CH_2.OH \qquad CH_3-CH_2-CH_2-CH.OH-CH_3 \qquad CH_3-CH_2-CH.OH-CH_2-CH_3$$

Primary (B.P. 137°) α-Secondary (B.P. 118·5°) β-Secondary (B.P. 116°-117°)

Amyl alcohol.

Halogen substitution products of the hydrocarbons, like the oxygen compounds, boil at a lower temperature the nearer the halogen approaches the middle of the carbon chain. In the case of isomers with more than one halogen atom, the compound in which the halogens are closest together has the lowest boiling point:—

$CH_2Cl—CH_2Cl$ Ethylene chloride (B.P. 85°)

$CH_3—CHCl_2$ Ethidine chloride (B.P. 58°)

Corresponding methylketones, methyl esters, and acid chlorides have almost the same boiling points (Schröder):—

		B.P.
Acetone	$CH_3.CO.CH_3$	56·3°
Methyl acetate	$CH_3.CO.OCH_3$	56·3°
Acetyl chloride	$CH_3.CO.Cl$	55°–56°
Propylmethyl ketone	$C_3H_7.CO.CH_3$	102·3°
Methyl butyrate	$C_3H_7.CO.OCH_3$	102°–105°
Butyryl chloride	$C_3H_7CO.Cl$	100°–101·5°

The groups —$CO.CH_3$, —$CO.OCH_3$, and —$CO.Cl$ exert the same influence on the boiling point.

A similar agreement has been observed in the boiling points of corresponding phenols and amido compounds (Markwald):—

	B.P.
$C_6H_5.OH$	183°
$C_6H_5.NH_2$	183°
$C_6H_4(CH_3)OH(p)$	198°
$C_6H_4(CH_3)NH_2(p)$	198°

A number of other uniformities have been shown to exist, but no general law is known expressing the relation between volatility and atomic linking.

CHAPTER XI

HEAT OF COMBUSTION AND HEAT OF FORMATION

Thermal phenomena go hand in hand with chemical phenomena. Numerous thermo-chemical researches have been made of late years, particularly by Berthelot and J. Thomsen; as the result, it has been found that the principles of the mechanical theory of heat may be applied to explain many chemical phenomena. As regards *organic* compounds alone, only little is known of their thermo-chemical behaviour. An important problem connected with this subject is the discovery of the relations between chemical constitution and thermal properties.

Isomeric compounds with different constitutions have different heats of combustion.—The reason for this is very simple. Heat of combustion may be divided into two factors, viz.(1) the sum of the heats of combustion of the elements contained in the compound(2) and the quantity of heat required to overcome the mutual attractions of the atoms in the molecule. The first of these factors is the same for isomeric compounds, but the second may differ; it must however be the same as the *heat of formation*, that is to say, the quantity of heat absorbed or evolved on the formation of the compound. Heat of formation may be either positive or negative.

Thomsen has determined the heats of combustion of a number of simple hydrocarbons, and has calculated from these data their heats of formation; from the numbers thus obtained he has attempted to estimate the thermal values of the different kinds of bonds between two carbon atoms. He found for

the first valency	+	14805°
„ second „	+	228°
„ third „	–	14345°[1]

Thomsen used these numbers in order to determine how the carbon atoms are linked together in hydrocarbons such as benzene, which contain little hydrogen. From the above data different values would be obtained by calculation for the heats of combustion and formation of benzene, according to whether its constitution were represented by Kekulé's formula with three double and three single bonds, or by a formula with nine single bonds. Calculated heat of formation (for constant pressure):—

According to Kekulé's formula —59200c.
„ formula with single bonds —15490c.

The heat of combustion for six atoms of carbon and six atoms of hydrogen is:—

$$6(C, O_2) + 3(H_2, O) = 6 \cdot 96960 + 3 \times 68360 = 786840c.$$

The theoretical heat of combustion in the first case (Kekulé) would be 786840 + 59200 = 846040c.; and in

---

[1] This only holds on the understanding that in ethylene and acetylene respectively, a double and triple bond exists between the carbon atoms.

the second case 786840 + 15490 = 802330c. Thomsen found the heat of combustion of benzene to be 805800c, and concluded therefore that in benzene the carbon atoms are linked by nine simple bonds, and not by three double and three single ones, as Kekulé's formula indicates.

The above serves to show how far thermo-chemical numbers may be applied to the solution of constitutional problems in organic chemistry.

All researches prove that unsaturated compounds possess a greater heat of combustion than saturated ones; their heats of formation are therefore less, and their energy greater, than that of compounds containing carbon atoms linked only by single bonds. The thermal behaviour of unsaturated compounds also shows that the so-called *double bond is a weaker*, *not a stronger*, *form of atomic attraction than the simple bond.*

CHAPTER XII

OPTICAL PROPERTIES

Refraction of light.—Different liquid organic compounds refract light differently. If i be the angle of incidence and r the angle of refraction, the *refractive index*, which is constant for every compound, is $n = \frac{\sin i}{\sin r}$. The *specific refractive energy* of a compound is given by the expression $\frac{n-1}{d}$, where d = the density of the substance. The product of this empirically found quantity with the molecular weight, is termed the *molecular refractive energy* or *refraction-equivalent.*

The molecular refractive energy of a number of organic compounds has been determined, chiefly by Landolt, Gladstone, Brühl, &c.; it has been found to increase by about 7·6—7·8 for every additional CH_2 in homologous series of compounds:—

		$\frac{n-1}{d}.m$	Difference.
Ethyl alcohol	$C_2H_5.OH$	20·70	
			7·60
Propyl alcohol	$C_3H_7.OH$	28·30	
			7·81
Butyl alcohol	$C_4H_9.OH$	36·11	
			7·78
Amyl alcohol	$C_5H_{11}.OH$	43·89	

Isomeric saturated compounds have the same, or nearly the same, refractive energy, which is therefore *independent of the atomic grouping.* The theoretical refraction-equivalents of the *elementary atoms* have been calculated from a comparison of the molecular refractive energy of different saturated compounds. The following results have been obtained ($\lambda = \infty$):—

The atomic refraction for 1 atom of C = 4·86 (5).
„ „ „ „ 1 „ H = 1·29 (1·3).
„ „ „ „ 1 „ O = 2·71 (2·8).
„ „ „ „ 1 „ N = 5·35 (4·1).

The refraction equivalent of a saturated molecule is equal to the sum of the refraction equivalents of the atoms contained in it. The molecular refractive energy of *unsaturated* compounds is greater than that calculated from the refraction equivalents of their constituent atoms; each double bond causes an increase of 1·78 in the refractive power (Brühl). The molecular refractive power of benzene = 42·16, the formula C_6H_6 requires 36·90; the difference 5·26 would appear to point to the existence of three double bonds in the molecule.

Compounds containing a doubly linked oxygen atom show a greater refractive energy than the theory would indicate. Brühl calculated the atomic refraction for $\overset{\|}{O} = 3{\cdot}29$ (3·40).

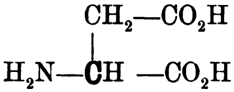
Sulphur also shows a refraction equivalent varying according to the manner in which the atom is linked.

The refractive power of solid bodies may be calculated from the refractive power of their solutions, provided of course that the solvent exerts no chemical action on the substance under examination.

Circular polarisation. (Optical rotatory power).—Many organic substances have the power, when in the liquid state or in solution, of turning the plane of polarisation of a ray of light to the left or to the right. Compounds which show *circular polarisation* are termed *optically active.* Optical activity is particularly shown by a number of substances which occur in nature, such as, for instance, vegetable acids, carbohydrates, ethereal oils, &c.; a number of optically active substances have however been artificially prepared.

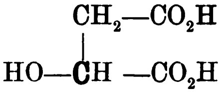
It has been discovered that certain compounds, such as turpentine oil, and camphor, retain their optical activity when in the gaseous state; the activity is therefore dependent on the grouping of the atoms composing the separate molecules, not on the constitution as represented on a plane surface, but upon the *geometrical structure.* Optically active substances may often be converted into isomeric inactive bodies without any alteration in chemical constitution occurring.

All optically active substances contain one or more *asymmetric* carbon atoms (see p. 39), (Le Bel, Van 't Hoff); their derivatives retain their activity so long as the carbon atom remains asymmetric; if the asymmetry be lost the activity ceases: —



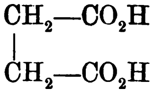
$$\begin{array}{l} \qquad\quad CH_2-CO_2H \\ \qquad\quad | \\ H_2N-CH-CO_2H \end{array}$$

Aspartic acid
active



$$\begin{array}{l} \qquad CH_2-CO_2H \\ \qquad | \\ HO-CH-CO_2H \end{array}$$

Malic acid
active

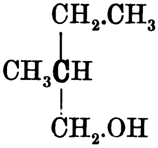


$$\begin{array}{l} CH_2-CO_2H \\ | \\ CH_2-CO_2H \end{array}$$

Succinic acid
inactive.

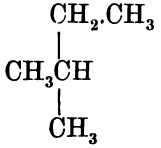
Active aspartic acid is converted into active malic acid by the action of nitrous acid; by treating malic acid with hydriodic acid, succinic acid is formed, which is inactive.

The following further examples may be given :—



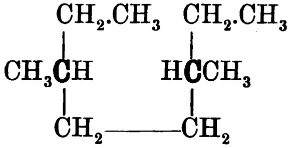
$$\begin{array}{c} \mathrm{CH_2.CH_3} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH_2.OH} \end{array}$$

Amyl alcohol
active



$$\begin{array}{c} \mathrm{CH_2.CH_3} \\ | \\ \mathrm{CH_3CH} \\ | \\ \mathrm{CH_3} \end{array}$$

Dimethylethylmethane
inactive



$$\begin{array}{ccc} \mathrm{CH_2.CH_3} & & \mathrm{CH_2.CH_3} \\ | & & | \\ \mathrm{CH_3CH} & & \mathrm{HCCH_3} \\ | & & | \\ \mathrm{CH_2} & \text{———} & \mathrm{CH_2} \end{array}$$

Diamyl
active.

Certain inactive substances may be split up into two forms showing opposite activity; for instance, dextro- and lævo-rotatory tartaric acids can be obtained from racemic acid.

Certain inactive acids give an active acid when they are exposed to the action of some organised ferment (Lewkowitsch); the one component of the inactive acid is destroyed by the ferment; this is the case, for instance, with lactic and dioxypropionic acids.

It should be noted that all compounds containing an asymmetric carbon atom do not occur in an optically active form; this applies more particularly to a number of substances which have only been prepared artificially.

The *specific rotatory power* $[a] = \frac{100a}{l\,r\,d}$, where

a = the observed angle of rotation of the plane of polarisation of light of given wave length.
l = the length of the column of liquid in decimetres.
d = the density of the liquid referred to water at 4°.
r = percentage of active substance.

The specific rotatory power is constant for the same substance, but only if the temperature remain unchanged; a rise in temperature frequently causes a decrease in rotatory power.

The specific rotatory power of an active substance depends largely on the solvent, and on the concentration of the solution. Certain active bodies show opposite rotatory power when dissolved in different solvents. Asparagine and aspartic acid are lævo-rotatory in alkaline solutions, and dextro-rotatory in acid ones.

The specific rotatory power is an important characteristic of many organic compounds; the conditions under which it was determined must be given—in particular the kind of light, the temperature, and the nature and quantity of the solvent, should be stated. The direction of rotation is indicated by + (right) and − (left). Extensive researches have been conducted of late years by W. H. Perkin, sen., on the rotatory power of liquid organic compounds such as hydrocarbons, alcohols, ethers, acids, &c., when under magnetic influence. The quantity $\frac{r\,m}{r_1\,m_1\,d}$ is termed the *magnetic molecular rotatory power*, m = the molecular weight, d the density, and r the magnetic rotatory power of the substance, whilst r_1 indicates the molecular rotatory power of water calculated under the same conditions as r, and m_1 is the molecular weight of water. All the determinations were made with yellow monochromatic light.

From the numerous deductions which Perkin has drawn from his researches the following may be selected. In all homologous series, the magnetic rotatory power increases in proportion to the number of carbon atoms; if this number be designated by n, then the magnetic molecular rotatory power equals $a + n$ 1·023; in this expression the number 1·023 indicates the constant increase for each CH_2 group, a is a number different for each homologous series but constant for the same one. It has been determined for many different series, as for example:—

Normal hydrocarbons C_nH_{2n+2} = 0·508
Iso ,, ,, = 0·621
Normal primary alcohols $C_nH_{2n+2}O$ = 0·699
,, acids $C_nH_{2n}O_2$ = 0·393.

The calculated magnetic molecular rotatory power for different members of different series agrees in general with the results obtained by direct experiment; this physical property may therefore be applied with advantage in certain cases to determine the constitution of compounds.

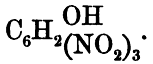
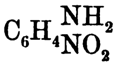
CHAPTER XIII

PHOSPHORESCENCE

MANY organic substances when shaken with air in presence of alkalis become luminous in the dark; a faint greenish light is emitted. This property was first observed in the case of the aromatic aldehyde lophine. Radziszewski has investigated the phosphorescent phenomena of organic substances, and has found that this property is possessed chiefly by bodies which may be easily oxidised, such as the aromatic aldehydes. Phosphorescence is connected with the production of ozone. Radziszewski concludes that during the slow oxidation of an aldehyde the molecule of oxygen is split up, one atom going to the aldehyde, thus $R.CHO + O_2 = R.CO.OH + O$, whilst the remaining atom unites with a second molecule of oxygen to form ozone. The presence of ozone was shown by the bleaching of an indigo solution. According to Radziszewski organic compounds become luminous in the dark when *their alkaline solutions unite with active oxygen*; it is on this account that terpenes and other hydrocarbons, which are sometimes called ozone carriers, after they have been exposed in air to the action of sunlight, show phosphorescence in presence of alkalis. Radziszewski also believes that the power possessed by certain animals of becoming luminous in the dark, depends on a slow oxidation and ozone production.

CHAPTER XIV

RELATION BETWEEN COLOUR AND CONSTITUTION

MANY organic substances absorb or reflect all rays of light to the same extent; they are therefore *colourless* or *white*. Other bodies possess the property of absorbing part of the rays, the remainder being either reflected or transmitted; these are the *coloured* substances, and both the natural and artificial ones are, almost without exception, benzene derivatives. Already a number of interesting observations have been made on the relations between colour and constitution. All aromatic hydrocarbons are colourless, as are also the compounds in which one atom of hydrogen has been replaced by OH, NO_2, or NH_2. If however two atoms of hydrogen be replaced, the behaviour of the compound towards light depends upon whether the two substituting groups are alike or not; in the former case the compounds are colourless, in the latter they are in general coloured. Compounds containing only OH and NH_2 groups form an exception to the above rule. Phenol $C_6H_5.OH$ is colourless, but its nitro compounds are intensely yellow, for instance, trinitrophenol or picric acid  $C_6H_2{}^{OH}_{(NO_2)_3}$. Aniline $C_6H_5.NH_2$ and nitrobenzene $C_6H_5.NO_2$ are also colourless, but nitroaniline  $C_6H_4{}^{NH_2}_{NO_2}$ is yellow.

In many cases the colour appears to be dependent on the presence of certain atomic groups in the molecule. This applies for example to the quinones which contain the group —O—O—, as well as to the azo compounds which are distinguished by the group —N=N— joining two organic groups.

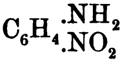
It may be mentioned that reducing agents, such as nascent hydrogen, as a rule convert coloured bodies into colourless compounds; hydrogen is either directly added, or it replaces oxygen in the original substance:—

$$C_6H_5.N=N.C_6H_5$$

Azobenzene
coloured

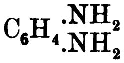
$$C_6H_5.NH—NH.C_6H_5$$

Hydrazobenzene
colourless



$$C_6H_4\begin{matrix}.NH_2\\.NO_2\end{matrix}$$

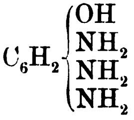
Nitroaniline
coloured



$$C_6H_4\begin{matrix}.NH_2\\.NH_2\end{matrix}$$

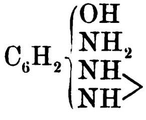
Diamidobenzene
colourless.

Such colourless compounds become reconverted into coloured ones by oxidation (loss of hydrogen):—



$$C_6H_2\begin{cases}OH\\NH_2\\NH_2\\NH_2\end{cases}$$

Triamidophenol
colourless



$$C_6H_2\begin{cases}OH\\NH_2\\\left.\begin{matrix}NH\\NH\end{matrix}\right>\end{cases}$$

Diimidoamidophenol
coloured.

Graebe and Liebermann concluded, from the above and similar facts, that the colour depends upon certain atomic groups such as NO_2, N_2, O_2; these groups resemble each other in the fact that their atoms are more closely linked together than is necessary for the existence of the molecule. An intimate linking of carbon to nitrogen or oxygen, caused by inner condensation, is found in the rosanilines, aurins, phthaleïns, and other similar dyes. If this close linking be destroyed, as happens if hydrogen be taken up, the colour disappears.

The carbon atoms are very much more closely linked together in the benzene derivatives than in the fatty compounds, and if this of itself be not sufficient to account for colour, it is at any rate remarkable that coloured bodies should almost always be aromatic compounds.

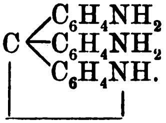
A distinction must be drawn between *coloured substances* and *colouring matters*, or *dyes*. The peculiar property which these latter compounds possess of colouring animal and vegetable substances depends upon their power of uniting with the animal or vegetable fibres. Witt has shown that the property of acting as dyes depends upon the presence of two groups; the one may be termed the true *chromophor*, the second makes the compound acid or basic, thus causing it to *form salts*. The above-mentioned groups NO_2, N_2, O_2, are chromophors. Compounds containing only the chromophors are called *chromogenes*; they are not yet dyes, but they become so on the introduction of a salt-forming group such as OH or NH_2.

Azobenzene is coloured; it is however not a dye, but only a chromogene. Oxyazobenzene and amidoazobenzene possess marked dyeing properties.

$C_6H_5.N_2.C_6H_5$	$C_6H_5.N_2.C_6H_4.OH$	$C_6H_5.N_2.C_6H_4.NH_2$
Azobenzene chromogene	Oxyazobenzene dye	Amidoazobenzene dye.

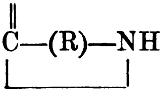
Nitrobenzene is also only a chromogene, but its oxy- and amido- compounds are dyes.

Besides the above-mentioned chromophores a number of others are known; they are contained in the more complicated natural and artificial dyes. The simplest representative of the true aniline dyes is pararosaniline:



$$C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH.\end{cases}$$

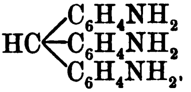
The group



$$\overset{\|}{C}\text{—(R)—}NH$$

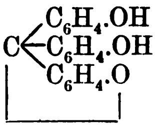
is here the chromophore.

If this group be split up by means of hydrogen, colourless paraleucaniline is obtained:—



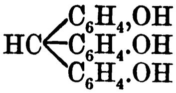
$$HC\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2.\end{cases}$$

Aurin has a similar composition; it yields leucaurin when treated with hydrogen:—



$$C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.O\end{cases}$$

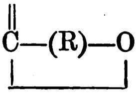
Aurin dye



$$HC\begin{cases}C_6H_4,OH\\C_6H_4.OH\\C_6H_4.OH\end{cases}$$

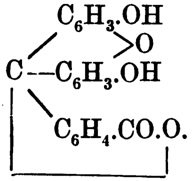
Leucaurin colourless.

The group

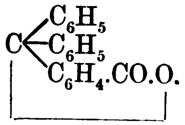


$$\overset{\|}{C}\text{—(R)—}O$$

is here the chromophore; it occurs also in the phthaleïn dyes:—

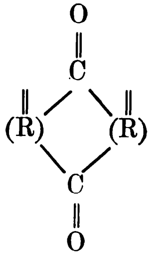


The chromogene of this dye is phthalophenon:—



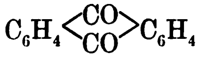
It contains the above-mentioned chromophore, but only becomes a dye on the introduction of hydroxyl groups.

The chromophore



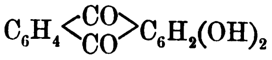
occurs in alizarine and purpurine.

The chromogene of this compound is anthrachinone:



$$C_6H_4\begin{matrix}<CO>\\ <CO>\end{matrix}C_6H_4$$

Anthrachinone
chromogene



$$C_6H_4\begin{matrix}<CO>\\ <CO>\end{matrix}C_6H_2(OH)_2$$

Alizarine
dye.

As a rule the salts of dyes have a stronger colour than the free acid or basic compounds.

The intensity of colour increases with the number of salt-forming groups, as for example :—

Amidoazobenzene	$C_{12}H_9N_2(NH_2)$	:	light yellow.
Diamidoazobenzene	$C_{12}H_8N_2(NH_2)_2$	:	orange.
Triamidoazobenzene	$C_{12}H_7N_2(NH_2)_3$	:	brown.

The replacement of amido hydrogen by hydrocarbon radicles causes a definite change in the colour. As the number of introduced radicles increases, the colours of the compounds often change in the following order: yellow, red, violet, blue. By the addition of successive phenyl groups to rosaniline, the colour alters as under:

Rosaniline	$C_{20}H_{19}N_3$	red.
Phenylrosaniline	$C_{20}H_{18}(C_6H_5)N_3$	red-violet.
Diphenylrosaniline	$C_{20}H_{17}(C_6H_5)_2N_3$	blue-violet.
Triphenylrosaniline	$C_{20}H_{16}(C_6H_5)_3N_3$	blue.

The *fluorescence* which is shown by many organic compounds, both dyes and others, is also dependent on the constitution.

PART III

GENERAL BEHAVIOUR OF ORGANIC COMPOUNDS

CHAPTER XV

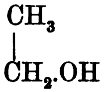
OXIDATION

By oxidation is meant not only the combination of oxygen with a compound, but also the splitting off of hydrogen and replacement of it by oxygen. The final oxidation product of the carbon of organic compounds is carbon dioxide. *Combustion* is the term usually applied to the complete oxidation of an organic compound to carbon dioxide. Each organic compound, with the exception of the most highly oxidised, can pass through several oxidation phases before it is completely burnt, so that the numerous organic oxygen compounds may be regarded as such partial oxidation products.

All organic compounds containing oxygen attached to the carbon may be looked upon as being oxidation products of the hydrocarbons; they cannot all be prepared by direct oxidation of the hydrocarbons, but they may be derived from them as *theoretical oxidation products*. The oxidation process must be considered as proceeding in such a way that the oxygen inserts itself between the hydrogen and carbon, thus forming hydroxyl.

$$\begin{array}{l} CH_3 \\ | \\ CH_3 \end{array}$$

Ethane



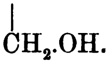
$$\begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array}$$

Ethyl alcohol.

The first (theoretical) oxidation products of the hydrocarbons are the *monovalent alcohols*, or *phenols* as they are called when the hydroxyl is linked to a benzene nucleus. In reality such an oxidation of the hydrocarbons to alcohols can only occur under certain conditions.

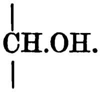
An alcohol is primary, secondary, or tertiary, according to whether the oxidation has taken place in connection with a carbon atom which is linked to one, two, or three other carbon atoms.

The first named contain the group



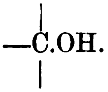
$$\begin{array}{l} | \\ CH_2.OH. \end{array}$$

The secondary alcohols contain the group



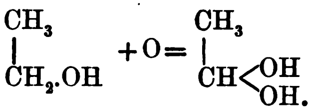
$$\begin{array}{l} | \\ CH.OH. \\ | \end{array}$$

The tertiary the group



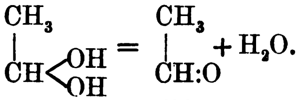
$$\begin{array}{l} \;\;| \\ -C.OH. \\ \;\;| \end{array}$$

If an alcohol be further oxidised, the oxygen as a rule becomes attached to the carbon atom which is already oxidised, hydroxyl being again formed in the first place:—



$$\begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array} + O = \begin{array}{l} CH_3 \\ | \\ CH<{}^{OH}_{OH}. \end{array}$$

Experience has however shown that compounds *containing more than one free hydroxyl attached to the same carbon atom are not stable*; they split off water and become converted into oxides:—



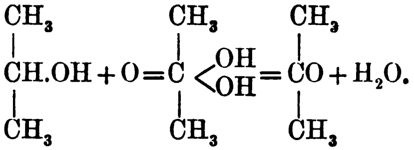
$$\begin{array}{l} CH_3 \\ | \\ CH<{}^{OH}_{OH} \end{array} = \begin{array}{l} CH_3 \\ | \\ CH:O \end{array} + H_2O.$$

Aldehyde

The first oxidation products of the primary alcohols are the *aldehydes*, which are characterised by the presence of the group

$$\begin{array}{l} | \\ CH:O. \end{array}$$

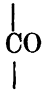
A similar process occurs if a secondary alcohol be oxidised:—



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array} + O = \begin{array}{l} CH_3 \\ | \\ C<{}^{OH}_{OH} \\ | \\ CH_3 \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + H_2O.$$

Secondary propyl alcohol Acetone (ketone)

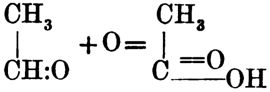
Secondary alcohols give on oxidation *ketones*, which all contain the group



$$\begin{matrix}|\\CO\\|\end{matrix}$$

linked to two hydrocarbon radicles.

The oxidised carbon atom of the aldehydes, but not that of the ketones, can take up another atom of oxygen without the molecule being destroyed:—



$$\begin{matrix}CH_3\\|\\CH{:}O\end{matrix} + O = \begin{matrix}CH_3\\|\\C\begin{matrix}=O\\-OH\end{matrix}\end{matrix}$$

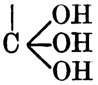
Acetic acid.

Aldehydes give on oxidation *carboxylic acids* which are characterised by the group

$$\begin{matrix}|\\CO.OH\end{matrix}$$

Carboxyl.

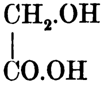
Strictly speaking the carboxylic acids must be regarded as being trihydrates with the group



Ortho-acids.

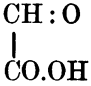
This group however at once splits off water, and becomes converted into ordinary carboxyl (meta-acids).

The ortho-acids are only known in the form of esters; all free carboxylic acids belong to the meta series. In the formation of acetic acid one of the carbon atoms of ethane is entirely oxidised; it cannot take up more oxygen without being split off as carbon dioxide. The second carbon atom may pass through exactly the same phases of oxidation as the first:—



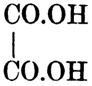
$$\begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array}$$

Alcohol acid
(Glycollic acid)



$$\begin{array}{l}CH:O\\ |\\ CO.OH\end{array}$$

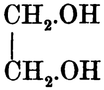
Aldehyde acid
(Glyoxylic acid)



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array}$$

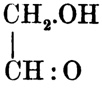
Divalent acid
(Oxalic acid).

In addition to the above compounds the following ones may also be regarded as oxidation products of the hydrocarbon C_2H_6:—



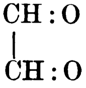
$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array}$$

Divalent alcohol
(Glycol)



$$\begin{array}{l}CH_2.OH\\ |\\ CH:O\end{array}$$

Alcohol aldehyde

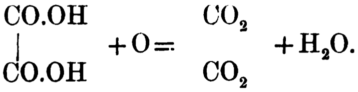


$$\begin{array}{l}CH:O\\ |\\ CH:O\end{array}$$

Double aldehyde
(Glyoxal).

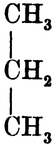
All other oxygen compounds containing two atoms of carbon are simple derivatives of some one of the above-mentioned ten compounds.

The highest oxidation product of ethane is oxalic acid, and if this be further oxidised, carbon dioxide and water are produced:—



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + O = \begin{array}{l}CO_2\\ \\ CO_2\end{array} + H_2O.$$

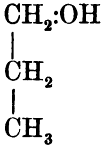
The following is a list of the theoretical oxidation products of propane. Compounds which have not yet been prepared are given in brackets:—



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

Propane

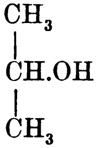
1.



$$\begin{array}{l}CH_2{:}OH\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

Primary
propyl alcohol

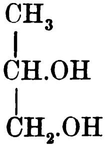
2.



$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_3\end{array}$$

Secondary
propyl alcohol

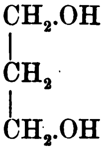
3.



$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array}$$

Propylidene
glycol.

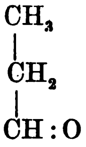
4.



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

Propylene glycol

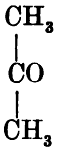
5.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH:O \end{array}$$

Propyl-aldehyde

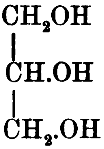
6.



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$$

Acetone

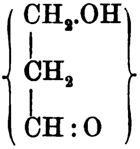
7.



$$\begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

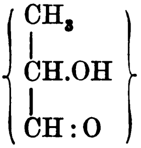
Glycerine.

8.



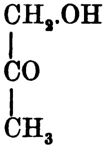
$$\left\{ \begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ CH:O \end{array} \right\}$$

9.



$$\left\{ \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH:O \end{array} \right\}$$

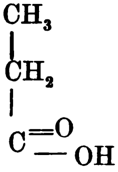
10.



$$\begin{array}{l} CH_2.OH \\ | \\ CO \\ | \\ CH_3 \end{array}$$

Acetol

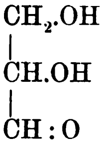
11.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ C\begin{array}{l} =O \\ -OH \end{array} \end{array}$$

Propionic acid.

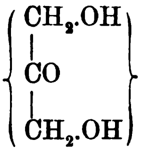
12.



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH:O \end{array}$$

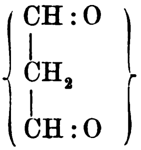
Glyceric aldehyde.

13.



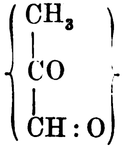
$$\left\{ \begin{array}{l} CH_2.OH \\ | \\ CO \\ | \\ CH_2.OH \end{array} \right\}$$

14.



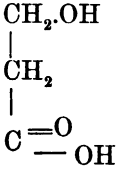
$$\left\{ \begin{array}{l} CH:O \\ | \\ CH_2 \\ | \\ CH:O \end{array} \right\}$$

15.



$$\left\{ \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH:O \end{array} \right\}$$

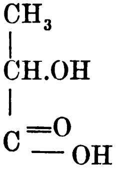
16.



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2 \\ | \\ C\begin{array}{l} =O \\ -OH \end{array} \end{array}$$

Ethylenelactic acid

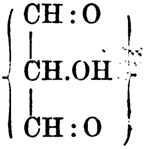
17.



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ C\begin{array}{l} =O \\ -OH \end{array} \end{array}$$

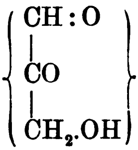
Ethidenelactic acid.

18.



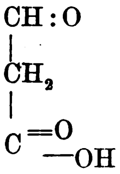
$$\left\{ \begin{array}{l} CH:O \\ | \\ CH.OH \\ | \\ CH:O \end{array} \right\}$$

19.



$$\left\{\begin{array}{l} \mathrm{CH:O} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2.OH} \end{array}\right\}$$

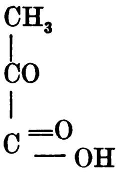
20.



$$\begin{array}{l} \mathrm{CH:O} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

Formyl-acetic acid

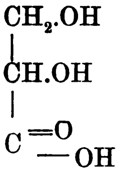
21.



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

Pyroracemic acid

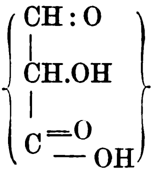
22.



$$\begin{array}{l} \mathrm{CH_2.OH} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

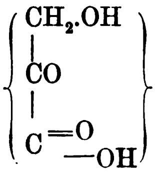
Glyceric acid.

23.



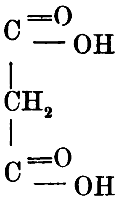
$$\left\{\begin{array}{l} \mathrm{CH:O} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}\right\}$$

24.



$$\left\{\begin{array}{l} \mathrm{CH_2.OH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}\right\}$$

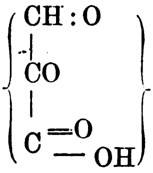
25.



$$\begin{array}{l} \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

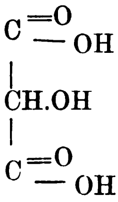
Malonic acid.

26.



$$\left\{\begin{array}{l} \mathrm{CH:O} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}\right\}$$

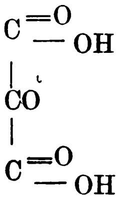
27.



$$\begin{array}{l} \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

Oxymalonic acid

28.

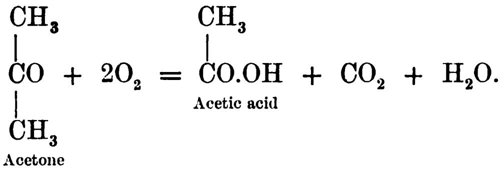


$$\begin{array}{l} \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{C}\begin{smallmatrix} =\mathrm{O} \\ -\mathrm{OH} \end{smallmatrix} \end{array}$$

Mesoxalic acid.

This list shows how great the number of the possible organic oxygen compounds is; the compounds are all derived from one hydrocarbon which only contains three carbon atoms. In spite of the formidable number of substances, great simplicity prevails in their arrangement, because all organic oxygen compounds containing the oxygen linked to carbon, are either alcohols, aldehydes, ketones, acids, or combinations or derivatives of these substances.

Oxidising operations, as they can be practically carried out, often give results differing greatly from those which would be anticipated from theory. If, for instance, a ketone be treated with a powerful oxidising agent, the oxygen does not attack the carbon atoms which are not oxidised; it combines with the carbon atom which is already linked to oxygen, thus causing a disruption of the carbon chain :—

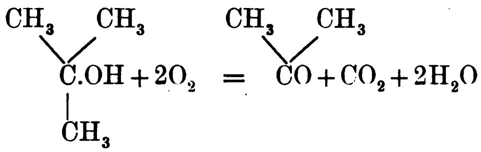


$$\underset{\text{Acetone}}{\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}} + 2O_2 = \underset{\text{Acetic acid}}{\begin{array}{c} CH_3 \\ | \\ CO.OH \end{array}} + CO_2 + H_2O.$$

The theoretical oxidation products of acetone, Nos. 10, 13, 15, &c., in the above list, are not formed by direct oxidation of this compound. Ketones are decomposed by oxidation into *acids containing less carbon.*

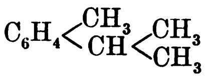
If a tertiary alcohol be treated with an energetic oxidising medium, the oxygen also attacks the carbon atom which is linked to the hydroxyl group, and the carbon chain is broken, because otherwise the oxygen could not attach itself to this carbon atom. Tertiary alcohols on oxidation do not give any compounds specially characteristic of themselves; they decompose with the formation of acids containing less carbon.

Tertiary butyl alcohol gives, in the first place, acetone and carbon dioxide :—



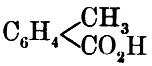
The acetone is then further oxidised to acetic acid and carbon dioxide. The difference in behaviour of primary, secondary, and tertiary alcohols towards oxidising agents, is very characteristic for these compounds.

Hydrocarbons with open carbon chains show considerable powers of resistance to the action of oxidising agents; if the action of these be very energetic, the hydrocarbon is completely burnt. As a rule, in the case of the aromatic compounds, only the open side-chains attached to the benzene nucleus are oxidised, but the action proceeds so far as to cause the formation of carboxyl which remains linked to the aromatic nucleus—for example, toluene $C_6H_5.CH_3$, and ethylbenzene $C_6H_5.C_2H_5$, are both oxidised to benzoic acid. If weaker oxidising agents be employed, the oxidation may only be a partial one—for instance, from cymene



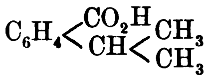
$$C_6H_4\begin{matrix}\diagup CH_3 \\ \diagdown CH\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix}\end{matrix}$$

besides methyl benzoic acid



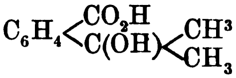
$$C_6H_4\begin{matrix}\diagup CH_3 \\ \diagdown CO_2H\end{matrix}$$

the following oxidation products have been obtained:—



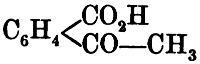
$$C_6H_4\begin{matrix}\diagup CO_2H \\ \diagdown CH\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix}\end{matrix}$$

Isopropyl benzoic acid



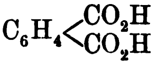
$$C_6H_4\begin{matrix}\diagup CO_2H \\ \diagdown C(OH)\begin{matrix}\diagup CH^3 \\ \diagdown CH_3\end{matrix}\end{matrix}$$

Oxypropyl benzoic acid.



$$C_6H_4\begin{matrix}\diagup CO_2H \\ \diagdown CO\text{—}CH_3\end{matrix}$$

Acetyl benzoic acid



$$C_6H_4\begin{matrix}\diagup CO_2H \\ \diagdown CO_2H\end{matrix}$$

Terephthalic acid.

The nature and position of the side-chains of aromatic compounds may exert great influence on the course of the oxidation; negative groups in the ortho position to a hydrocarbon side-chain may entirely hinder its oxidation. (*See* influence of affinity within the molecule.)

If an unsaturated compound of the methane series be oxidised, the carbon chain is, as a rule, broken at the position of the double bond:—

$$CH_3.CH : CH.CO_2H + 2O_2 = CH_3.CO_2H + CO_2H.CO_2H$$

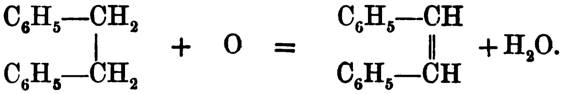
Crotonic acid Acetic acid Oxalic acid.

$$CH_2 : CH.CH_2.OH + 3O_2 = CH_2O_2 + C_2H_2O_4 + H_2O.$$

Allyl alcohol Formic acid Oxalic acid

Many oxidation products contain no oxygen; the oxidation may consist in a simple withdrawal ot hydrogen.

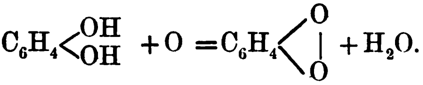
The hydrocarbon dibenzyl becomes converted by oxidation into another hydrocarbon called toluylene.



$$\begin{matrix} C_6H_5-CH_2 \\ | \\ C_6H_5-CH_2 \end{matrix} + O = \begin{matrix} C_6H_5-CH \\ \| \\ C_6H_5-CH \end{matrix} + H_2O.$$

Dibenzyl Toluylene

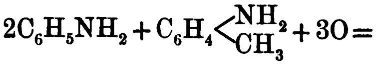
In such processes hydroxyl is probably first formed, and then split off in combination with an atom of hydrogen as water, as for instance in the conversion of leuco bases into dye bases. The oxidation of hydroquinones to quinones is peculiar; two hydroxyl hydrogen atoms are split off, the dihydrate being thereby converted into a peroxide:—



$$C_6H_4{<}\begin{matrix} OH \\ OH \end{matrix} + O = C_6H_4{<}\begin{matrix} O \\ | \\ O \end{matrix} + H_2O.$$

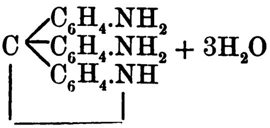
Hydroquinone Quinone

A noteworthy reaction is that of *synthesis* by oxidation. The formation of aniline dyes by the oxidation of aromatic amido-compounds is a synthetical process:—



$$2C_6H_5NH_2 + C_6H_4{<}\begin{matrix} NH_2 \\ CH_3 \end{matrix} + 3O =$$

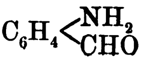
Aniline *p*-toluidine



$$C{<}\begin{matrix} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH \end{matrix} + 3H_2O$$

Pararosaniline

The reaction may however be explained by supposing that from the toluidine an aldehyde



$$C_6H_4{<}\begin{matrix} NH_2 \\ CHO \end{matrix}$$

is first formed, and that this then condenses with the aniline. (*See* aldehyde condensation.)

In the above reactions it is always the carbon which is oxidised; the oxidation may however proceed in other ways. For example, oxygen attacks the sulphur of mercaptans, sulphonic acids being formed :—

$$\underset{\text{Mercaptan}}{C_2H_5SH + 3O} \quad = \quad \underset{\text{Ethyl sulphonic acid.}}{C_2H_5.SO_2OH}$$

The sulphides are converted (by nitric acid) into sulphine oxides and sulphones :—

$$\underset{\substack{\text{Diethyl}\\ \text{sulphide}}}{(C_2H_5)_2S} \qquad \underset{\substack{\text{Diethyl sulphine}\\ \text{oxide}}}{(C_2H_5)_2SO} \qquad \underset{\text{Diethyl sulphone.}}{(C_2H_5)_2SO_2}$$

Of other oxidations which do not affect the carbon, the conversion of the phosphines into phosphine oxides may be mentioned :—

$$\underset{\text{Triethylphosphine}}{P(C_2H_5)_3 + O} \quad = \quad \underset{\text{Triethylphosphine oxide,}}{P(C_2H_5)_3O.}$$

as well as the transformation of nitroso- into nitro-compounds.

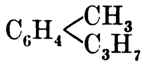
As the nature of the oxidising agent frequently exercises great influence on the course of the reaction, a brief account is given in the following pages of the action of ordinary oxidising agents, and of the cases in which they are usually employed.

(1) *Free oxygen* acts upon easily oxidisable substances. In presence of heated or spongy platinum, air oxidises primary alcohols to aldehydes, and aldehydes in contact with air are gradually converted into acids.

Free oxygen in presence of sodium hydrate oxidises many organic compounds; in such reactions the oxygen is first of all made active. In this manner benzene is converted, though only to a slight extent, into phenol:

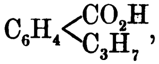
$$C_6H_6 + O \quad = \quad C_6H_5.OH.$$

Cymene



$$C_6H_4<^{CH_3}_{C_3H_7}$$

gives propylbenzoic acid



$$C_6H_4<^{CO_2H}_{C_3H_7}, \text{ \&c.}$$

It should be noticed that the same reaction occurs in the animal organism, in alkaline blood.

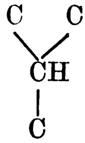
Silver oxide easily changes aldehydes into acids, metallic silver being precipitated :—

$$2CH_3.CH{:}O + 3Ag_2O = 2CH_3.CO.OAg + H_2O + 2Ag_2.$$

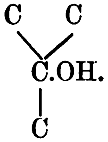
A delicate test for the presence of aldehydes is based on this reaction (precipitation of silver from ammoniacal solution). Polyvalent alcohols of the fatty series, such as glycerine or carbohydrates, are oxidised by silver oxide to glycollic acid $CH_2OH.CO_2H$.

Manganese dioxide with dilute sulphuric acid oxidises alcohols to aldehydes and acids, but it is seldom employed.

Potassium permanganate.—This reagent in *acid* solution causes complete combustion, but in *alkaline* solution its action is less energetic; it is used for the oxidation of aromatic ortho-hydrocarbons which would be burnt if a more powerful agent were employed. Compounds containing hydrogen linked to a tertiary carbon atom have the hydrogen converted into hydroxyl by the action of potassium permanganate in alkaline solution (R. Meyer). The group



becomes changed into the group



The reason why on oxidation only the group $R_3{\equiv}CH$ should be hydroxylated is easily seen. It has already been mentioned, when discussing the general process of oxidation, that in the groups $R_2{=}CH_2$ and $R{-}CH_3$ one hydrogen atom is first converted into hydroxyl; the resulting primary and secondary alcohols with the groups $=CH.OH$ and $-CH_2.OH$ are however at once further oxidised with formation of ketones (aldehydes) and acids. A more complete oxidation of the tertiary alcohols ($R_3{\equiv}C.OH$) does not occur. It is also found that the group CH_2 is oxidised to CO by potassium permanganate:—

$$\underset{\text{Diphenyl methane}}{C_6H_5.CH_2.C_6H_5} + O_2 = \underset{\text{Diphenyl ketone}}{(C_6H_5)_2CO} + H_2O.$$

6) *Chromic acid* is very generally employed for the preparation of aldehydes, ketones, and acids, from alcohols, for the oxidation of aromatic hydrocarbons, with the exception of ortho-compounds, as well as in the

production of quinones &c. Chromic acid is sometimes used in the form of anhydride in glacial acetic acid solution; usually however a mixture of sulphuric acid and potassium bichromate answers the purpose. For the oxidation of aromatic hydrocarbons a mixture of 4 parts $K_2Cr_2O_7$ and 6 parts of H_2SO_4 diluted with twice its volume of water is found to be most suitable. In the case of alcohols a more dilute solution is necessary, for instance 3 parts $K_2Cr_2O_7$, 1 part H_2SO_4, and 10 parts H_2O.

Many organic compounds, such as oxyacids, ketones, &c., may be decomposed by chromic acid mixture, oxidation products containing less carbon being obtained; the constitution of a compound may often be determined from the nature and composition of these bodies.

Chromyl chloride, alone, acts very violently; its action is milder if it be dissolved in a considerable quantity of carbon disulphide; in this form it is specially used for the conversion of benzene homologues into aldehydes (Etard).

The double compounds of hydrocarbon and chromyl-chloride which are first formed are decomposed with water, the aldehydes being produced :—

$$3C_6H_5.CH_3(CrO_2Cl_2)_2$$
$$=3C_6H_5.CH{:}O+2Cr_2Cl_6+2CrO_3+3H_2O.$$

Nitric acid has both a directly oxidising and a nitrating action.

1. *Dilute* nitric acid is usually employed for oxidation; an acid diluted with two molecules of water acts less energetically than chromic acid mixture. Compounds

of the methane series are in general strongly oxidised by the *concentrated* acid, being often entirely or partially converted into carbon dioxide or oxalic acid :—

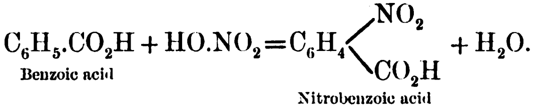
$$\underset{\text{Lactic acid}}{C_3H_6O_3} + 5O = \underset{\text{Oxalic acid}}{C_2H_2O_4} + CO_2 + 2H_2O.$$

$$\underset{\text{Sugar}}{C_6H_{12}O_6} + 9O = \underset{\text{Oxalic acid}}{3C_2H_2O_4} + 3H_2O.$$

In certain circumstances nitric acid acts like an alkaline solution of potassium permanganate in so far that it oxidises the hydrogen of a tertiary carbon atom to hydroxyl.

2. Many substances, particularly aromatic compounds, are converted into *nitro compounds* by the action of concentrated nitric acid, or of a mixture of nitric and sulphuric acids. The hydrogen linked to the carbon is replaced by the group NO_2, the radicle of nitric acid.

$$\underset{\text{Benzene}}{C_6H_6} + HO.NO_2 = \underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + H_2O.$$



$$\underset{\text{Benzoic acid}}{C_6H_5.CO_2H} + HO.NO_2 = \underset{\text{Nitrobenzoic acid}}{C_6H_4\begin{array}{l}\diagup NO_2 \\ \diagdown CO_2H\end{array}} + H_2O.$$

Phenols and aromatic amido compounds may be very easily nitrated, the action of even dilute nitric acid being one of substitution.

The presence of nitro groups in a substance increases the difficulty of further nitration, and in any case not more than three nitro groups can be introduced into a compound.

The disposition of the aromatic substances to form nitro compounds is so great that even easily oxidisable bodies like benzaldehyde are nitrated, not oxidised, by concentrated nitric acid.

Certain regularities have been observed in the formation of nitro compounds. If for example a substance contain alkyl or hydroxyl groups, large quantities of the para compound are obtained and very little of the ortho. The substitution takes place however almost entirely in the meta position if a nitro, carboxyl, or aldehyde group be present. Ordinary phenol gives *p*- and *o*-nitrophenol, toluene gives *p*- and *o*-nitrotoluene. But nitrobenzene forms *m*-dinitrobenzene, and benzoic acid *m*-nitrobenzoic acid &c.

Certain compounds of the methane series, such as for instance acids containing a tertiary carbon atom, are also nitrated by nitric acid.

Lead nitrate in aqueous solution converts the chlorides of the alcohol radicles into aldehydes.

$$\underset{\text{Benzoyl chloride}}{2C_6H_5.CH_2Cl} + Pb(NO_3)_2$$
$$= \underset{\text{Benzaldehyde}}{2C_6H_5.CHO} + PbCl_2 + H_2O + N_2O_3.$$

Nitrous acid is specially used to prepare *oxy-compounds* from primary *amido compounds* ($R—NH_2$); the amido compound must be dissolved in water.

$$\underset{\text{Amine}}{C_2H_5.NH_2} + HO.NO = \underset{\text{Alcohol}}{C_2H_5.OH} + N_2 + H_2O$$
$$\underset{\text{Amido-acetic acid}}{CH_2(NH_2).CO_2H} + HO.NO$$
$$= \underset{\text{Oxyacetic acid}}{CH_2(OH).CO_2H} + N_2 + H_2O.$$

Under certain conditions, especially with aromatic amido-compounds, *diazo-compounds* are obtained by this reaction; these easily give off nitrogen and pass into oxy-compounds; they may be regarded therefore as being intermediate products of the action of nitrous acid upon amido-compounds.

$$\underset{\text{Aniline nitrate}}{C_6H_5.NH_2.HNO_3} + HO.NO = \underset{\text{Diazobenzene nitrate}}{C_6H_5.N_2.ONO_2} + 2H_2O,$$

$$C_6H_5.\,\vdots\,N_2.\,\vdots\,ONO_2 + H\,\vdots\,OH = \underset{\text{Phenol}}{C_6H_5.OH} + N_2 + HNO_3.$$

The action of nitrous acid on *secondary amines* is one of substitution, *nitrosoamines* being formed :—

$$(CH_3)_2.NH + HO.NO = (CH_3)_2.N.NO + H_2O.$$

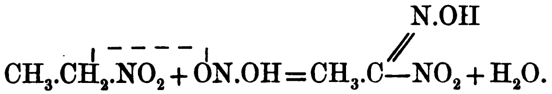
Tertiary amines are either unaffected by nitrous acid, or nitroso compounds are formed by the substitution of hydrogen linked to the carbon :—

$$\underset{\text{Dimethylaniline}}{C_6H_5.N(CH_3)_2} + HO.NO = \underset{\text{Nitrosodimethylaniline}}{C_6H_4(NO).N(CH_3)_2} + H_2O.$$

If in any of the above reactions a definite quantity of nitrous acid be required, sulphuric acid and potassium or sodium nitrite are used instead of the free gas.

Nitro compounds are differently affected by nitrous acid according to whether they are primary ($R.CH_2.NO_2$), secondary ($R_2:CH.NO_2$), or tertiary ($R_3\vdots C.NO_2$).

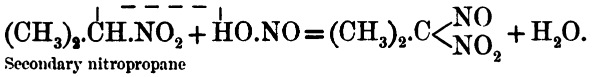
Primary nitro compounds are converted into *nitrolic* *acids* (oximid-compounds) which dissolve in alkalis with an intense *red* colour :—



$$CH_3.CH_2.NO_2 + ON.OH = CH_3.C\begin{matrix}N.OH\\ /\!/ \\ \end{matrix}\!\!-NO_2 + H_2O.$$

Nitroethane Ethylnitrolic acid

Secondary nitro compounds give *pseudo-nitrols* with nitrous acid ; these are soluble in alkalis, giving a deep blue colour.



$$(CH_3)_2.CH.NO_2 + HO.NO = (CH_3)_2.C\begin{matrix}<NO\\ <NO_2\end{matrix} + H_2O.$$

Secondary nitropropane

Propanepseudonitrol

Tertiary nitro compounds do not react with nitrous acid. A delicate method for the detection of primary, secondary, and tertiary alcohols is founded on the above reactions. The alcohols are converted into iodides and treated with silver nitrite ; the nitro compounds which are formed are distilled off and mixed with potassium nitrite and sulphuric acid ; on adding excess of potassium hydrate the liquid becomes either red or blue, or remains unchanged, according to whether the alcohol was a primary, secondary, or tertiary one. Only the alcohols with a low molecular weight show these colour reactions.

As mentioned above, silver nitrite is used to convert iodides into nitro compounds :—

$$C_2H_5I + AgNO_2 = C_2H_5.NO_2 + AgI.$$

These compounds are isomeric, not identical, with nitrous acid ethers.

Under certain conditions *potassium hydrate* (sodium hydrate) acts as an oxidising agent; this result is only achieved at high temperatures and is always accompanied by evolution of hydrogen (Potash fusion).

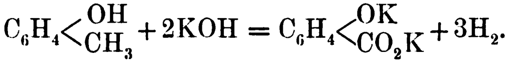
Primary alcohols are converted into acids by fusion with alkalis:—

$$\underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH} + KOH = \underset{\text{Palmitic acid}}{C_{16}H_{31}O.OK} + 2H_2.$$

Alkaline hydrates also oxidise phenols at high temperatures. The reaction differs according to the composition of the phenol: ordinary phenol is converted into diphenol, hydrogen being evolved; resorcinol yields diresorcinol, but some phlorglucinol is also formed by direct oxidation; in the case of the cresols the hydrocarbon side chain is oxidised:—

$$\underset{\text{Phenol}}{2C_6H_5OH} + 2KOH = \underset{\substack{\text{Potassium}\\ \text{diphenolate}}}{C_{12}H_8O_2K_2} + 2H_2O + H_2.$$

$$\underset{\text{Resorcinol}}{C_6H_4(OH)_2} + 3KOH = \underset{\substack{\text{Potassium}\\ \text{phloroglucinolate}}}{C_6H_3(OK)_3} + 2H_2O + H_2.$$



$$\underset{\text{Cresol}}{C_6H_4\text{<}\substack{OH\\ CH_3}} + 2KOH = \underset{\substack{\text{Potassium}\\ \text{oxybenzoate}}}{C_6H_4\text{<}\substack{OK\\ CO_2K}} + 3H_2.$$

Unsaturated compounds are decomposed by fusion with caustic potash; the carbon chain is usually broken at the position of the double bond, the products being oxidised to acids. Hydrosorbic acid for instance gives acetic and butyric acids:—

$$CH_3.CH{:}CH.CH_2.CH_2.CO_2H + 2KOH$$
$$= CH_3.CO_2K + C_3H_7.CO_2K + H_2.$$

Action of halogens.—The halogens seldom act as direct oxidisers of organic compounds; their action is however closely related to true oxidation processes, and may therefore be conveniently discussed in this connection. Organic halogen compounds are the most important mediums for indirect oxidation. Free halogens, especially chlorine and bromine, easily *combine directly* with *unsaturated* compounds:—

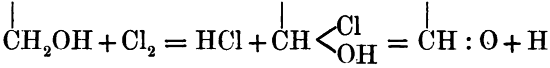
$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

$$\underset{\text{Acrylic acid}}{C_3H_4O_2} + Br_2 = \underset{\text{Dibrompropionic acid.}}{C_3H_4Br_2O_2}$$

Chlorine has an *oxidising* action in presence of water, primary alcohols being converted into aldehydes by loss of hydrogen:—

$$C_2H_6O + Cl_2 = C_2H_4O + 2HCl.$$

In all probability the hydrogen is not directly eliminated; substitution first takes place and then hydrochloric acid is split off from the compound:—



$$\overset{|}{C}H_2OH + Cl_2 = HCl + \overset{|}{C}H{<}{}^{Cl}_{OH} = \overset{|}{C}H : O + HCl. + HCl$$

The formation of chloral from ethyl alcohol and chlorine may be explained in this way, substitution of the hydrogen of the second carbon atom taking place simultaneously. Certain ethers behave in a similar manner; benzylethyl ether gives with chlorine benzaldehyde and chlorethyl.

The action of chlorine is generally one of *substitution*; it expels and replaces hydrogen atom by atom:—

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$

$$C_2H_5Cl + Cl_2 = C_2H_4Cl_2 + HCl, \&c.$$

When chlorine acts upon hydrocarbons, the substitution does *not* proceed regularly step by step, so that the whole of the hydrocarbon is first converted into the monosubstitution product, this into the disubstitution compound, and so on. The substance consists during the reaction of a mixture of unaltered hydrocarbon and many of its different substitution products. It should be noted that aromatic compounds may be much more easily chlorinated than fatty bodies. Substitution proceeds best in direct sunlight or if the chlorine act *in statu nascendi.* ($KClO_3$ or MnO_2 and HCl.)

The reaction is also helped by the presence of iodine; chloriodide is first formed, and is then decomposed by the organic body, $C_6H_6 + ClI = C_6H_5.Cl + HI$.

Chloriodide is again formed from the hydriodic acid and free chlorine, $HI + Cl_2 = HCl + ICl$.

A small quantity of iodine is therefore sufficient to bring about the chlorination of a large amount of substance. Antimony chloride, ferric chloride, and aluminium or molybdenum chlorides may be used instead of iodine. Certain free metals, such as gold, aluminium, zirconium, tin, &c., act in the same way. They first become converted into chlorides and are then reduced.

These substances act as *chlorine transferrers*; a complete substitution of the hydrogen in hydrocarbons—for instance, from C_6H_6 to C_6Cl_6—only occurs in the presence of such bodies.

The manner in which these substances act is not yet entirely known. It is however probable that addition compounds of the chlorides and hydrocarbons are first formed and then decomposed, substitution by the chlorine occurring at the same time:—

$$C_6H_5.CH_3 + Fe_2Cl_6 = C_6H_5(Fe_2Cl_6).CH_3.$$
$$C_6H_5(Fe_2Cl_6).CH_3 + Cl_2 = C_6H_4Cl.CH_3 + HCl + Fe_2Cl_6.$$

The complete chlorination of aromatic compounds generally results in the formation of hexchlorobenzene, the side-chains being all split off—for example, ethylbenzene $C_6H_5.C_2H_5$ gives C_6Cl_6 and C_2Cl_6.

Bromine acts like chlorine, only more mildly. In order to obtain substitution products of a fatty compound, it is often necessary to heat with bromine in a sealed tube. Bromine acts upon aromatic compounds much more easily.

Iodine in general does not substitute directly. This arises from the fact that iodine compounds when heated with hydriodic acid split off iodine and take up hydrogen:—

$$\underset{\text{Monoiodacetic acid}}{CH_2I.CO_2H} + HI = \underset{\text{Acetic acid}}{CH_3.CO_2H} + I_2.$$

As hydriodic acid is formed by the process of substitution, the replacement by iodine does not occur unless the hydriodic acid which is formed be neutralised. This may be accomplished by the addition of iodic acid or mercuric oxide.

The action of a mixture of iodic acid and iodine is one of substitution:—

$$5C_6H_6 + HIO_3 + 4I = 5C_6H_5I + 3H_2O.$$

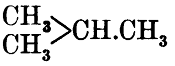
It has been observed, curiously enough, that concentrated sulphuric acid may act as an iodine transferrer. Monoiodobenzene when treated with sulphuric acid gives di-iodo benzene, and benzenesulphonic acid.

As a rule, the halogens only replace *hydrogen which is directly linked to carbon.* Acetic acid only yields the following substitution products:—

$$CH_2Cl.CO_2H\ ;\ CHCl_2.CO_2H\ ;\ CCl_3.CO_2H.$$

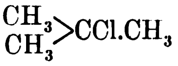
In exceptional cases halogens replace hydroxyl hydrogen in phenols, but never carboxyl hydrogen. If chlorine or iodine act on sodium phenate, chloro or iodophenol is obtained; $C_6H_5.OI$ is however first formed, and then by rearrangement $C_6H_4I.OH$. If chlorine or bromine act on aromatic hydrocarbons at high temperatures, the halogen enters the side-chain if one be present; at low temperatures on the other hand, the hydrogen of the benzene nucleus is replaced. From toluene $C_6H_5.CH_3$ benzyl chloride $C_6H_5.CH_2Cl$ is obtained by treatment with chlorine at high temperatures, but at low temperatures chlorotoluene $C_6H_4Cl.CH_3$ is formed. The same difference is noticed if the substitution be carried out in darkness or in sunlight: in the first case the hydrogen of the benzene nucleus is replaced, in the second that of the side chain.

If chlorine act at low temperatures on aromatic hydrocarbons such as toluene and its homologues, addition compounds are first formed, from which substitution products are produced by the splitting off of hydrochloric acid when the temperature rises (Seelig). In hydrocarbons of the fatty series the halogens first replace the hydrogen of the carbon atom which is linked to the least hydrogen. For example isobutane when treated with chlorine gives only tertiary butyl chloride :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CH_3$$

Isobutane



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CCl.CH_3$$

Tertiary butyl chloride.

Normal saturated hydrocarbons however give both secondary and primary substitution products. As a rule if halogens act on carboxylic acids, the hydrogen of the carbon atom which is linked to the carboxyl group will be replaced. Propionic acid

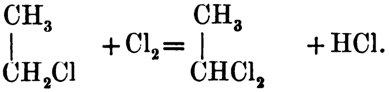
$$CH_3.CH_2.CO_2H$$

when treated with chlorine gives *a*-chloropropionic acid $CH_3.CHCl.CO_2H$; butyric acid $CH_3.CH_2.CH_2.CO_2H$ by the action of bromine yields *α*-brombutyric acid

$$CH_3.CH_2.CHBr.CO_2H.$$

The halogens usually unite with the carbon atom possessing the most negative character.

If chlorine or bromine enter a compound which already contains one of these elements, they usually unite with the carbon atom which is already linked to a halogen :--



$$\begin{matrix}CH_3\\|\\CH_2Cl\end{matrix}+Cl_2=\begin{matrix}CH_3\\|\\CHCl_2\end{matrix}+HCl.$$

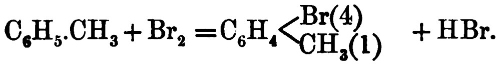
Ethylchloride Ethidene chloride

In the same way monochloracetone by the action of chlorine gives unsymmetrical di- and tri- chloracetone

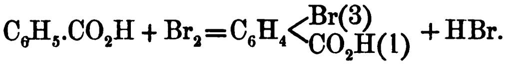
$$CH_3.CO.CHCl_2 \text{ and } CH_3.CO.CCl_3.$$

Certain rules have also been noticed in the case of the halogen substitution of aromatic compounds.

If a compound contain such a group as NH_2, alkyle, OH, or halogen, the action of a halogen causes the formation of the para-compound (1-4) in large quantities, and of the ortho compound (1-2) to a smaller extent. If however the groups NO_2, CO_2H, CHO, or SO_3H be present, the meta-compound (1-3) is the chief product. Toluene gives when brominated *p*-bromtoluene, but benzoic acid yields *m*-brombenzoic acid :—

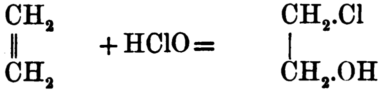


$$C_6H_5.CH_3 + Br_2 = C_6H_4 < \begin{matrix} Br(4) \\ CH_3(1) \end{matrix} + HBr.$$



$$C_6H_5.CO_2H + Br_2 = C_6H_4 < \begin{matrix} Br(3) \\ CO_2H(1) \end{matrix} + HBr.$$

Like the halogens, *hypochlorous and hypobromous acids* add themselves directly to unsaturated compounds :



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HClO = \begin{matrix} CH_2.Cl \\ | \\ CH_2.OH \end{matrix}$$

Ethylene Ethylene chlorhydrine.

Indirect oxidation.—The introduction of hydroxyl into a compound is easily accomplished by first replacing the hydrogen with a halogen, and then treating the substance with moist silver oxide, lead oxide, alkaline hydrate, alkaline carbonate, or water, at a higher temperature :—

$$2C_2H_5I + Ag_2O + H_2O = 2C_2H_5OH + 2AgI.$$

$$\underset{\text{Monochloracetic acid}}{CH_2Cl.CO_2H} + H_2O = \underset{\text{Glycollic acid}}{CH_2OH.CO_2H} + HCl.$$

Tertiary alkyl haloids react in this way most easily; for instance tertiary butyl iodide, when treated with water at ordinary temperatures, is converted quantitatively into the corresponding alcohol.

Halogens may also be replaced by oxygen by means of sulphuric or anhydrous oxalic acids; this latter is very convenient to use for converting acid chlorides into the corresponding anhydrides. (Anschutz):—

$$\underset{\text{Benzalchloride}}{C_6H_5.CHCl_2} + H_2SO_4 = \underset{\text{Benzaldehyde}}{C_6H_5.CHO} + 2HCl + SO_3.$$

$$2\underset{\text{Benzoylchloride}}{C_6H_5.COCl} + H_2C_2O_4$$

$$= \underset{\text{Benzoic anhydride}}{(C_6H_5.CO)_2O} + 2HCl + CO_2 + CO.$$

Aromatic haloid compounds containing the halogen in the side-chain resemble the alkylhaloids in the ease with which the halogen may be replaced; if however the halogen be linked to the benzene nucleus, as in chlorobenzene C_6H_5Cl, it is as a rule very difficult or impossible to replace it directly by hydroxyl; it is therefore convenient to convert aromatic compounds into sulphonic acids by the action of concentrated or fuming sulphuric acid, the sulphonic acids being then fused with potassium hydrate:—

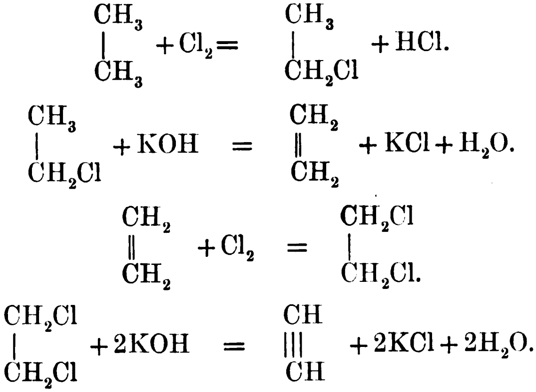
$$C_6H_6 + HO.SO_3H = C_6H_5.SO_3H + H_2O.$$

$$\underset{\substack{\text{Monobenzene}\\ \text{sulphonic acid}}}{C_6H_5.SO_3H} + 2KOH = C_6H_5.OH + K_2SO_3 + H_2O.$$

Another special method for the indirect hydroxylation of aromatic compounds is by the nitration of the substance, reduction of the nitro to the amido compound, and treatment of the latter with nitrous acid (see p. 117).

An indirect *withdrawal of hydrogen* may also be accomplished by means of the halogen compounds.

Concentrated caustic potash solution causes the splitting off of halogen hydrides from many halogen compounds. Acetylene may be prepared from ethane by the following reactions :—



$$\begin{array}{c}CH_3\\ |\\ CH_3\end{array} + Cl_2 = \begin{array}{c}CH_3\\ |\\ CH_2Cl\end{array} + HCl.$$

$$\begin{array}{c}CH_3\\ |\\ CH_2Cl\end{array} + KOH = \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + KCl + H_2O.$$

$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + Cl_2 = \begin{array}{c}CH_2Cl\\ |\\ CH_2Cl.\end{array}$$

$$\begin{array}{c}CH_2Cl\\ |\\ CH_2Cl\end{array} + 2KOH = \begin{array}{c}CH\\ |||\\ CH\end{array} + 2KCl + 2H_2O.$$

CHAPTER XVI

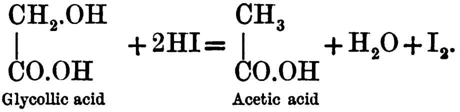
REDUCTION

By *reduction* is meant the opposite of oxidation; it includes splitting off of oxygen, addition of hydrogen, or replacement of oxygen by hydrogen.

(1) Certain oxygen compounds, especially phenols and quinones, give up their oxygen when heated with *zinc dust* (mixture of Zn and ZnO):—

$$\underset{\text{Phenol}}{C_6H_5.OH} + Zn = \underset{\text{Benzene}}{C_6H_6} + ZnO.$$

(2 *Hydriodic acid* (B.P. 127°) is very generally used in order to replace alcoholic hydroxyl by hydrogen; the reaction takes place at high temperatures, and is rendered much easier by the addition of phosphorus:—



$$\underset{\text{Glycollic acid}}{\begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array}} + 2HI = \underset{\text{Acetic acid}}{\begin{array}{l}CH_3\\ |\\ CO.OH\end{array}} + H_2O + I_2.$$

Iodoacetic acid is first formed, and this gives free iodine and acetic acid with hydriodic acid (see p. 123).

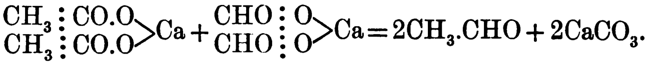
With a large excess of *concentrated* hydriodic acid, acids may even be reduced to the corresponding hydrocarbons. If hydriodic acid act on alcohols at ordinary temperatures the corresponding iodides are formed; in the case of polyvalent alcohols all the hydroxyls are reduced except one, which is replaced by iodine, and this one is always linked to a secondary carbon atom; such alcohols therefore yield secondary alkyl iodides when treated with hydriodic acid.

$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + 5HI = \underset{\substack{\text{Secondary}\\ \text{propyl iodide}}}{C_3H_7I} + 3H_2O + 2I_2.$$

$$\underset{\text{Mannite}}{C_6H_8(OH)_6} + 11HI = \underset{\substack{\text{Secondary}\\ \text{hexyl iodide}}}{C_6H_{13}I} + 6H_2O + 5I_2.$$

Phosphorus iodide PI_3 acts like hydriodic acid.

(ii) Monobasic acids are reduced to aldehydes, if their calcium or barium salts be heated with *calcium* or *barium formates.* The formic acid is oxidised to carbon dioxide, but the reaction may be looked upon as consisting in a mutual decomposition of the salts, such as is represented in the following formulæ :—



$$\underset{\text{Acetate}}{\begin{matrix} CH_3 \vdots CO.O \\ CH_3 \vdots CO.O \end{matrix}}\!>\!Ca + \underset{\text{Formate}}{\begin{matrix} CHO \vdots O \\ CHO \vdots O \end{matrix}}\!>\!Ca = \underset{\text{Aldehyde}}{2CH_3.CHO} + 2CaCO_3.$$

Hydrogen in a nascent state reduces many organic substances; nitro compounds are converted into amido compounds by its action :—

$$C_2H_5.NO_2 + 3H_2 = C_2H_5.NH_2 + 2H_2O.$$

Aldehydes are reduced to primary, and ketones to secondary alcohols by addition of hydrogen :—

$$\underset{\text{Aldehyde}}{C_2H_4O} + H_2 = \underset{\text{Alcohol.}}{C_2H_6O}$$

$$\underset{\text{Acetone}}{C_3H_6O} + H_2 = \underset{\substack{\text{Secondary}\\ \text{propyl alcohol.}}}{C_3H_8O}$$

Certain acids may be reduced by hydrogen to aldehydes. Acids of the sugar group are converted into sugars (E. Fischer).

Acid nitriles (cyanides) combine directly with hydrogen to form amines:—

$$C_2H_5.CN + 2H_2 = C_2H_5.CH_2.NH_2$$

Propionitrile — Propylamine.

As the nitriles may be prepared from the acids, and the amines can easily be converted into alcohols (see p. 117), this reaction renders it possible to reduce an acid to the corresponding alcohol. Nitriles can however be prepared from alcohols containing less carbon, so that the above reaction also serves to convert an alcohol into its next higher homologue.

Most, if not all, unsaturated compounds combine directly with hydrogen to form saturated bodies.

Hydrogen *in a nascent state* replaces the halogens in halogen compounds; it causes an *inverse substitution*:—

$$CH_2Cl.CO_2H + H_2 = CH_3.CO_2H + HCl.$$

Chloracetic acid — Acetic acid

$$CH_3.COCl + H_2 = CH_3.COH + HCl.$$

Acetyl chloride — Aldehyde

$$C_2H_5.SO_2Cl + H_2 = C_2H_5.SO_2H + HCl.$$

Ethylsulphonic chloride — Ethylsulphinic acid

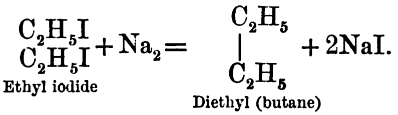
According to circumstances sodium amalgam and water, zinc or tin and hydrochloric acid, &c., &c., are used for these reductions.

Halogen compounds may easily be obtained from the corresponding oxygen compounds. Alcohols can be converted, by means of hydrochloric, hydrobromic, or hydriodic acids into the corresponding halogen compounds, and by the use of the *halogen compounds of phosphorus* ($PCl_3, PBr_3, PI_3, PCl_5$) the oxygen of almost all compounds may be replaced by halogens:—

$$C_2H_5.OH + \quad Cl = C_2H_5Cl + H_2O.$$
$$3CH_3.CO.OH + PBr_3 = 3CH_3.COBr + H_3PO_3.$$
$$C_2H_4O + PCl_5 = C_2H_4Cl_2 + POCl_3.$$

As has already been mentioned the halogens in these compounds may be replaced by hydrogen, and thus an *indirect reduction* accomplished.

Metallic *sodium* may also be used to eliminate halogens from organic compounds; it often happens that the halogens are taken from two molecules, and that the resulting groups unite together to form one molecule. The reaction can only be carried out in an anhydrous solution (dry ether).



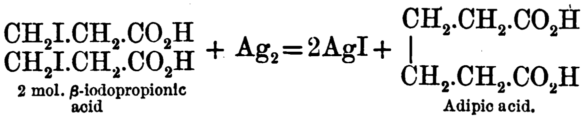
$$\begin{matrix} C_2H_5I \\ C_2H_5I \end{matrix} + Na_2 = \begin{matrix} C_2H_5 \\ | \\ C_2H_5 \end{matrix} + 2NaI.$$

Ethyl iodide — Diethyl (butane)

$$C_6H_5Br + CH_3I + Na_2 = NaI + NaBr + C_6H_5.CH_3$$

Monobromobenzene — Toluene.

Finely divided (molecular) *silver* acts like sodium:—



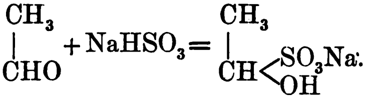
$$\begin{matrix} CH_2I.CH_2.CO_2H \\ CH_2I.CH_2.CO_2H \end{matrix} + Ag_2 = 2AgI + \begin{matrix} CH_2.CH_2.CO_2H \\ | \\ CH_2.CH_2.CO_2H \end{matrix}$$

2 mol. β-iodopropionic acid — Adipic acid.

Many important syntheses of organic compounds are founded upon this action of sodium and silver.

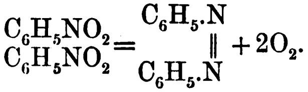
In certain cases *sulphurous* acid and sulphites are employed as reducing agents, for instance in the preparation of hydroquinones from quinones, and of hydrazines from diazo compounds.

Hydrogen sodium sulphite is also used as a test for aldehydes and ketones, with which it forms crystalline compounds generally rather insoluble in water:—



$$\begin{array}{l}CH_3\\ |\\ CHO\end{array}+NaHSO_3=\begin{array}{l}CH_3\\ |\\ CH<^{SO_3Na}_{OH}\end{array}.$$

Alcoholic potash reduces certain oxygen compounds. For example, nitro bodies are converted into azo compounds, the alcohol being at the same time oxidised to aldehyde by the oxygen of the nitro group:—



$$\begin{array}{l}C_6H_5NO_2\\ C_6H_5NO_2\end{array}=\begin{array}{c}C_6H_5.N\\ \|\\ C_6H_5.N\end{array}+2O_2.$$

CHAPTER XVII

DEHYDRATION PROCESSES

MANY of the reactions between organic compounds are accompanied by a splitting off of water. In some cases this takes place spontaneously, but in others the aid of high temperatures is necessary, or the action of *dehydrating agents*, such as sulphuric acid, hydrochloric acid, zinc chloride, phosphorus pentoxide, acetic anhydride, sodium acetate, &c.

If a reaction occurs between two compounds, each containing hydroxyl, water is generally split off, as for instance in the formation of *salts* from acids and bases, or of esters from acids and alcohols, $CH_3.CO.OH + CH_3.OH = CH_3.CO.OCH_3 + H_2O$; in the formation of *ethers* from two molecules of alcohol, $2C_2H_5.OH = (C_2H_5)_2O + H_2O$; and of *anhydrides* from two molecules of acid, $2CH_3.CO.OH = (C_2H_3O)_2O + H_2O$. Mineral acids (sulphuric acid, phosphoric acid, &c.), easily form esters with alcohols. Organic acids act in the same way at high temperatures, but the yield is as a rule very small; a complete reaction is only brought about by the presence of substances which are capable of uniting with water, such as sulphuric acid or zinc chloride.

Sulphuric acid is generally used in the formation of ethers; it forms with the alcohol ethylsulphuric acid; this decomposes with free alcohol at a definite temperature (temperature of the formation of ether), ether and sulphuric acid being produced:—

$$C_2H_5.OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

Polyvalent alcohols may form partial ethers; the substances called polyglycols, polyglycerides, di- and polysaccharoses (carbohydrates), are examples of such compounds.

The formation of anhydrides from two molecules of organic acids is not possible by simple splitting off of water, but, like the ethers and esters, the acid anhydrides may be obtained from the halogen compounds (indirect anhydride formation). Esters are produced by the action of acid chlorides upon alcohols; ethers by the action of alkyl haloids upon sodium alcoholate, and acid anhydrides by acting with acid chlorides on free acids or their salts.

$$CH_3.COCl + HO.C_2H_5 = \underset{\text{Ester}}{CH_3.CO.OC_2H_5} + HCl.$$

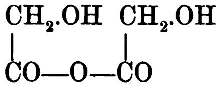
$$C_2H_5I + NaOC_2H_5 = \underset{\text{Ether}}{(C_2H_5)_2O} + NaI.$$

$$CH_3.COCl + HO.CO.CH_3 = \underset{\text{Acid anhydride}}{(CH_3CO)_2O} + HCl.$$

Oxyacids, which are at once acids and alcohols, may unite to form anhydrides with another molecule of a similar kind in three different ways: they may form acid, ether, or ester anhydrides, which latter may be simple or double anhydrides; such double anhydrides are termed *lactides*. The anhydrides of glycollic acid,

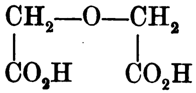
$$CH_2OH.CO_2H,$$

which is the simplest oxyacid, may be taken as examples.



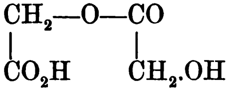
$$\begin{array}{lcl} CH_2.OH & & CH_2.OH \\ | & & | \\ CO & -O- & CO \end{array}$$

Glycollic anhydride



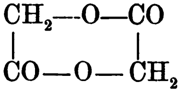
$$\begin{array}{lcl} CH_2 & -O- & CH_2 \\ | & & | \\ CO_2H & & CO_2H \end{array}$$

Diglycollic acid.



$$\begin{array}{lcl} CH_2 & -O- & CO \\ | & & | \\ CO_2H & & CH_2.OH \end{array}$$

Glycoglycollic acid
(First ester anhydride)



$$\begin{array}{lcl} CH_2 & -O- & CO \\ | & & | \\ CO & -O- & CH_2 \end{array}$$

Glycolide
(Second ester anhydride).

The formation of *amides* is also a dehydration process; acids and ammonia unite to form an ammonium salt which gives up water when heated:—

$$CH_3.CO_2NH_4 = CH_3.CONH_2 + H_2O.$$

This result may also be achieved indirectly by means of the acid chlorides:—

$$CH_3.COCl + NH_3 = CH_3.CONH_2 + HCl.$$

If the *amines* be regarded as derivatives of the corresponding hydroxyl compounds, they must also be looked upon as being anhydrides.

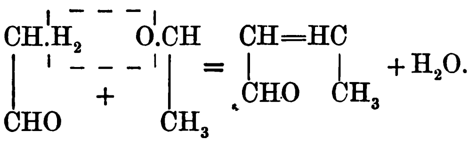
$$C_2H_5OH + NH_3 = C_2H_5NH_2 + H_2O.$$

The direct substitution of hydroxyl by the amido group can only be carried out in certain exceptional cases (a few of the phenols). The change is brought about by the action of ammonia, or by strongly heating with zinc-ammonium chloride. The amines may be obtained indirectly however from the halogen derivatives of the alcohols, especially the iodine compounds :—

$$C_2H_5I + NH_3 = C_2H_5NH_2 + HI.$$

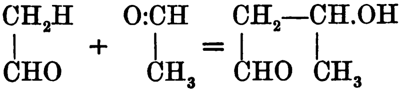
Condensation.—The splitting off of water may also take place in such a way that the oxygen from one molecule unites with the hydrogen which is linked to a carbon atom in the other, thus causing *a carbon atom in the one molecule to become united directly with a carbon or nitrogen atom in the other molecule.* Such a reaction is termed a *condensation* in the restricted sense.

Condensation phenomena are very numerous. The substances which show this property in the greatest degree are the aldehydes and ketones. In such cases the aldehyde or ketone oxygen splits off with two of the hydrogen atoms of the other reacting body. In the first place *aldehydes* may condense *together.* Two molecules of ordinary aldehyde when treated with zinc chloride give croton aldehyde :—



$$\begin{array}{l} CH.H_2 \\ | \\ CHO \end{array} + \begin{array}{l} O.CH \\ | \\ CH_3 \end{array} = \begin{array}{ll} CH{=} & HC \\ | & | \\ CHO & CH_3 \end{array} + H_2O.$$

An oxyaldehyde called aldol is however first formed,



$$\begin{array}{l} CH_2H \\ | \\ CHO \end{array} + \begin{array}{l} O{:}CH \\ | \\ CH_3 \end{array} = \begin{array}{ll} CH_2{-} & CH.OH \\ | & | \\ CHO & CH_3 \end{array}$$

Aldol,

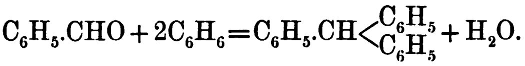
from which crotonic aldehyde is produced by loss of water. Benzaldehyde and ordinary aldehyde give cinnamic aldehyde by condensation:—

$$C_6H_5.CHO + CH_3.CHO = C_6H_5.CH{:}CH.CHO + H_2O.$$

Aldehydes and *ketones* condense in a similar manner. The aldehydes give up oxygen.

$$C_6H_5.CHO + CH_3.CO.CH_3 = \underset{\text{Methylcumyl ketone}}{C_6H_5CH{:}CH.CO.CH_3} + H_2O.$$

Dilute sodium hydrate solution is a useful medium for causing the condensation of aldehydes and ketones. Aldehydes react with aromatic *hydrocarbons* in such a way that the oxygen unites with an atom of hydrogen from each of two hydrocarbon molecules:—

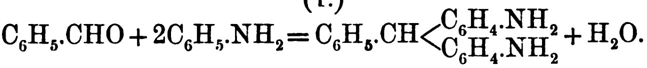


$$C_6H_5.CHO + 2C_6H_6 = C_6H_5.CH\textless\begin{matrix}C_6H_5\\C_6H_5\end{matrix} + H_2O.$$

Triphenylmethane

Aldehydes react in the same manner with *phenols* and *amines*. In the latter case the aldehyde oxygen may unite either with the amido hydrogen, or with that attached to the carbon nucleus:—

(1.)

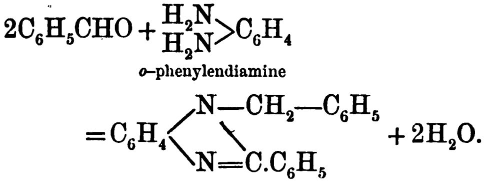


$$C_6H_5.CHO + 2C_6H_5.NH_2 = C_6H_5.CH\textless\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH_2\end{matrix} + H_2O.$$

Diamidotriphenylmethane

(2.)

$$C_6H_5.CHO + H_2N.C_6H_5 = \underset{\text{Benzylideneaniline}}{C_6H_5.CH:N.C_6H_5} + H_2O.$$



$$2C_6H_5CHO + \begin{matrix} H_2N \\ H_2N \end{matrix}\!\!>C_6H_4$$

o-phenylendiamine

$$= C_6H_4\begin{matrix} \diagup N{-}CH_2{-}C_6H_5 \\ \diagdown N{=}C.C_6H_5 \end{matrix} + 2H_2O.$$

Phenylbenzaldehydine

Hydrazines react still more easily with aldehydes. It is on this account that simple phenylhydrazine may be used as a test for aldehydes (E. Fischer).

$$C_6H_5.CH{:}O + NH_2.NH.C_6H_5$$
$$= C_6H_5.CH{:}N.NH.C_6H_5 + H_2O.$$

Benzaldehydephenylhydrazone

A closely allied reaction with separation of water is that which occurs between aldehydes and *hydroxylamine* (V. Meyer), isonitroso compounds (aldoximes) being formed :—

$$C_2H_5.CH{:}O + H_2NOH = C_2H_5.CH{:}NOH + H_2O.$$

Propyl aldehyde

The action of aldehydes upon *acids* (sodium salts) in presence of acid anhydrides is very interesting, because it is a synthetical method for the preparation of unsaturated acids (Perkin's reaction) :—

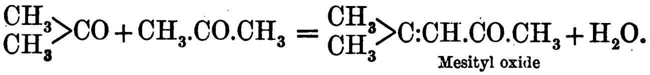
$$C_6H_5.CHO + CH_3.CO_2H = C_6H_5CH{:}CH.CO_2H + H_2O.$$

Cinnamic acid

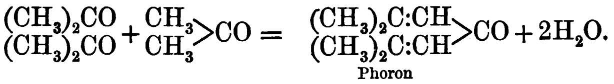
Only a $-\overset{|}{C}H_2$ or $-CH_3$ group which is linked to carboxyl, reacts in this way with aldehydes.

This reaction is a general one both for aromatic and fatty aldehydes ; in this case also unstable oxy-compounds are first formed (aldol condensation) and it appears probable that this occurs in all aldehyde condensations.

Ketones may condense together. If hydrochloric acid be passed into acetone, water is split off, and mesityl oxide and phoron are formed:—



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CO + CH_3.CO.CH_3 = \underset{\text{Mesityl oxide}}{\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C{:}CH.CO.CH_3} + H_2O.$$



$$\begin{matrix}(CH_3)_2CO\\(CH_3)_2CO\end{matrix} + \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CO = \underset{\text{Phoron}}{\left.\begin{matrix}(CH_3)_2C{:}CH\\(CH_3)_2C{:}CH\end{matrix}\right>CO} + 2H_2O.$$

If sulphuric acid act on acetone, the condensation goes still further; three molecules of acetone combine with loss of three molecules of water:—

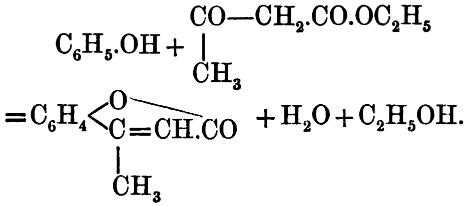
$$3CO(CH_3)_2 = C_6H_3(CH_3)_3 + 3H_2O.$$

The resulting compound is termed mesitylene or trimethylbenzene; it contains the carbon atoms linked in a ring as they are in the benzene derivatives.

Other ketones which contain a methyl group behave in a similar manner; acetophenone $C_6H_5.CO.CH_3$ for instance gives triphenylbenzene $C_6H_3(C_6H_5)_3$.

Ketones react with amines and hydroxylamine like aldehydes (see above); hydroxylamine gives rise to acetoximes.

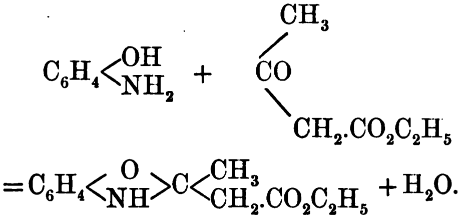
Ketonic acids such as pyroracemic acid $CH_3.CO.CO_2H$, or acetoacetic ether $CH_3.CO.CH_2.CO_2C_2H_5$ condense in the same manner as ketones. Acetoacetic ether unites with phenols at ordinary temperatures in presence of some dehydrating agent; as alcohol is split off at the same time compounds called cumarines are formed (Von Pechmann).



$$C_6H_5.OH + \begin{array}{l} CO—CH_2.CO.OC_2H_5 \\ | \\ CH_3 \end{array}$$

$$= C_6H_4 \begin{array}{l} <O \\ <C{=}CH.CO \\ \;\;| \\ \;\;CH_3 \end{array} + H_2O + C_2H_5OH.$$

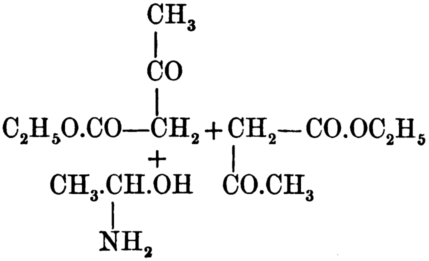
Acetoacetic ether condenses with orthoamidophenol according to the following equation :—



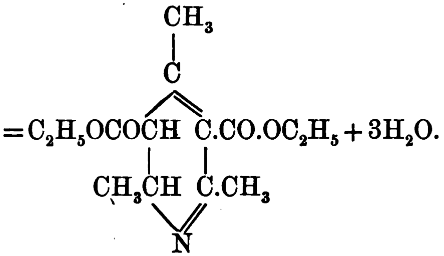
$$C_6H_4<\begin{array}{l} OH \\ NH_2 \end{array} + CO\begin{array}{l} \diagup CH_3 \\ \diagdown CH_2.CO_2C_2H_5 \end{array}$$

$$= C_6H_4<\begin{array}{c} O \\ NH \end{array}>C<\begin{array}{l} CH_3 \\ CH_2.CO_2C_2H_5 \end{array} + H_2O.$$

Acetoacetic ether gives pyridine compounds with aldehyde ammonia (Hantzsch) :—



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ & CO & \\ & | & \\ C_2H_5O.CO— & CH_2 & + CH_2—CO.OC_2H_5 \\ & + & \quad\;\; | \\ CH_3.CH.OH & & \quad CO.CH_3 \\ | & & \\ NH_2 & & \end{array}$$

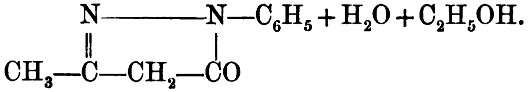


(1-3-5) Trimethyldihydropyridinedicarboxylic ether.

Certain ketonic acid ethers condense with phenylhydrazine to form pyrazolon compounds :—[1]

$$C_6H_5.NH.NH_2 + CH_3—CO—CH_2—CO.OC_2H_5 =$$

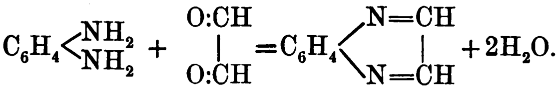
Phenylhydrazine Acetoacetic ether



(1-3) Phenylmethylpyrazolon

Here, as also in some other of the above-mentioned reactions, an intramolecular splitting off of water or alcohol occurs, particularly from the intermediate condensation products which are first formed.

All compounds which contain two adjoining carbonyl groups, —CO—CO—, react with *o*-diamines to form quinoxalines (Duisberg). Glyoxal gives simple quinoxaline, benzil gives diphenylquinoxaline, &c.



Glyoxal Quinoxaline

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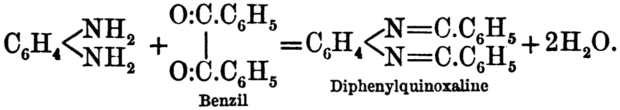
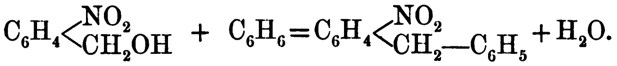
[1] These were formerly called quinizine compounds.



$$C_6H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix} + \underset{\text{Benzil}}{\begin{matrix}O{:}C.C_6H_5\\ |\\ O{:}C.C_6H_5\end{matrix}} = \underset{\text{Diphenylquinoxaline}}{C_6H_4{<}\begin{matrix}N{=}C.C_6H_5\\N{=}C.C_6H_5\end{matrix}} + 2H_2O.$$

Certain *alcohols* also condense with other substances, such as hydrocarbons, the hydroxyl group being split off with one hydrogen atom of the hydrocarbon.

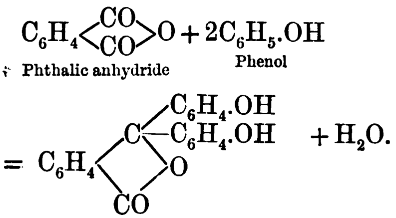
Paranitrobenzyl alcohol gives with benzene, in presence of sulphuric acid, *p*-nitrodiphenylmethane :—



$$C_6H_4{<}\begin{matrix}NO_2\\CH_2OH\end{matrix} + C_6H_6 = C_6H_4{<}\begin{matrix}NO_2\\CH_2{-}C_6H_5\end{matrix} + H_2O.$$

Oxyacids such as lactic or malic acids condense with amines and phenols, but the reactions are more complicated than the foregoing.

Amongst other compounds which are easily condensed, the *anhydrides* of certain acids such as phthalic and succinic acids must be mentioned. In the condensation of these substances it is not the anhydride oxygen which is split off, but one of the carbonyl oxygen atoms; these bodies combine remarkably easily with phenols and amines :—



$$\underset{\text{Phthalic anhydride}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O} + \underset{\text{Phenol}}{2C_6H_5.OH}$$

$$= C_6H_4{<}\begin{matrix}C{<}\begin{matrix}C_6H_4.OH\\C_6H_4.OH\end{matrix}\\CO\end{matrix}{>}O + H_2O.$$

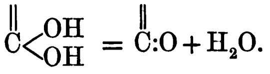
Phenolphthaleïne

From the above typical examples of different condensation processes, it is plain that they furnish a means of preparing higher molecular compounds from simple ones, and there is no doubt that condensations play a great part in the building up of many of the complicated compounds found in animal and vegetable organisms.

Intramolecular splitting off of water.—In the reactions hitherto discussed water has always been formed by the combination of two or more molecules, but it may also be split off within a *single* molecule, *inner anhydrides* or *inner condensation products* being produced. These intramolecular processes have been thoroughly investigated, particularly of late years (Von Baeyer, Fittig, &c.):—

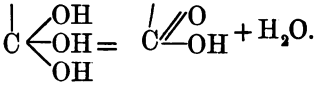
Only examples of the more important of these reactions will be given here.

Compounds containing two or three hydroxyls attached to the *same* carbon atom immediately split off water, one oxygen atom becoming at the same time doubly linked to the carbon:—



$$\overset{\|}{\mathrm{C}}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} = \overset{\|}{\mathrm{C}}{:}\mathrm{O} + \mathrm{H_2O}.$$

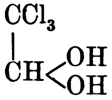
Conversion of aldehyde and ketone hydrates into aldehydes and ketones.



$$\overset{|}{\mathrm{C}}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix} = \overset{|}{\mathrm{C}}\begin{matrix}\mathrm{\!/\!\!/O}\\ \mathrm{-OH}\end{matrix} + \mathrm{H_2O}.$$

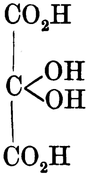
Change of ortho- into meta- acids.

The aldehyde and ketone hydrates are only stable if a neighbouring carbon atom be linked to strongly negative groups or atoms. Many aldehydes and ketones containing halogens occur as hydrates, as also do several aldehyde and ketonic acids :—



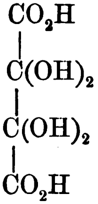
$$\begin{array}{l} CCl_3 \\ | \\ CH<\begin{matrix}OH\\OH\end{matrix} \end{array}$$

Chloral hydrate



$$\begin{array}{l} CO_2H \\ | \\ C<\begin{matrix}OH\\OH\end{matrix} \\ | \\ CO_2H \end{array}$$

Dioxymalonic acid
(Hydrate of mesoxalic acid)

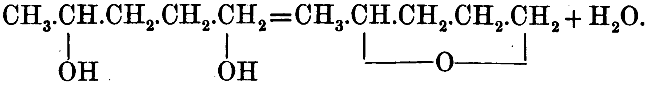


$$\begin{array}{l} CO_2H \\ | \\ C(OH)_2 \\ | \\ C(OH)_2 \\ | \\ CO_2H \end{array}$$

Dioxytartaric acid.

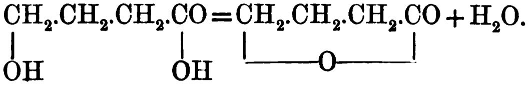
These compounds however give up water more or less readily on heating.

Dihydrates in which hydroxyls are separated by two or three carbon atoms split off water with difficulty; if however there be *four* or *five* carbon atoms between the hydroxyl groups, water is easily lost. The resulting anhydrides differ according to the nature of the compound from which they are derived; the splitting off of water causes the formation of either an internal ether, an internal ester, or an internal acid anhydride. Divalent alcohols form *alcoholic anhydrides* (internal ethers), oxy-acids give *lactones* (internal esters), and dibasic acids yield *acid anhydrides* :—



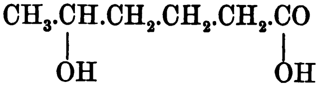
$$CH_3.\underset{\displaystyle OH}{\underset{|}{CH}}.CH_2.CH_2.\underset{\displaystyle OH}{\underset{|}{CH_2}} = CH_3.\underbrace{CH.CH_2.CH_2.CH_2}_{O} + H_2O.$$

γ-Pentyleneglycol Anhydride



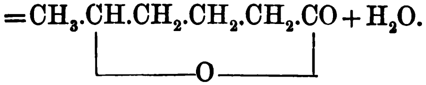
$$\underset{\displaystyle OH}{\underset{|}{CH_2}}.CH_2.CH_2.\underset{\displaystyle OH}{\underset{|}{CO}} = \underbrace{CH_2.CH_2.CH_2.CO}_{O} + H_2O.$$

γ-Oxybutyric acid Butyrolactone



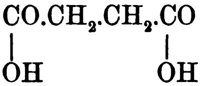
$$CH_3.\underset{\overset{|}{OH}}{CH}.CH_2.CH_2.\underset{\overset{|}{OH}}{CO}$$

δ-Oxycaproic acid



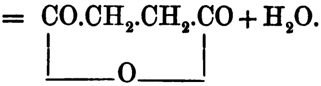
$$= \underbrace{CH_3.CH.CH_2.CH_2.CO}_{O} + H_2O.$$

δ-Caprolactone



$$\underset{\overset{|}{OH}}{CO}.CH_2.CH_2.\underset{\overset{|}{OH}}{CO}$$

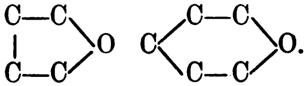
Succinic acid



$$= \underbrace{CO.CH_2.CH_2.CO}_{O} + H_2O.$$

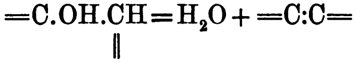
Anhydride

All these anhydrides contain the atoms linked in a ring composed of four or five carbon atoms and one oxygen atom :—



The above reactions hold generally for γ- and δ-oxy-compounds of the fatty series, and for ortho-compounds of the aromatic series. Many of these oxycompounds (particularly the γ-oxyacids) give up water spontaneously at ordinary temperatures, others require the action of heat, or of dehydrating substances.

The splitting off of water may take place in such a way that the hydroxyl or oxygen of one carbon atom unites with the hydrogen of an adjacent carbon atom; in such cases the carbon atoms usually become doubly linked. *Unsaturated* compounds are formed in this manner according to the following general equation :—



$$=\mathrm{C.OH.}\underset{\|}{\mathrm{CH}}=\mathrm{H_2O}+=\mathrm{C{:}C}=$$

In this way for example β-oxybutyric acid gives crotonic acid :—

$$\mathrm{CH_3.CH(OH).CH_2.CO_2H=CH_3.CH{:}CH.CO_2H+H_2O.}$$

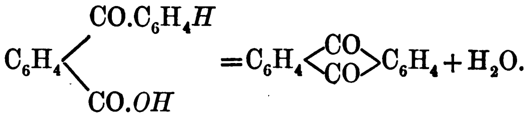
This reaction is specially characteristic for β-oxy-acids.

The formation of aldehydes and ketones from polyhydroxyl compounds by the action of dehydrating agents, depends probably upon a similar reaction ; unsaturated alcohols are formed as intermediate products, and these become further changed by a rearrangement of the atoms :—

$$\mathrm{CH_2OH.CH_2OH=CH_2{:}CH.OH=CH_3.CH{:}O+H_2O.}$$

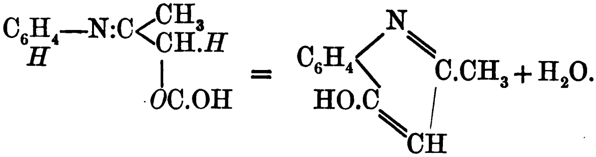
The formation of unsaturated compounds by the splitting off of water does not take place spontaneously, but requires the help of high temperatures, or the action of some dehydrating agent such as sulphuric acid, hydrogen potassium sulphate, zinc chloride, phosphorus trichloride, &c.

If water be formed from hydroxyl or oxygen and hydrogen which are not linked to adjoining carbon atoms, the *inner condensation* is accompanied by a *circular closing* of the carbon chain. *o*-Benzoylbenzoic acid for instance gives anthraquinone by treatment with sulphuric acid :—



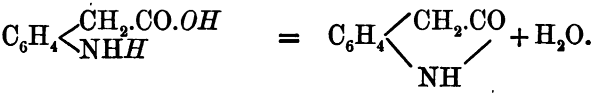
$$C_6H_4\begin{cases}CO.C_6H_4H\\CO.OH\end{cases} = C_6H_4{<}{}^{CO}_{CO}{>}C_6H_4 + H_2O.$$

Aniline and acetoacetic ether give aniline-acetoacetic acid; this loses water and forms oxymethylquinoline:—

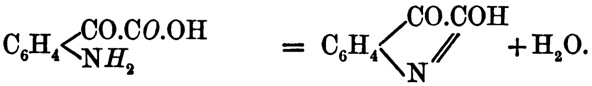


Many syntheses of quinoline compounds and similar substances containing condensed pyridine or benzene nuclei are founded upon analogous reactions (see p. 142). The hydrogen atom which is taken from the benzene nucleus always occupies the ortho-position relative to the side-chain. It is worthy of note that this reaction as a rule can only be carried out if the oxygen be separated from the hydrogen by *five* or *six* atoms which are linked together.

An inner condensation occurs in the case of certain aromatic *nitrogen* compounds of the ortho-series, the hydrogen linked to nitrogen combines with the oxygen linked to carbon, and a union of carbon and nitrogen is effected. In this manner ortho-amido acids form inner anhydrides which are called *lactames* or *lactimes*, according to whether the hydroxyl or the oxygen of the carboxyl group reacts:—



o-Amidophenylacetic acid **Oxindol (Lactame)**

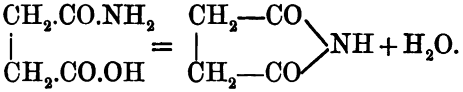


$$C_6H_4{<}\begin{matrix}CO.C\mathit{O}.OH\\ N\mathit{H}_2\end{matrix} = C_6H_4{<}\begin{matrix}CO.COH\\ N\end{matrix} + H_2O.$$

Isatic acid **Isatin (Lactime)**

Lactames correspond to lactones.

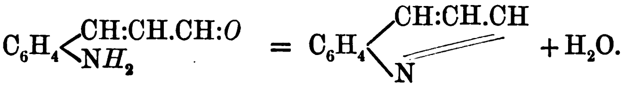
Acid imides, corresponding to acid anhydrides, are formed by amido acids in which the carboxyl group is separated from the amido group by two or three carbon atoms:—



$$\begin{matrix}CH_2.CO.NH_2\\ |\\ CH_2.CO.OH\end{matrix} = \begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}{>}NH + H_2O.$$

Succinamic acid **Succinimide**

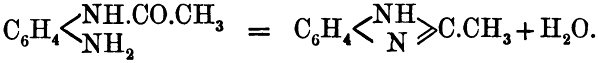
An inner condensation of *o*-amido aldehydes and ketones may also be easily accomplished, the reaction being exactly similar to that involved in the formation of lactimes:—



$$C_6H_4{<}\begin{matrix}CH{:}CH.CH{:}\mathit{O}\\ N\mathit{H}_2\end{matrix} = C_6H_4{<}\begin{matrix}CH{:}CH.CH\\ N\end{matrix} + H_2O.$$

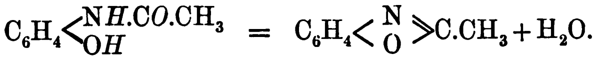
o-Amidocinnamic aldehyde **Quinoline**

Anhydrides are also obtained from acetyl substituted *o*-diamines and *o*-amidophenols (Hobrecker and Hübner):—



$$C_6H_4{<}\begin{matrix}NH.CO.CH_3\\ NH_2\end{matrix} = C_6H_4{<}\begin{matrix}NH\\ N\end{matrix}{>}C.CH_3 + H_2O.$$

Acetyl o-phenylenediamine **Ethenylphenyleneamidine**



$$C_6H_4{<}\begin{matrix}N\mathit{H}.C\mathit{O}.CH_3\\ \mathit{OH}\end{matrix} = C_6H_4{<}\begin{matrix}N\\ O\end{matrix}{>}C.CH_3 + H_2O.$$

Acetyl o-amidophenol **Ethenylamidophenol**

In these cases also water is only split off with ease if the oxygen be separated from the hydrogen by a chain of *five* or *six* atoms.

The substances formed by the inner condensation of aromatic monoamido compounds are either *indol* or *quinoline* compounds, according to whether the ring which is formed contains five or six atoms, including one nitrogen atom. Indol itself may be regarded as the anhydride of a hydroxy amido compound:—

$$C_6H_4\left\langle\begin{matrix}CH{:}CH.OH\\ NH_2\end{matrix}\right. = \underset{\text{Indol}}{C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle CH} + H_2O.$$

In the formation of all these different kinds of inner anhydrides and condensation products, where water is split off from atomic groups which are not linked to the same, or adjoining, carbon atoms, a circular closing of a previously open atomic chain occurs. This chain is, with very few exceptions, always composed of five or six atoms, which may either be all carbon atoms or may include atoms of nitrogen, oxygen, or sulphur. The tendency of an open chain to pass into a ring formation is governed chiefly by the *number* of atoms linked together; their nature and the manner in which they are joined are only of secondary importance.

Amongst intramolecular reactions accompanied by loss of water the conversion of *amides* into *nitriles* remains to be noticed; this reaction only takes place by the help of powerful dehydrating agents.

$$\underset{\text{Acetamide}}{CH_3.CONH_2} = \underset{\text{Acetonitril}}{CH_3{-}CN} + H_2O.$$

CHAPTER XVIII

SPLITTING OFF OF HALOGEN HYDRIDES

THIS process is completely analogous to dehydration, and also occurs between either one or two molecules. The products of the reaction are usually the same as those obtained in the preparation of anhydrides.

The indirect processes of dehydration which have already been discussed, and upon which depend the formation of ethers, esters, acid anhydrides, amido compounds, and amines, from halogen compounds, all cause the formation and splitting off of halogen hydrides, because the halogen of one molecule unites with the hydrogen of a hydroxyl or ammonia residue attached to a second molecule.

The following reactions proceed in a similar manner to condensations with loss of water.

Organic halogen compounds, in presence of aluminium chloride or bromide, act on aromatic hydrocarbons in such a way that the halogen unites with a hydrogen atom of the hydrocarbon, and the group which was previously attached to the halogen takes the place of the hydrogen atom (Friedel and Crafts' reaction):—

$$C_6H_6 + CH_3Cl = C_6H_5.CH_3 + HCl.$$

In this manner six CH_3 groups may be successively introduced into benzene.

Chloroform and benzene, in presence of aluminium chloride, give triphenyl methane:—

$$CHCl_3 + 3C_6H_6 = (C_6H_5)_3CH + 3HCl.$$

If carbonyl chloride act upon hydrocarbons in presence of aluminium chloride, acid chlorides and ketones are formed synthetically:—

$$C_6H_6 + COCl_2 = \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl.$$

$$2C_6H_6 + COCl_2 = \underset{\text{Benzophenone}}{C_6H_5.CO.C_6H_5} + 2HCl.$$

The action of aluminium chloride is apparently catalytic; in all probability however it combines with the hydrocarbon, and the substance which is formed is then decomposed by the halogen compound (Gustavson).

$$C_6H_6 + Al_2Cl_6 = C_6H_5.Al_2Cl_5 + HCl.$$
$$C_6H_5.Al_2Cl_5 + CH_3Cl = C_6H_5.CH_3 + Al_2Cl_6.$$

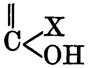
Aluminium chloride and bromide are largely used for syntheses of the above nature.

The presence of zinc dust may also cause a reaction between aromatic hydrocarbons and chlorides (Zincke):

$$\underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + C_6H_6 = \underset{\text{Diphenylmethane}}{C_6H_5.CH_2.C_6H_5} + HCl.$$

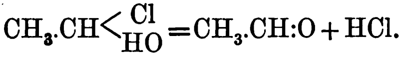
The splitting off of halogen hydrides *within the molecule* takes place partly at ordinary temperatures, and partly by warming with water or alkalis.

Compounds containing the group



$$\overset{\|}{\mathrm{C}}<^{\mathrm{X}}_{\mathrm{OH}}\quad(\mathrm{X}=\text{halogen})$$

are just as little capable of existence as the corresponding dihydrates; they evolve halogen hydrides :—



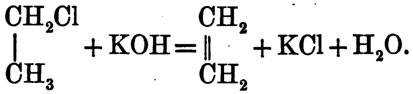
$$\mathrm{CH_3.CH}<^{\mathrm{Cl}}_{\mathrm{HO}}=\mathrm{CH_3.CH{:}O+HCl.}$$

The formation of chloral from alcohol, by the action of chlorine, depends upon this reaction (see p. 121). If a halogen and an amido group be linked to the same carbon atom, a halogen hydride is split off and an imido compound formed. For instance, by the action of phosphorus pentachloride upon acetamide, a compound $CH_3.CCl_2.NH_2$ is obtained; hydrochloric acid is however at once evolved with formation of acetchlorimide, but this compound readily loses a second molecule of hydrochloric acid, the final product being therefore a nitrile (Wallach) :—

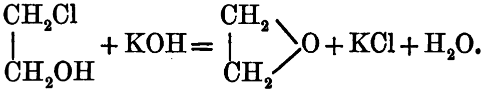
$$CH_3.CONH_2+PCl_5=CH_3.CCl_2NH_2+POCl_3.$$
$$CH_3.CCl_2NH_2=CH_3.CCl{:}NH+HCl.$$
$$CH_3.CCl{:}NH=CH_3.CN+HCl.$$

The conversion of the amides into nitriles by means of phosphorus pentachloride is therefore an indirect process of dehydration (see p. 150).

By treating halogen compounds with water or alkalis the halogen hydrides are split off, or else the halogen is replaced by hydroxyl or oxygen.



$$CH_2Cl{-}CH_3 + KOH = CH_2{=}CH_2 + KCl + H_2O.$$

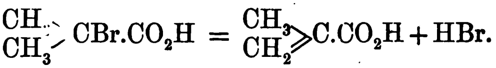


Ethylene chlorhydrin   Ethylene oxide

This last reaction, especially the action of alkalis upon halogen substituted alcohols, may be regarded as taking place in such a way that the hydroxyl hydrogen is first replaced by metal, and then the metallic chloride is split off.

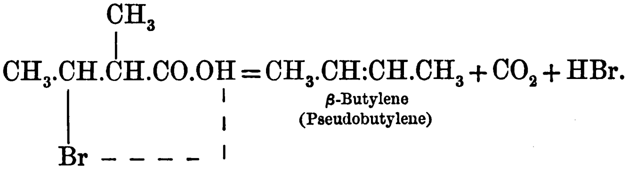
The splitting off of halogen hydrides from substituted fatty acids by treating with water or alkalis, proceeds in different ways according to the relative position of the halogen to carboxyl.

By this treatment the substituted acids usually give oxyacids which are formed by the replacement of the halogen by hydroxyl; a few of them yield unsaturated acids, hydrogen being taken from an adjoining carbon atom.



Bromoisobutyric acid   Methacrylic acid

If the halogen take the β-position, hydrogen is split off from the carboxyl group, *unsaturated hydrocarbons and carbon dioxide* being formed (Fittig):—

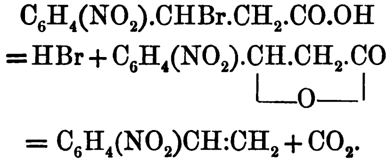


$$CH_3.CH.CH(CH_3).CO.OH = CH_3.CH{:}CH.CH_3 + CO_2 + HBr.$$

β-Butylene (Pseudobutylene)

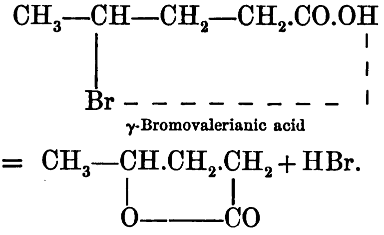
β-Bromomethylethylacetic acid

Unstable β-lactones are formed as intermediate products, but they decompose as above into a hydrocarbon and carbon dioxide. The β-lactones of nitro-acids are somewhat more stable. Ortho-, meta-, and para-nitro phenylbromopropionic acids give lactones when treated in the cold with soda solution; on heating however carbon dioxide and nitrostyrolenes are formed:—



$$\begin{aligned}&C_6H_4(NO_2).CHBr.CH_2.CO.OH\\ &= HBr + C_6H_4(NO_2).\underbrace{CH.CH_2.CO}_{O}\\ &= C_6H_4(NO_2)CH{:}CH_2 + CO_2.\end{aligned}$$

If the halogen be linked to the third carbon atom reckoned from the carboxyl (the γ position), the hydrogen of the carboxyl combines with the halogen; in this case however no carbon dioxide is evolved, but a stable lactone is produced (γ-lactones, see p. 145):—



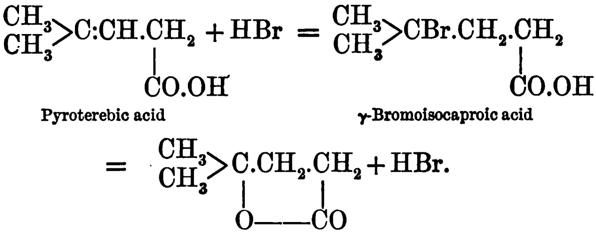
$$\underset{\displaystyle Br}{CH_3—\overset{}{CH}}—CH_2—CH_2.CO.OH$$

γ-Bromovalerianic acid

$$= CH_3—\underbrace{CH.CH_2.CH_2}_{O\text{———}CO} + HBr.$$

Valerolactone

Many γ-halogen acids are not at all stable but change spontaneously into lactones, a halogen hydride being split off. This explains the interesting fact that certain unsaturated acids yield isomeric lactones when treated with hydrobromic acid. A hydrobromic addition compound is first formed; this at once loses hydrobromic acid, a lactone being produced. Diallylmalonic, and pyroterebic acids act in this way:—

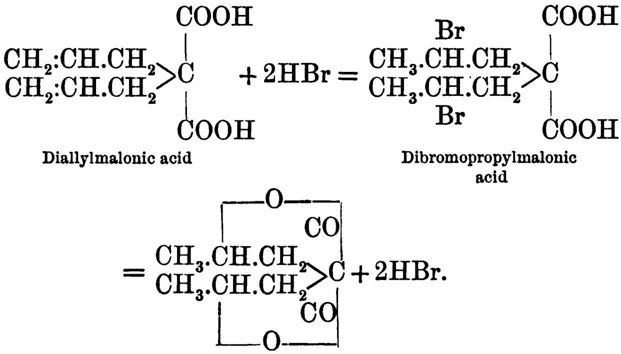


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{:}CH.\underset{\displaystyle \overset{|}{CO.OH}}{CH_2} + HBr = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CBr.CH_2.\underset{\displaystyle \overset{|}{CO.OH}}{CH_2}$$

Pyroterebic acid γ-Bromoisocaproic acid

$$= \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\underset{\displaystyle O\text{———}CO}{\underset{|\qquad\quad |}{C.CH_2.CH_2}} + HBr.$$

Isocaprolactone



$$\begin{matrix}CH_2{:}CH.CH_2\\CH_2{:}CH.CH_2\end{matrix}\!\!>\overset{\displaystyle COOH}{\underset{\displaystyle COOH}{C}} + 2HBr = \begin{matrix}CH_3.\overset{Br}{CH}.CH_2\\CH_3.\underset{Br}{CH}.CH_2\end{matrix}\!\!>\overset{\displaystyle COOH}{\underset{\displaystyle COOH}{C}}$$

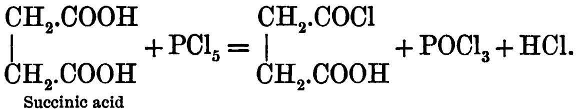
Diallylmalonic acid Dibromopropylmalonic acid

$$= \begin{matrix}\overset{\displaystyle \ulcorner\text{——}O\text{——}\urcorner}{CH_3.CH.CH_2}\\\underset{\displaystyle \llcorner\text{——}O\text{——}\lrcorner}{CH_3.CH.CH_2}\end{matrix}\!\!>\overset{\displaystyle CO}{\underset{\displaystyle CO}{C}} + 2HBr.$$

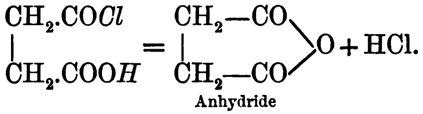
Nonodilactone

It thus appears that in the formation of lactones, the splitting off of halogen hydrides corresponds completely to the splitting off of water.

The formation of inner acid anhydrides by the loss of halogen hydrides has not been directly proved, because the monochlorides of dibasic acids are unknown; but in spite of this it may be supposed that the production of anhydrides by the action of phosphorus chloride on certain dibasic acids depends upon the above reaction; the action of phosphorus chloride is only indirect, as in the case of the amides :—



$$\underset{\text{Succinic acid}}{\begin{array}{l}CH_2.COOH\\ |\\ CH_2.COOH\end{array}} + PCl_5 = \begin{array}{l}CH_2.COCl\\ |\\ CH_2.COOH\end{array} + POCl_3 + HCl.$$



$$\begin{array}{l}CH_2.CO\mathit{Cl}\\ |\\ CH_2.COO\mathit{H}\end{array} = \underset{\text{Anhydride}}{\begin{array}{l}CH_2-CO\diagdown\\ |\qquad\qquad\quad O\\ CH_2-CO\diagup\end{array}} + HCl.$$

CHAPTER XIX

HYDRATION PROCESSES

THESE are the opposite of anhydric processes; water is taken up during their progress, and in general a complex molecule is split up into two or more simple ones; the anhydrides in particular easily combine with water, corresponding hydroxyl compounds being formed. These reactions are brought about by means of *dilute acids*, particularly sulphuric and hydrochloric acids. *Alkalis* too may act in the same way in certain cases. It occasionally happens that the combination with water takes place so easily, that nothing but *water* is needed to bring about the change. Enzymotic processes (*i.e.* processes of fermentation by means of 'unorganised ferments') are of this order, but for convenience they are discussed in another chapter. The esters are most easily decomposed into their components, alcohols and acids: the term *saponification* is usually applied to this operation. It is best accomplished by the action of alkalis, but it may also be brought about by heating with dilute mineral acids, or with water.

$$CH_3.CO. \vdots OC_2H_5 + KOH = CH_3CO.OK + C_2H_5.OH.$$

Alcoholic solution of potassium hydrate (sodium hydrate) is very convenient for the saponification of esters insoluble in water.

The word saponification is derived from the process of soap-making—that is to say, of the preparation of the alkaline salts of fatty acids from fats. Fats consist of the fatty acid ethers of the trivalent alcohol glycerine; by the action of alkalis, alkaline salts of the fatty acids are formed, and the glycerine is set free :—

$$\underset{\text{Tristearin}}{C_3H_5(OC_{18}H_{35}O)_3} + 3KOH = \underset{\substack{\text{Potassium stearate}\\ \text{(soap)}}}{3C_{18}H_{35}OOK} + \underset{\text{Glycerine.}}{C_3H_5(OH)_3}$$

Ethers are not so easily decomposed as esters. Ordinary ether must be heated with water to 150° in order to be reconverted into alcohol.

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

The ethers of the glucoses (simple sugars), the di- and poly-saccharoses as they are called, combine with water more easily. Cane sugar, for instance, is split up by dilute mineral acids into grape and fruit sugars :

$$\underset{\text{Cane sugar}}{C_6H_{11}O_5—O—C_6H_{11}O_5} + H_2O = \underset{\substack{\text{Grape sugar}\\ \text{(Dextrose)}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fruit sugar}\\ \text{(Lævulose).}}}{C_6H_{12}O_6}$$

Starch when treated in a similar manner is converted into dextrose, though the change proceeds more slowly :—

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

The glucosides, which are ethereal compounds of sugar and other substances, mostly combine with water when treated with dilute mineral acids, or in certain cases, by the action of dilute alkalis.

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Saligenin}}{C_7H_8O_2} + \underset{\text{Grape sugar.}}{C_6H_{12}O_6}$$

Acid anhydrides, which are formed by the withdrawal of water from two molecules of acid, are easily converted into the corresponding acids by the action of water or alkalis :—

$$\underset{\text{Acetic anhydride}}{CH_3.CO.O.CO.CH_3} + H_2O = \underset{\text{Acetic acid.}}{2CH_3.CO_2H}$$

All *acid amides* are easily hydrated by means of acids or alkalis, the organic acid and ammonia being regenerated :—

$$\underset{\text{Acetamide}}{CH_3.CONH_2} + H_2O = CH_3.CO.OH + NH_3.$$

The amido acids, like the amines, show a much greater power of resisting the action of acids and alkalis, and it is difficult or impossible to hydrate them. Amines and amidoacids containing acid radicles (which may be regarded as substituted amides) are however easily decomposed into their components.

$$\underset{\substack{\text{Hippuric acid}\\ \text{(Benzoylglycocoll)}}}{C_6H_5.CO—NH.CH_2.CO_2H} + H_2O$$

$$= \underset{\text{Glycocoll}}{NH_2.CH_2.CO_2H} + \underset{\text{Benzoic acid.}}{C_6H_5.CO_2H}$$

Sulphonic acids, which may be regarded as being acid esters of unsymmetrical sulphurous acid, are not changed by boiling with alkalis, but by fusion they are easily decomposed, water (alkali) being taken up :—

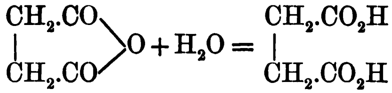
$$\underset{\substack{\text{Monobenzene}\\ \text{sulphonic acid}}}{C_6H_5.SO_2OH} + 2KOH = \underset{\text{Phenol}}{C_6H_5OH} + K_2SO_3 + H_2O.$$

A peculiar hydration process takes place if an aldehyde be treated with alkalis; part of the aldehyde is converted into an alcohol, another part into the corresponding acid:—

$$\underset{\text{Benzaldehyde}}{2C_6H_5.CHO} + KOH = \underset{\text{Benzylalcohol}}{C_6H_5.CH_2OH} + \underset{\text{Potassium benzoate.}}{C_6H_5.CO_2K}$$

Compounds formed by condensation and splitting off of water (see p. 137) are very stable. It is difficult, and often impossible, to induce them to combine with water to form the substances from which they were originally made; their stability depends on the properties of the carbon bond.

Water may be taken up without the molecule being decomposed. Many *internal anhydrides* for instance combine with water, a hydrate being again formed. Internal *acid anhydrides* are very easily converted into the corresponding acids by treatment with water or alkalis:



$$\begin{array}{l} CH_2.CO \\ | \\ CH_2.CO \end{array}\!\!>O + H_2O = \begin{array}{l} CH_2.CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

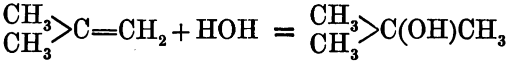
Succinic anhydride Succinic acid.

The *lactones* are, as a rule, only to a slight extent reconverted into oxyacids by the action of water, but they are easily acted upon by soluble basic hydrates with formation of salts of the corresponding oxyacids.

Lactames behave like lactones.

Alcohol anhydrides (alkylenoxides) formed by direct splitting off of water, show considerable resistance to the action of water. Of the remaining alkylenoxides, those glycols are most easily regenerated in which the oxygen is attached to a tertiary carbon atom (Eltekow).

Some *unsaturated* compounds take up water, and in such cases the hydroxyl always attaches itself to the carbon atom which is linked to the least hydrogen:—



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH_2 + HOH = \begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH)CH_3$$

Isobutylene Trimethyl carbinol.

Unsaturated hydrocarbons combine with sulphuric acid in an exactly similar way; H goes to one carbon atom, and OSO_3H to another, that namely to which less hydrogen is attached.

Amongst the remaining hydration processes, the conversion of the *nitriles* (cyanides) into amides by the action of acids may be mentioned. The amides themselves, as already shown, take up more water and form acids and ammonia.

$$CH_3{-}CN + H_2O = CH_3{-}CONH_2$$

Acetonitril Acetamide.

CHAPTER XX

ADDITION OF HALOGEN HYDRIDES

DILUTE hydrochloric, like dilute sulphuric acid, causes the decomposition of anhydride compounds without the halogen hydride becoming linked to the compound. Esters are however decomposed by heating with concentrated halogen hydrides in such a way that the alkyl haloid and free acid are formed:—

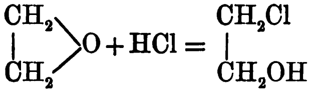
$$CH_3.CO.OC_2H_5 + HI = CH_3.CO.OH + C_2H_5I.$$

Ethers react in an analogous manner, especially with hydriodic acid:—

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

As regards internal anhydrides, by the action of concentrated halogen hydrides (especially hydrobromic acid) many lactones are converted into corresponding halogen-substituted acids, addition products being first formed.

Alcohol anhydrides also combine directly with halogen hydrides, halogen hydrins being produced:—



$$\left.\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\right\rangle O + HCl = \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$$

Ethylene oxide Ethylene chlorhydrin

Halogen hydrides combine tolerably easily with unsaturated compounds. As the affinity of hydrogen for halogens decreases with increase of atomic weight, this addition takes place most easily with hydriodic acid. When halogen hydrides add themselves to unsaturated compounds, the halogen goes to the carbon atom combined with the least hydrogen, and the hydrogen to the carbon richest in hydrogen. Such reactions therefore only give secondary and tertiary halogen compounds (see p. 125).

$$CH_3.CH{:}CH_2 + HI = CH_3.CHI.CH_3.$$

If *unsaturated acids* combine with halogen hydrides, the opposite action occurs; as a rule the halogen goes to the carbon atom linked to the most hydrogen, or if the acid contain the group CH=CH, to the carbon atom furthest from carboxyl :—

$$\underset{\text{Acrylic acid}}{CH_2{:}CH.CO_2H} + HI = \underset{\beta\text{-Iodopropionic acid.}}{CH_2I.CH_2.CO_2H}$$

$$\underset{\text{Crotonic acid}}{CH_3.CH{:}CH.CO_2H} + HI = \underset{\beta\text{-Iodobutyric acid.}}{CH_3.CHI.CH_2.CO_2H}$$

α-iodo acids are simultaneously formed in small quantities.

CHAPTER XXI

UNION OF CARBON WITH CARBON

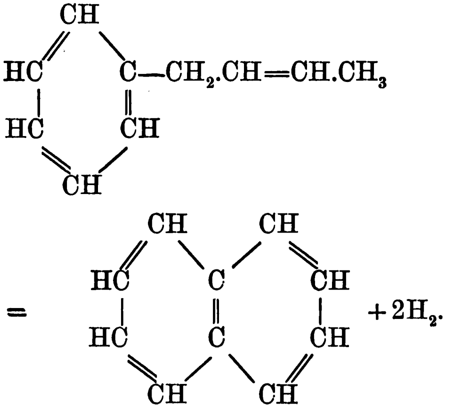
AN enlargement of the carbon chain may be brought about in various ways. There are many methods of introducing carbon into organic compounds in such a way that it shall attach itself to the carbon already present in the chain. Some of the reactions belonging to this class have already been mentioned, particularly the condensations of two or more molecules which are accompanied by a splitting off of water, as well as the actions of halogen compounds on aromatic hydrocarbons in presence of aluminium chloride or bromide. Many synthetical condensation processes which lead to an enlargement of the carbon chain proceed in other ways.

If hydrocarbons be exposed to high temperatures, by passing them through red-hot tubes, hydrocarbons of higher molecular weight are often formed, hydrogen being usually evolved. In this manner acetylene is converted into benzene, which itself gives, if it be passed through red-hot tubes, diphenyl and other more condensed hydrocarbons:—

$$3C_2H_2 = C_6H_6.$$

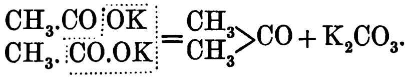
$$2C_6H_6 = C_6H_5.C_6H_5 + H_2.$$

If phenylbutylene be exposed to high temperatures it forms naphthalene; in this reaction the carbon chain is not enlarged, but two carbon atoms which were previously free unite together. The open side-chain (butylene radicle) attacks the benzene nucleus and a close carbon ring is produced.



Many other pyrogenetic reactions proceed analogously; in all cases the open side-chain links itself to the benzene nucleus in the ortho-position, a closed carbon chain of *five* or *six* members being formed.

An important pyrogenetic synthesis is that which causes the formation of ketones, by heating the salts of organic acids:—



$$\begin{matrix} CH_3.CO\,\boxed{OK} \\ CH_3.\boxed{CO.OK} \end{matrix} = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CO + K_2CO_3.$$

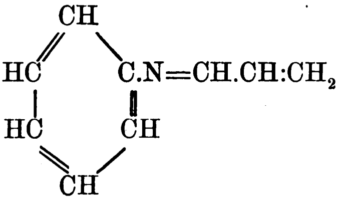
Amongst the numerous condensation processes accompanied by loss of water or oxidation, mention may be made of Skraup's general method for the synthetical production of quinolines, by heating aromatic amido-compounds with glycerine and sulphuric acid. Ordinary quinoline is obtained from aniline according to the equation

$$C_6H_5.NH_2 + C_3H_8O_3 = C_6H_4N(C_3H_3) + 3H_2O + H_2.$$

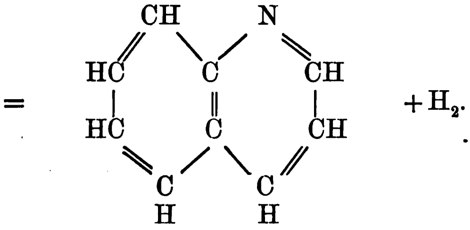
It is probable that acrolein is first formed from the glycerine by loss of water; acrolein-aniline is then produced, from which hydrogen is split off giving quinoline. The presence of nitrobenzene, which acts as an oxidiser, helps the reaction.

$$\underset{\text{Glycerine}}{C_3H_8O_3} = \underset{\text{Acrolein}}{C_3H_4O} + 2H_2O.$$

$$C_3H_4O + C_6H_5.NH_2 = \underset{\text{Acrolein-aniline}}{C_6H_5.N{:}CH.CH{:}CH_2} + H_2O.$$



Acrolein-aniline

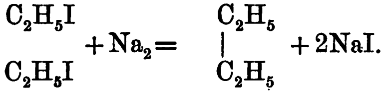


Quinoline

The toluidines give methyl-quinolines, and chloro-, bromo-, and iodo-anilines yield corresponding substituted quinolines. Many other condensations which are accompanied by oxidation are probably caused by the intermediate formation of an aldehyde which then condenses in the usual manner, so for example in the formation of rosaniline from aniline and toluidine (see pp. 138 and 111).

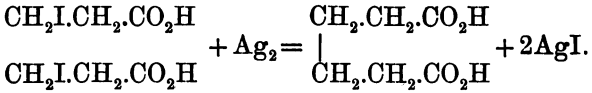
Some of the remaining simple methods for enlarging the carbon nucleus are given in the following pages:

If sodium or finely divided silver act upon organic halogen compounds a synthesis takes place, the halogen is eliminated, and the molecular residues unite to form one molecule:



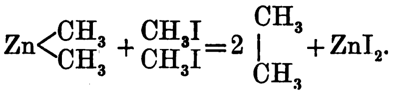
$$\underset{\text{Ethyl iodide}}{\begin{array}{c} C_2H_5I \\ C_2H_5I \end{array}} + Na_2 = \underset{\substack{\text{Butane} \\ \text{(Diethyl)} \\ \text{(Würtz).}}}{\begin{array}{c} C_2H_5 \\ | \\ C_2H_5 \end{array}} + 2NaI.$$

$$\underset{\text{Brombenzene}}{C_6H_5Br} + CH_3I + Na_2 = \underset{\substack{\text{Toluene} \\ \text{(Fittig).}}}{C_6H_5.CH_3} + NaI + NaBr.$$



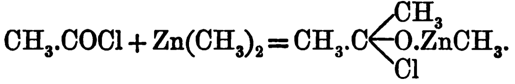
$$\underset{\beta\text{-Iodpropionic acid}}{\begin{array}{c} CH_2I.CH_2.CO_2H \\ CH_2I.CH_2.CO_2H \end{array}} + Ag_2 = \underset{\text{Adipic acid (J. Wislicenus)}}{\begin{array}{l} CH_2.CH_2.CO_2H \\ | \\ CH_2.CH_2.CO_2H \end{array}} + 2AgI.$$

Another method depends upon the ease with which organic zinc compounds (zinc alkyles) react. With halogen and many oxygen compounds, they are decomposed in such a way that the halogen or oxygen unites with the zinc, and the molecular residues combine together. Hydrocarbons may be prepared synthetically in this manner:—

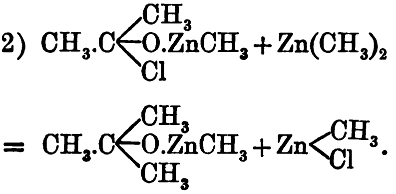


$$Zn\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} + \begin{matrix}CH_3I\\ CH_3I\end{matrix} = 2\begin{matrix}CH_3\\ |\\ CH_3\end{matrix} + ZnI_2.$$

Acid chlorides and zinc alkyles give tertiary alcohols (Butleroff). This rather complicated reaction takes place in three stages, as represented by the following formulæ:—

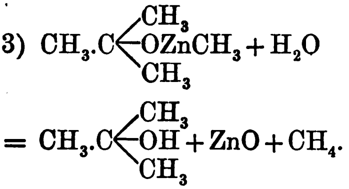
1) 

$$CH_3.COCl + Zn(CH_3)_2 = CH_3.C\begin{matrix}\diagup CH_3\\ -O.ZnCH_3\\ \diagdown Cl\end{matrix}.$$

2) 

$$CH_3.C\begin{matrix}\diagup CH_3\\ -O.ZnCH_3\\ \diagdown Cl\end{matrix} + Zn(CH_3)_2$$

$$= CH_3.C\begin{matrix}\diagup CH_3\\ -O.ZnCH_3\\ \diagdown CH_3\end{matrix} + Zn\begin{matrix}\diagup CH_3\\ \diagdown Cl\end{matrix}.$$

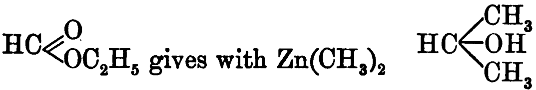
3) 

$$CH_3.C\begin{matrix}\diagup CH_3\\ -OZnCH_3\\ \diagdown CH_3\end{matrix} + H_2O$$

$$= CH_3.C\begin{matrix}\diagup CH_3\\ -OH\\ \diagdown CH_3\end{matrix} + ZnO + CH_4.$$

Trimethyl carbinol

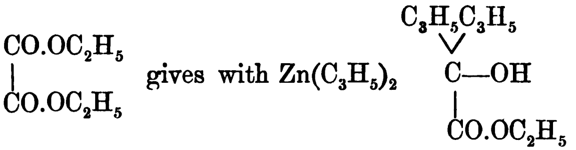
In an exactly analogous way, secondary alcohols are obtained from formic ethers by the action of zinc alkyles.



$$HC\begin{matrix}\diagup O\\ \diagdown OC_2H_5\end{matrix}\ \text{gives with}\ Zn(CH_3)_2\quad HC\begin{matrix}\diagup CH_3\\ -OH\\ \diagdown CH_3\end{matrix}$$

Secondary propyl alcohol.

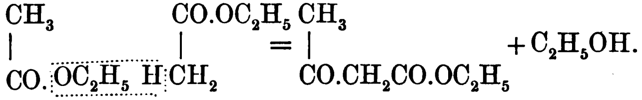
Amongst other reactions of a similar kind, the one which takes place between zinc alkyles, or zinc and alkyl iodides, and oxalic ether should be mentioned; an oxygen atom is replaced by two alkyles, oxyacid ethers being formed (Frankland and Duppa).



$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{array} \quad \text{gives with } Zn(C_3H_5)_2 \quad \begin{array}{c} C_3H_5C_3H_5 \\ \vee \\ C—OH \\ | \\ CO.OC_2H_5 \end{array}$$

Oxalic ether Diallyloxalicethyl ester.

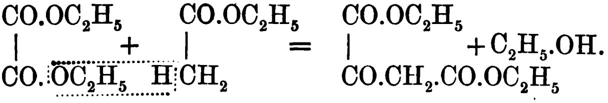
An interesting synthesis of ketonic acids depends upon the action of metallic sodium upon carboxylic acid ethers; the sodium causes the formation and splitting off of one molecule of alcohol from two ester molecules. The most familiar reaction of this kind is that resulting in the formation of acetoacetic ether:—



$$\begin{array}{l} CH_3 \\ | \\ CO.\boxed{OC_2H_5 \; H}CH_2 \end{array} \begin{array}{l} CO.OC_2H_5 \\ | \\ \end{array} = \begin{array}{l} CH_3 \\ | \\ CO.CH_2CO.OC_2H_5 \end{array} + C_2H_5OH.$$

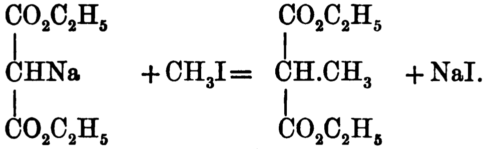
The reaction does not proceed so simply as the formula indicates; sodium-acetoacetic ether is first formed instead of the free ester.

Propionyl-propionic, and succino-succinic ethers are obtained in the same way, from propionic and succinic ethers respectively. In the same manner two different esters may condense; aceto-oxalic ether is formed by the action of sodium upon oxalic and acetic ethers (W. Wislicenus):—

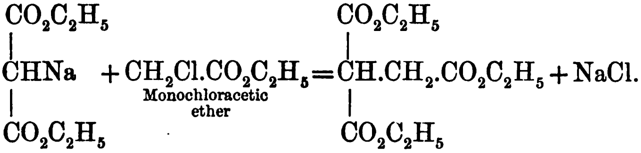


$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{array} + \begin{array}{l} CO.OC_2H_5 \\ | \\ H\,CH_2 \end{array} = \begin{array}{l} CO.OC_2H_5 \\ | \\ CO.CH_2.CO.OC_2H_5 \end{array} + C_2H_5.OH.$$

The hydrogen of malonic ether may be replaced by sodium. The resulting sodium-malonic ether acts easily upon halogen compounds. A synthetical method which is often used for the preparation of acids is founded upon this reaction (Conrad):—



$$\begin{array}{l} CO_2C_2H_5 \\ | \\ CHNa \\ | \\ CO_2C_2H_5 \end{array} + CH_3I = \underset{\text{Methylmalonic ether}}{\begin{array}{l} CO_2C_2H_5 \\ | \\ CH.CH_3 \\ | \\ CO_2C_2H_5 \end{array}} + NaI.$$

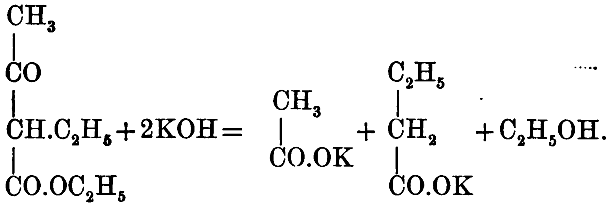


$$\begin{array}{l} CO_2C_2H_5 \\ | \\ CHNa \\ | \\ CO_2C_2H_5 \end{array} + \underset{\text{Monochloracetic ether}}{CH_2Cl.CO_2C_2H_5} = \underset{\text{Acetomalonic ether}}{\begin{array}{l} CO_2C_2H_5 \\ | \\ CH.CH_2.CO_2C_2H_5 \\ | \\ CO_2C_2H_5 \end{array}} + NaCl.$$

The corresponding acids may be easily obtained by saponification of the esters.

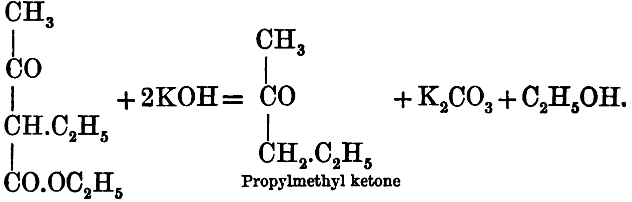
Sodium-acetoacetic ether $CH_3.CO.CHNa.CO_2C_2H_5$ acts exactly like sodium-malonic ether; from it different acids and ketones may be prepared by the action of halogen compounds, and treatment of the product of reaction with alkalis (Frankland and Duppa, J. Wislicenus):—

$$CH_3.CO.CHNa.CO_2C_2H_5 + C_2H_5I$$
$$= \underset{\text{Ethylacetoacetic ether}}{CH_3.CO.CH(C_2H_5).CO_2.C_2H_5} + NaI.$$



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH.C_2H_5} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} + \mathrm{2KOH} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO.OK} \end{array} + \begin{array}{l} \mathrm{C_2H_5} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OK} \end{array} + \mathrm{C_2H_5OH}.$$

Potassium butyrate

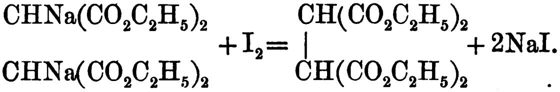


$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH.C_2H_5} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} + \mathrm{2KOH} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2.C_2H_5} \end{array} + \mathrm{K_2CO_3} + \mathrm{C_2H_5OH}.$$

Propylmethyl ketone

Benzoylacetic ether $\mathrm{C_6H_5.CO.CH_2.CO_2C_2H_5}$, acetondicarboxylic ether $\mathrm{C_2H_5.O.CO.CH_2.CO.CH_2.CO.O.C_2H_5}$, and other esters containing the group $\mathrm{CH_2}$ linked to two CO or certain other negative groups, react in the same way as the above-mentioned esters.

It has already been stated (p. 168) that sodium acts upon halogen compounds in such a manner that the halogen unites with the sodium, and synthetical products are formed; the result is strictly analogous if halogens (bromine, iodine) be allowed to act upon the above sodium compounds—the sodium is eliminated and the residues unite together:—



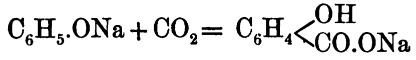
$$\begin{array}{l} \mathrm{CHNa(CO_2C_2H_5)_2} \\ \\ \mathrm{CHNa(CO_2C_2H_5)_2} \end{array} + \mathrm{I_2} = \begin{array}{l} \mathrm{CH(CO_2C_2H_5)_2} \\ | \\ \mathrm{CH(CO_2C_2H_5)_2} \end{array} + \mathrm{2NaI}.$$

Sodium-malonic ether   Acetylene-tetracarboxylic ether

Carbon may be introduced into many organic compounds by the help of simple carbon compounds such as carbon dioxide, carbonyl chloride, chloroform, &c. Certain organic compounds combine directly with carbon dioxide, carbon becoming linked to carbon.

$$CH_3.Na + CO_2 = CH_3.CO.ONa$$

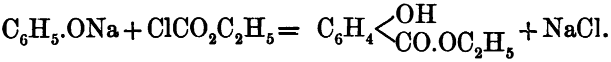
Sodium methyl — Sodium acetate.



$$C_6H_5.ONa + CO_2 = C_6H_4\left\langle\begin{matrix}OH\\CO.ONa\end{matrix}\right.$$

Sodium phenolate — Sodium salicylate (Kolbe).

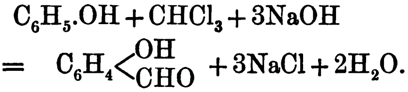
Sodium and chlorocarboxylic ethers have a similar action on phenols (Würtz):—



$$C_6H_5.ONa + ClCO_2C_2H_5 = C_6H_4\left\langle\begin{matrix}OH\\CO.OC_2H_5\end{matrix}\right. + NaCl.$$

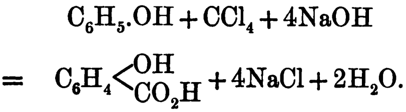
Salicylic ethyl ether

Chloroform and sodium hydrate convert phenols into oxyaldehydes (Reimer):—



$$C_6H_5.OH + CHCl_3 + 3NaOH$$
$$= C_6H_4\left\langle\begin{matrix}OH\\CHO\end{matrix}\right. + 3NaCl + 2H_2O.$$

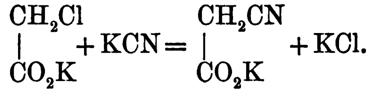
By an analogous reaction, oxyacids are obtained by the action of carbon tetrachloride and sodium hydrate upon phenols:—



$$C_6H_5.OH + CCl_4 + 4NaOH$$
$$= C_6H_4\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right. + 4NaCl + 2H_2O.$$

Salicylic acid

A method, which is often employed in order to increase the size of carbon chains, consists in the addition of the cyanogen group $\overset{|}{CN}$; this is accomplished by the action of potassium cyanide upon halogen compounds, alkyl sulphates, sulphonic acids, or diazo compounds:—



$$\begin{array}{l}CH_2Cl\\ |\\ CO_2K\end{array} + KCN = \begin{array}{l}CH_2CN\\ |\\ CO_2K\end{array} + KCl.$$

Potassium chloracetate — Potassium cyanacetate

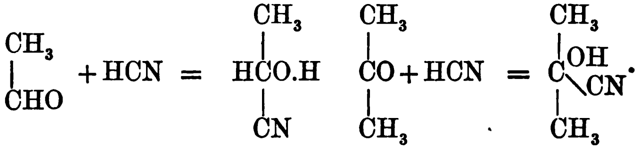
$$C_2H_5.O.SO_3K + KCN = C_2H_5CN + K_2SO_4.$$

Potassium ethylsulphate — Propionitril

If a compound contain several halogen atoms a corresponding number of cyanogen groups may add themselves, unless *two halogen atoms be linked to the same carbon atom.*

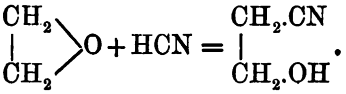
Ethylene chloride $CH_2Cl.CH_2Cl$ gives a corresponding dicyanide, but ethidene chloride does not react in this way with potassium cyanide.

The cyanogen group may be introduced into aldehydes and ketones by simple treatment with hydrocyanic acid; a direct addition takes place.



$$\begin{array}{l}CH_3\\ |\\ CHO\end{array} + HCN = \begin{array}{c}CH_3\\ |\\ HCO.H\\ |\\ CN\end{array} \qquad \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + HCN = \begin{array}{l}CH_3\\ |\\ C\begin{smallmatrix}OH\\ CN\end{smallmatrix}\\ |\\ CH_3\end{array}.$$

Ethylene oxide reacts in a similar way:—



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + HCN = \begin{array}{l}CH_2.CN\\ |\\ CH_2.OH\end{array}.$$

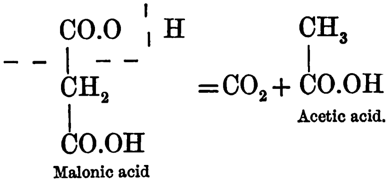
It has already been mentioned under hydration processes that the nitrogen of cyanogen compounds can be easily split off by treatment with alkalis or dilute acids, the cyanogen groups being converted into carboxyl (see p. 162). By means of this reaction it is possible to pass from alcohols, aldehydes, and lactones to acids containing more carbon, and from monobasic acids to dibasic ones richer in carbon.

On the other hand, the cyanides can be easily transformed into amines (see p. 131), the synthesis of alcohols being thus accomplished.

CHAPTER XXII

DISRUPTION OF CARBON BONDS

MANY organic acids lose carbon dioxide when heated. The di- and poly-basic acids with two carboxyl groups attached to the *same carbon atoms* evolve carbon dioxide by slight heating (to about 150°):—

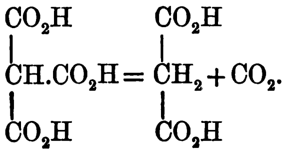


$$\begin{array}{l} \mathrm{CO.O} \mid \mathrm{H} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OH} \end{array} = \mathrm{CO_2} + \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO.OH} \end{array}$$

Malonic acid — Acetic acid.

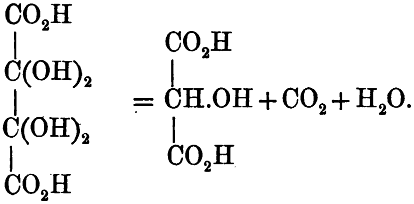
$$\underset{\text{Isosuccinic acid}}{\mathrm{CH_3.CH(COOH)_2}} = \mathrm{CO_2} + \underset{\text{Propionic acid.}}{\mathrm{CH_3.CH_2.CO.OH}}$$

Carbon dioxide is of course split off still more easily from acids with three carboxyl groups linked to the same carbon atom. Methenyltricarboxylic acid decomposes as soon as formed, into malonic acid and carbon dioxide:—



$$\begin{array}{l} \mathrm{CO_2H} \\ | \\ \mathrm{CH.CO_2H} \\ | \\ \mathrm{CO_2H} \end{array} = \begin{array}{l} \mathrm{CO_2H} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO_2H} \end{array} + \mathrm{CO_2}.$$

Tetraoxysuccinic acid also at once gives up carbon dioxide, oxymalonic acid being obtained by internal rearrangement:—



$$\begin{array}{c} CO_2H \\ | \\ C(OH)_2 \\ | \\ C(OH)_2 \\ | \\ CO_2H \end{array} = \begin{array}{l} CO_2H \\ | \\ CH.OH + CO_2 + H_2O. \\ | \\ CO_2H \end{array}$$

Many other organic acids yield carbon dioxide by strongly heating with alkalis:—

$$CH_3.CO.OK + KOH = K_2CO_3 + CH_4.$$

This reaction takes place more easily and completely by heating the acid with sodium ethylate; in this way a paraffin $C_{17}H_{36}$ is obtained from stearic acid $C_{17}H_{35}.CO_2H$ (Mai).

Aromatic acids with the carboxyl linked to the benzene nucleus easily give off CO_2 on heating with quicklime:—

$$\underset{\text{Phthalic acid}}{C_6H_4(CO_2H)_2} = C_6H_6 + 2CO_2.$$

Carbon is occasionally split off from organic compounds as carbon monoxide; for instance, by the action of sulphuric acid upon citric acid:—

$$C_6H_8O_7 = \underset{\substack{\text{Acetone-} \\ \text{dicarboxylic} \\ \text{acid}}}{C_5H_6O_5} + CO + H_2O.$$

Many unsaturated acids are decomposed by fusion with potassium hydrate, the disruption taking place as a rule at the position of the double bond (see p. 120).

Many oxy- and ketonic-acids are decomposed by warming with potassium hydrate or sulphuric acid. Acetoacetic acid gives, with potassium hydrate, acetic acid:—

$$CH_3.CO\,\vdots\,.CH_2.CO_2H + 2KOH = 2CH_3.CO_2K + H_2O.$$

Or else acetone and carbonic acid:—

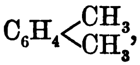
$$CH_3.CO.CH_2\,\vdots\,.CO_2H + 2KOH$$
$$= CH_3.CO.CH_3 + K_2CO_3 + H_2O.$$

Lactic acid yields aldehyde and formic acid when treated with sulphuric acid:—

$$CH_3.CH(O\,\vdots\,H).CO_2H = CH_3.CH{:}O + HCO_2H.$$

It has already been mentioned that the carbon chain is often broken by oxidation (see p. 108).

As stated above, organic radicles may be easily introduced into aromatic hydrocarbons by the action of aluminium chloride. This substance may however cause an opposite reaction, viz. the splitting off of hydrocarbon groups from aromatic hydrocarbons. Xylene



$$C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix},$$

for example, gives some toluene $C_6H_5.CH_3$, and benzene C_6H_6, when treated with aluminium chloride. A state of equilibrium, which is naturally dependent upon the conditions under which the reaction is performed, occurs between these different processes (Jacobsen).

CHAPTER XXIII

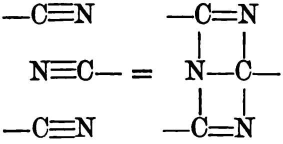
POLYMERISM

In the preceding pages it has been stated that many organic compounds polymerise; that is to say, a number of molecules unite together to form a single molecule. This often occurs spontaneously, but is frequently brought about by the action of a small quantity of some mineral substance such as sulphuric or hydrochloric acids, zinc chloride, sodium hydrate, &c.

Certain compounds, containing their atoms doubly linked, easily polymerise. Such substances are the cyanogen compounds, aldehydes, and unsaturated compounds.

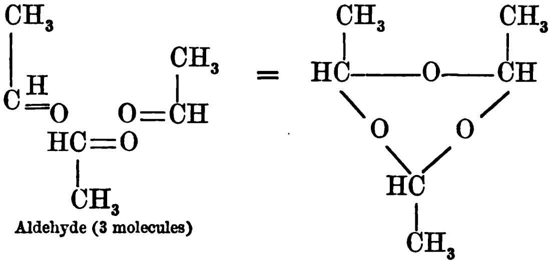
These phenomena are explained by the fact that the double or treble bonds are converted into single ones, so that two or three molecules of the substance may join together by means of the free valencies.

Cyanogen compounds easily form bodies possessing a triple molecular weight. The cyanogen group becomes converted into a tricyanogen group:—



$$\underset{\text{Cyanogen chloride}}{3CNCl} = \underset{\text{Cyanuric chloride}}{C_3N_3Cl_3} \quad : \quad \underset{\text{Cyanic acid}}{3CNOH} = \underset{\text{Cyanuric acid.}}{C_3N_3O_3H_3}$$

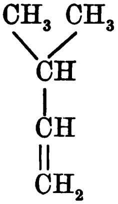
Ordinary *aldehyde* C_2H_4O easily polymerises to paraldehyde $C_6H_{12}O_3$:—



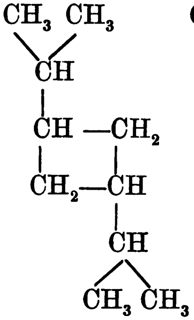
Aldehyde (3 molecules)

Paraldehyde.

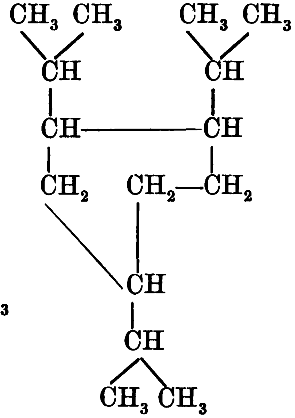
The *unsaturated* hydrocarbon isopropylethylene C_5H_{10} gives diamylene $C_{10}H_{20}$, and triamylene $C_{15}H_{30}$, when treated with sulphuric acid at ordinary temperatures :—



Isopropylethylene

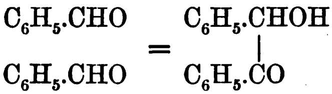


Diamylene



Triamylene.

Certain polymerisation phenomena are more correctly classed as condensation processes; for instance, the formation of aldol from aldehyde (see p. 137), or of benzoin by the action of potassium cyanide upon benzaldehyde :—



$$\begin{array}{l} C_6H_5.CHO \\ \\ C_6H_5.CHO \end{array} = \begin{array}{l} C_6H_5.CHOH \\ \qquad\quad | \\ C_6H_5.CO \end{array}$$

Benzaldehyde Benzoin.

Many polymerisations have not yet been sufficiently explained.

CHAPTER XXIV

INTRAMOLECULAR ATOMIC REARRANGEMENT

The peculiar resistance of the carbon bond has already been given as the reason for numerous cases of isomerism which occur amongst organic compounds. In spite of this it sometimes happens that an organic compound with a very unstable constitution passes into a more stable form by means of an internal rearrangement of the atoms. Many of these processes are without doubt the resultant of several successive reactions, though the intermediate products cannot always be isolated. Intramolecular rearrangements, and the metamorphosis of chemical compounds into isomeric substances have always been regarded with great interest by chemists.

Many rearrangements may be explained by what is called *tautomerism* (Laar). A substance is said to be tautomeric if it does not always possess the same unalterable constitution, but one which varies according to the circumstances in which it reacts with another compound. The constitution of such bodies may be expressed by two formulæ. Cyanamide, for example, is not represented solely by the formula $CN.NH_2$, or by the formula

$$\mathrm{C}\!\begin{array}{l}\diagup\!\!\!\!=\mathrm{NH}\\ \diagdown\!\!\!\!=\mathrm{NH}\end{array}$$

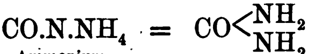
but by both; under certain conditions it behaves like true cyanamide, in other circumstances as carbondiimid.

In the same way acetoacetic ether may be represented by either of the following formulæ:—

$$\mathrm{CH_3.CO.CH_2.CO.OC_2H_5} \text{ and}$$
$$\mathrm{CH_3.C(OH){=}CH.CO.OC_2H_5}.$$

Tautomerism becomes isomerism if distinct compounds are known represented by each formula.

The first case of intramolecular rearrangement to be recorded was the conversion of ammonium cyanate into urea by warming the watery solution (Wöhler's synthesis of urea 1828):—

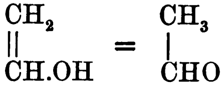


$$\mathrm{CO.N.NH_4} = \mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}$$

Ammonium cyanate — Urea.

This reaction appears to be a general one; the ammonium salt of the acid gives the diamide.

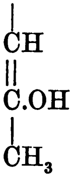
It may be stated that, as a general rule, alcohols containing the group $\mathrm{—CH{=}CH.OH}$ change spontaneously into aldehydes:—



$$\begin{array}{l}\mathrm{CH_2}\\ \|\\ \mathrm{CH.OH}\end{array} = \begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CHO}\end{array}$$

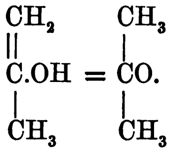
Vinyl alcohol — Aldehyde.

And that those with the group



$$\begin{array}{l}|\\ \mathrm{CH}\\ \|\\ \mathrm{C.OH}\\ |\\ \mathrm{CH_3}\end{array}$$

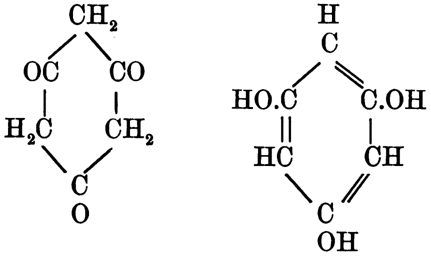
become converted into ketones :—



$$\begin{array}{lcl} \mathrm{CH_2} & & \mathrm{CH_3} \\ \| & & | \\ \mathrm{C.OH} & = & \mathrm{CO.} \\ | & & | \\ \mathrm{CH_3} & & \mathrm{CH_3} \end{array}$$

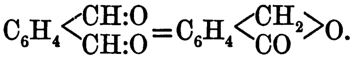
The generally accepted theory is that the above alcohols cannot exist as such—they become changed at the moment of their formation into aldehydes and ketones respectively (Erlenmeyer). It is probable however that many unsaturated alcohols and ketones are only tautomeric forms of the same compound, like acetoacetic ether (see above).

In the case of phloroglucinol and of certain other phenols it is necessary to assume the existence of secondary and tertiary forms, so called from the way in which the carbon atoms are linked :—



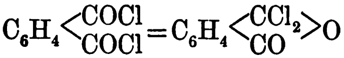
Secondary form Tertiary form
Phloroglucinol.

Compounds containing their atoms linked in the form of a ring are often more stable than isomerides with open chains, and it sometimes happens that these latter change into the first form. Phthalic aldehyde easily forms phthalide:



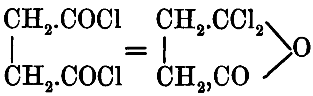
$$C_6H_4<\substack{CH:O\\CH:O}=C_6H_4<\substack{CH_2\\CO}>O.$$

A similar reaction probably takes place in the case of other phthalic compounds and of the analogous succinyl compounds. Symmetrical phthalyl and succinyl chlorides, and other similar acid chlorides, are converted into unsymmetrical compounds, unless, as is possible, both kinds of chlorides are only tautomeric forms:—



$$C_6H_4<\substack{COCl\\COCl}=C_6H_4<\substack{CCl_2\\CO}>O$$

(Phthalyl chloride).



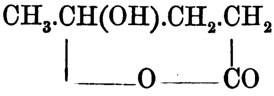
$$\begin{array}{l}CH_2.COCl\\|\\CH_2.COCl\end{array}=\begin{array}{l}CH_2.CCl_2\\|\\CH_2,CO\end{array}>O$$

(Succinyl chloride).

It also appears probable that corresponding aldehyde- and ketonic acids containing the oxygen linked to the third carbon atom counting from carboxyl, change, immediately on their formation, into compounds with their atoms linked in a circular form. In that case lævulinic acid would not be acetopropionic acid

$$CH_3.CO.CH_2.CH_2.CO_2H$$

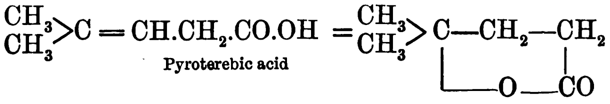
as generally represented, but an oxylactone



$$\begin{array}{l}CH_3.CH(OH).CH_2.CH_2\\ \qquad\quad |\_\_\_O\_\_\_|CO\end{array}$$

(Bredt).

Some unsaturated acids give isomeric lactones when heated:—

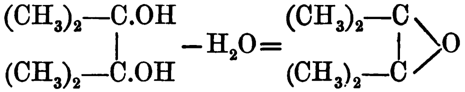


$$\begin{array}{l}CH_3\\CH_3\end{array}\!\!>C=CH.CH_2.CO.OH=\begin{array}{l}CH_3\\CH_3\end{array}\!\!>\begin{array}{l}C—CH_2—CH_2\\ |\qquad\qquad\ \ |\\ \llcorner\!\!—\!O—CO\end{array}$$

Pyroterebic acid

Isocaprolactone.

Most divalent alcohols are converted into aldehydes and ketones by the action of dehydrating agents. The double tertiary alcohols (pinacones) react particularly easily: they give ketones with dilute sulphuric acid; an alcohol anhydride is first formed, from which the ketones are produced by rearrangement:—



$$\begin{array}{l}(CH_3)_2—C.OH\\ \qquad\quad\ |\\ (CH_3)_2—C.OH\end{array}-H_2O=\begin{array}{l}(CH_3)_2—C\\ \qquad\quad\ |\\ (CH_3)_2—C\end{array}\!\!>O$$

Tetramethylethylene alcohol

$$=(CH_3)_3.C.CO.CH_3$$

Tertiary butylmethylketone.

Many other special cases of internal rearrangement have been observed, some of which may be mentioned. Allylthiocyanate is converted into allylthiocarbimide on heating; $N\equiv C—S.C_3H_5=S:C:N.C_3H_5$; in this reaction the sulphur and nitrogen change places. By heating phenylcarbylamine to 200°–220° it is changed into the isomeric benzonitrile, the isocyanogen group being transformed into the true cyanogen group:—

$$C_6H_5.NC=C_6H_5.CN.$$

Isocrotonic acid yields crotonic acid on distillation, the position of the double bond becoming altered:—

$$CH_2:CH.CH_2.CO.OH=CH_3.CH:CH.CO.OH.$$

Many other instances of hydrogen changing its position by moving from one carbon atom to another have been noticed. In many cases however the atomic rearrangement is only apparent. For example, ordinary crotonic acid

$$CH_3.CH{=}CH.CO.OH$$

is obtained by the saponification of allylcyanide

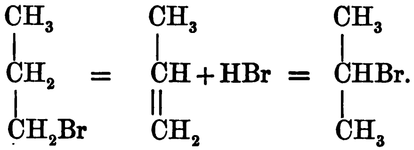
$$CH_2{=}CH.CH_2.CN$$

although isocrotonic acid would be expected. The natural conclusion is that an atomic rearrangement has taken place; it is probable however, from Pinner's researches, that on treating the cyanide with hydrochloric acid or potassium hydrate, monochlor- or oxybutyric acids are respectively formed; these split off hydrochloric acid or water as the case may be, ordinary crotonic acid being produced :—

$$CH_3.CHCl.CH_2.CO.OH = CH_3.CH{:}CH.CO.OH + HCl.$$

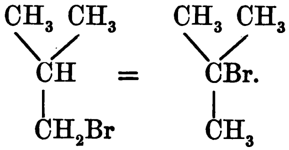
$$\begin{gathered}CH_3.CH(OH).CH_2.CO.OH\\ = CH_3.CH{:}CH.CO.OH + H_2O.\end{gathered}$$

Primary propyl bromide is converted into secondary propyl bromide by the action of aluminium bromide (Kekulé, Gustavson); at high temperatures the same change occurs without the intervention of aluminium bromide. The reaction may be explained by supposing that hydrobromic acid is first split off, and that it then adds itself in another way to the propylene which is simultaneously formed :—

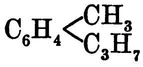


$$\begin{array}{ccccc} CH_3 & & CH_3 & & CH_3 \\ | & & | & & | \\ CH_2 & = & CH + HBr & = & CHBr. \\ | & & \| & & | \\ CH_2Br & & CH_2 & & CH_3 \end{array}$$

Secondary, as well as primary, propyl alcohol is formed by the action of nitrous acid upon primary propyl amine. Isobutyl bromide readily passes into tertiary butyl bromide :—



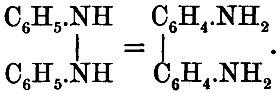
This reaction, as well as that of primary propyl bromide mentioned above, is probably caused by the tendency of the halogens to combine with that carbon atom which is linked to the least number of hydrogen atoms. Para-methyl-normal-propyl-benzene or cymene



$$C_6H_4{<}\begin{matrix} CH_3 \\ C_3H_7 \end{matrix}$$

is converted by oxidation (shaking with sodium hydrate and air) into *p*-isopropylbenzoic acid. On the other hand the *p*-isopropylbenzoic acid may be retransformed into ordinary cymene, the isopropyl group changing again into the normal propyl group. Other similar rearrangements have been observed in the cymyl and cumin series. A methyl group in the para-position to a normal propyl group, and a carboxyl in the same relative situation to an isopropyl group, appear to be best adapted for preserving the equilibrium of the molecule, hence the above rearrangements (Widman).

Hydrazobenzene derivatives are changed into benzidine compounds by the action of sulphuric acid or zinc chloride :—



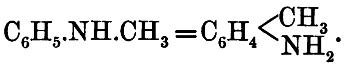
$$\begin{array}{c}C_6H_5.NH\\ | \\ C_6H_5.NH\end{array} = \begin{array}{c}C_6H_4.NH_2\\ | \\ C_6H_4.NH_2\end{array}.$$

A hydrogen atom from each benzene nucleus becomes attached to the nitrogen, the bond between the nitrogen atoms is dissolved, and two carbon atoms become linked together. Two nitrogen atoms, joined as they are in hydrazo-benzene, as a rule, render the atomic grouping very unstable.

Diazoamido compounds are easily converted into amidoazo compounds :—

$$C_6H_5.N_2.NH.C_6H_5 = C_6H_5.N_2.C_6H_4.NH_2.$$

A peculiar kind of transference of atoms was noticed by A. W. Hofmann and Martius in the case of aromatic amines. By strongly heating methylaniline (hydriodic acid salt) toluidine is produced :—



$$C_6H_5.NH.CH_3 = C_6H_4 < \begin{array}{l}CH_3\\ NH_2\end{array}.$$

Other secondary or tertiary aromatic amines behave in a similar way; the alcohol radicle changes places with a hydrogen atom of the benzene nucleus. Many cases of atoms or atomic groups shifting their position about the benzene nucleus have been observed. Isomeric disubstitution derivatives, ortho-, meta-, and para- compounds, are frequently changed one into another at high temperatures. Ortho-phenolsulphonic acid is entirely changed into para-phenolsulphonic acid by continued heating. In the same way potassium salicylate (ortho-compound) gives potassium para-oxybenzoate when heated to 220°, but at higher temperatures the opposite reaction takes place.

All three bromobenzenesulphonic acids and benzenedisulphonic acids (ortho-, meta-, and para-) give resorcinol, meta-dioxybenzene, when fused with potassium hydrate. By the oxidation of certain orthodialkyl benzenes with potassium permanganate terephthalic acid (para-compound) is formed in large quantities, and only a small amount of phthalic acid, the ortho-compound (Claus).

In considering these and other analogous reactions it is not needful to assume a direct atomic rearrangement; the product obtained may be the final result of a series of different processes.

CHAPTER XXV

VELOCITY AND LIMIT OF REACTIONS

If an alcohol be mixed with an acid an ester is produced, but the reaction is never completed by mere heating; certain quantities of the acid and of the alcohol remain unchanged.

$$aC_2H_5.OH + aCH_3.CO.OH = bH_2O + bCH_3.CO.OC_2H_5 + (a-b)\ (C_2H_5.OH + CH_3.CO.OH).$$

If the quantity of alcohol be increased, a larger portion of the acid will be reacted upon, and vice versâ. A definite equilibrium will be established between the amounts of the water and ester formed on the one hand, and of the free acid and alcohol on the other. The reaction reaches its *limit* and no further change takes place between the acid and alcohol. The same relations occur in many other reactions.

Menschutkin has closely investigated the quantitative course of the production of esters from monobasic organic acids and monovalent alcohols. If equal molecules of acetic acid and ethyl alcohol be heated to 154° *equilibrium* ensues after seventy-two hours. In the case of alcohols of higher molecular weight with the same acid, the reaction ceases after warming for ninety-six hours. By '*limiting value*' is meant the quantity of the mixture which is transformed. The term '*initial velocity*' is used to denote the quantity of ester produced at the end of the first hour. Both these values are different for saturated, unsaturated, primary, secondary, or tertiary alcohols, and they are smaller for unsaturated than for saturated alcohols.

		Initial velocity	Limiting value
Ethyl alcohol	$C_2H_5.OH$	46·81%	66·57%
Propyl alcohol	$C_3H_7.OH$	46·50%	66·85%
Allyl alcohol	$C_3H_5.OH$	36·12%	59·40%
Benzyl alcohol	$C_7H_7.OH$	37·98%	60·75%

In the case of primary alcohols the limiting values increase with the molecular weight :—

Ethyl alcohol	$C_2H_5.OH$	66·57%
Butyl ,,	$C_4H_9.OH$	67·30%
Octyl ,,	$C_8H_{17}.OH$	72·34%
Cetyl ,,	$C_{16}H_{33}.OH$	80·39%

The initial velocity of primary normal alcohols is very constant, about 47%; that of primary isoalcohols is rather less.

Secondary alcohols have a smaller initial velocity as well as a lower limiting value than the primary alcohols, and the difference is still more marked between these latter and tertiary alcohols :—

	Initial velocity	Limiting value
Secondary propyl alcohol	26·53%	60·52%
Tertiary butyl ,,	1·50%	6·59%

All these determinations were made with acetic acid.

The above factors are also influenced by the acid employed. Acids of normal structure,

$$R—CH_2—CO.OH,$$

possess the greatest initial velocity; tertiary acids,

$$R_3 \vdots C.CO_2H,$$

the least, and this value decreases with rising molecular weight, whilst the limiting value increases.

The ammonium salts of organic acids give amides on heating:—

$$R.CO.ONH_4 = R.CONH_2 + H_2O.$$

In this reaction too the primary acids have the greatest initial velocity and the tertiary ones the smallest; on the other hand the limiting value is not dependent upon the constitution of the acid. The formation of acetamide proceeds very rapidly at 155°; the initial velocity of the reaction is 50·90% and the limit value 81·46%. The production of benzamide (tertiary acid) is very slow, the initial velocity being only 0·75%.

Temperature exerts an important influence upon the speed of a reaction; the absolute initial velocity increases with the temperature. Menschutkin obtained the following values for the action of acetic acid upon alcohol:—

Temperature	Initial velocity
102°	13·50%
122°	24·78 „
142°	40·65 „
162°	52·90 „
182·5°	60·99 „
212·5°	63·98 „

The limiting value of etherification does not vary with the temperature (Berthelot). In the formation of amides (acetamide) however, both the initial velocity and limiting value increase with the temperature. The opposite result occurs in the formation of anilides (aniline and acids), the limiting value decreasing as the temperature rises. Certain other reactions have been investigated in this way, but not so completely as has the formation of esters and amides.

CHAPTER XXVI

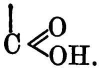
THE CHEMICAL INFLUENCE OF ELEMENTS ALREADY IN THE MOLECULE UPON THE AFFINITY OF NEIGHBOURING ATOMS.

ELEMENTS or groups of a strongly negative or positive character exert an influence upon the chemical nature or affinity of other elements contained in the molecule. This influence is greater the more closely the elements or groups are linked, or in other words, the shorter the atomic chain which intervenes between them.

The influence of one element upon another in the same molecule is most plainly seen in the case of organic hydroxyl compounds. The character of the hydroxyl, the affinity of its oxygen for metals, depends in the first instance upon the other elements which are linked to the same carbon atom. The hydroxyl has a weak basic character in the group

$$\overset{|}{C}H_2.OH$$

(alcohol) and an acid character in the group



$$\overset{|}{C}\lessgtr^{O}_{OH.}$$

The hydroxyl oxygen of the second group has a much greater tendency to unite with metals than that of the first. Oxygen and halogen atoms may increase the negative character of a hydroxyl even if they be not linked to the same carbon atom but to another one in the molecule situated close to the first. An accumulation of carbon atoms acts in the same way; for instance the phenols show a more acid character than the alcohols, because the hydroxyl is linked to a group poorer in hydrogen but richer in carbon:—

$C_6H_5.OH$	$C_2H_5.OH$
Phenol	Alcohol.

The phenols behave like true acids if negative groups be linked to the carbon atoms near the hydroxyl:

$$C_6H_2(NO_2)_3OH$$

Picric acid.

Polyvalent alcohols are less basic than monovalent alcohols, on account of the mutual influences of the different hydroxyls; polyvalent alcohols react more easily with metallic oxides, the hydroxyl hydrogen being replaced by metal.

If the hydrogen of an acid be replaced by halogens the carboxyl group is affected, the acidity or strength of the acid becoming greater; this is seen from a comparison of the heats of neutralisation of these compounds, and still more clearly and certainly from the affinity constants calculated from the electrical conductivity of the acids (Ostwald):—

		Affin. const. (K).
Acetic acid	$(CH_3.CO_2H)$	0·0018
Monochloracetic acid	$(CH_2Cl.CO_2H)$	0·1550
Dichloracetic ,,	$(CHCl_2.CO_2H)$	5·1400
Trichloracetic ,,	$(CCl_3.CO_2H)$	121·0000

The negative radicle NO_2 acts in the same way as the hydroxyl group though in a less degree.

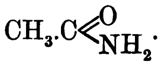
		K.
Acetic acid	$(CH_3.CO_2H)$	0·0018
Glycollic acid	$(CH_2.(OH).CO_2H)$	0·0152
Succinic acid	$(C_2H_4(CO_2H)_2)$	0·00665
Malic acid	$(C_2H_3(OH).(CO_2H)_2)$	0·0395
Racemic acid	$(C_2H_2(OH)_2(CO_2H)_2)$	0·097

The influence of negative groups upon the affinity of the oxygen of carboxyl for metals decreases in proportion as the distance of these groups from the carboxyl becomes greater; this is shown in a marked manner by a comparison of the ortho-, meta-, and para- substituted benzoic acids.

A basic group, such as an amidogen NH_2, in the molecule of an acid acts in the opposite way,—it decreases the activity of the acid very considerably. The affinity constant of *o*-amidobenzoic acid for instance is only one-sixth of that of benzoic acid.

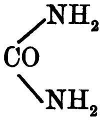
The affinity of the nitrogen in the NH_2 group is greatly dependent upon the other elements in the molecule.

Alkyl amines are strong bases; they combine with acids to form salts. On the other hand the amides, which contain oxygen linked to the same carbon atom as that to which the NH_2 group is joined, are neutral, and either form no salts at all, or only unstable ones:—



$$CH_3.C\begin{matrix}\diagup O \\ \diagdown NH_2\end{matrix}.$$

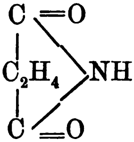
Urea



$$CO\begin{cases}NH_2\\NH_2\end{cases}$$

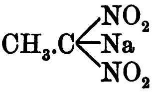
where the carbonyl influences *two* amido groups, forms stable salts, one NH_2 group uniting with the acid.

Acid imides, where the group NH is linked to *two* carbonyl groups, possess the character of weak acids; the imido-hydrogen may be easily replaced by metals.



Succinimide.

The affinity of carbon or nitrogen for metals decreases in presence of hydrogen, but increases by combination with groups containing oxygen; it is on this account that the hydrogen of the nitro ethanes may be replaced by metals.



$$CH_3.C\begin{cases}NO_2\\Na\\NO_2\end{cases}$$

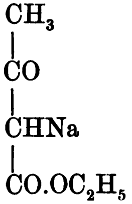
Sodium nitroethane.

The amido hydrogen of aniline $C_6H_5.NH_2$ may be replaced by sodium. The reaction only commences at a temperature of 200°; if however one of the hydrogen atoms of the NH_2 group be replaced by an acid radicle, the other one may be replaced by sodium at ordinary temperatures.

$$C_6H_5.N<\begin{matrix}Na\\CO.CH_3\end{matrix}$$

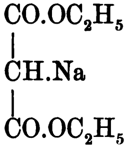
Sodium acetanilide.

The ease with which metals can replace the hydrogen attached to carbon in such compounds as malonic, acetoacetic, or benzoylacetic ethers, depends on the influence exerted upon the carbon by the neighbouring groups containing oxygen :—



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHNa \\ | \\ CO.OC_2H_5 \end{array}$$

Sodium acetoacetic ether

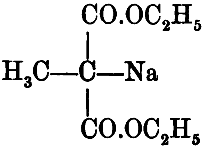


$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CH.Na \\ | \\ CO.OC_2H_5 \end{array}$$

Sodium malonic ether.

The influence of the phenyl (C_6H_5) and cyanide groups is similar to that of carboxyl, only less marked; so in desoxybenzoin $C_6H_5.CH_2.CO.C_6H_5$, and benzylcyanide $C_6H_5.CH_2.CN$, one atom of the hydrogen of the methylene group may easily be replaced by sodium, but, strange to say, phenylacetic ether $C_6H_5.CH_2.CO_2C_2H_5$ does not react with sodium (V. Meyer).

The tendency of carbon to combine with metals is more greatly decreased by metals than by hydrogen. It is only with the greatest difficulty that a second atom of hydrogen in sodium acetoacetic, or sodium malonic ethers can be replaced by metals, but if some organic radicle be introduced instead of the sodium the substitution by metals easily proceeds further :—



$$\begin{array}{rcl} & CO.OC_2H_5 & \\ & | & \\ H_3C— & C & —Na \\ & | & \\ & CO.OC_2H_5 & \end{array}$$

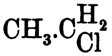
Sodium methylmalonic ether.

Hydrogen may be replaced by metals in hydrocarbons containing the group $-C{\equiv}CH$, but if in acetylene one atom of hydrogen be replaced by sodium, the substitution of the other is a matter of considerable difficulty. In dipropargyl

$$HC{\equiv}C.CH_2.CH_2.C{\equiv}CH$$

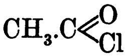
the hydrogen of the one CH group may be easily replaced even if the other CH group is already combined with a metal, the reason being that the two CH groups are situated so far apart in the atomic chain.

The energy with which halogens combine with carbon is greatly decreased by the presence of oxygen or negative groups. This is proved by such facts as the following. Halogen substituted hydrocarbons as a rule react with water with difficulty, but acid chlorides are easily decomposed, the halogen being replaced :—



$$CH_3.C\genfrac{}{}{0pt}{}{H_2}{Cl}$$

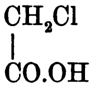
Ethyl chloride



$$CH_3.C{<}\genfrac{}{}{0pt}{}{O}{Cl}$$

Acetyl chloride.

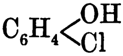
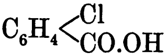
The halogen substituted fatty acids such as chloracetic acid



$$\begin{array}{l}CH_2Cl\\ |\\ CO.OH\end{array}$$

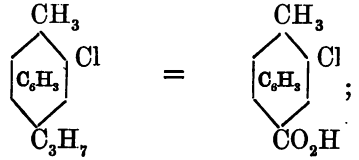
are more easily decomposed by water than the alkylhaloids.

Potassium hydrate does not act upon chlorobenzene, chlorotoluene, and other halogen substituted aromatic hydrocarbons, but chlorine substituted phenols and acids give up chlorine by fusion with this reagent, and the chlorine atoms in chloranil also react easily:—

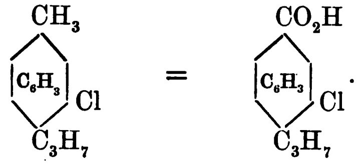
$C_6H_5.Cl$	 $C_6H_4{<}^{OH}_{Cl}$	 $C_6H_4{<}^{Cl}_{CO.OH}$	$C_6Cl_4O_2$
Chlorobenzene	Chlorophenol	Chlorobenzoic acid	Chloranil (Tetrachlorquinone).

Atoms or atomic groups may exert a 'protecting' influence upon other atomic groups, so that these latter will not be attacked by reagents which would have affected them in other circumstances. Negative atoms or groups in the ortho-position to hydrocarbon residues hinder the oxidation of these by acid oxidising agents.

For example, chlorocymene 1-2-4, CH_3 in 1, is converted by nitric acid into chlorotoluic acid:—



whilst the isomeric chlorocymene 1-3-4, CH_3 in 1, gives chloropropylbenzoic acid:—



In the oxidation of the toluidines the amido group exerts a protecting influence upon the methyl group

$$C_6H_4{<}^{CH_3}_{NH_2};$$

but if the amido hydrogen be replaced by an acid radicle, the methyl group is easily oxidised to carboxyl.

CHAPTER XXVII

THE CHEMICAL ACTION OF LIGHT

MANY organic silver salts are blackened by light, just like the inorganic compounds of this metal. A considerable number of organic colouring matters lose their colour and become bleached by the action of sunlight; the process by which the colours are destroyed is unknown. The action of light upon 'sensitive' organic substances has been little investigated generally, but a number of single observations of an interesting nature have been lately made on this subject. Ciamician and Klinger have observed that if a reducible substance be dissolved in an oxidisable medium and the solution subjected to the action of light, the dissolved substance will be reduced and the solvent oxidised. Quinones dissolved in alcohol, or in water containing some ether, remain unchanged in the dark but are reduced to hydroquinones by exposure to light, the alcohol or ether being oxidised to aldehyde. In similar circumstances nitrobenzene is converted into aniline, and the alcohol oxidised to aldehyde. Duchaux has made analogous observations with regard to the action of light upon alcoholic solutions of grape sugar. When the air was excluded one part of the sugar was oxidised to carbon-dioxide, oxalic acid, &c., whilst another part was reduced to alcohol. Klinger has also found that phenanthraquinone combines with aldehydes under the influence of sunlight. The synthetical action of light in this case is very remarkable; no similar action has ever previously been observed except in living plants.

It has long been known that hydrocarbons of the formula C_nH_{2n-6} had the power of converting oxygen into ozone when exposed to sunlight. The substitution of hydrogen by halogens is greatly facilitated by the action of direct sunlight. It is worthy of note that by the action of halogens upon aromatic hydrocarbons in direct sunlight, the hydrogen of the side chain is replaced, and not that of the benzene nucleus (Schramm).

CHAPTER XXVIII

ACTION OF HIGH TEMPERATURES

ALL organic compounds undergo change when exposed to high temperatures. Substances which are not gasifiable without decomposition are split up by simply heating, even if the air have not free access. Substances which are volatile without change must be heated to a temperature more or less above that at which they volatilise, in order that they may undergo decomposition; this is most conveniently effected by passing their vapour through heated, or sometimes red-hot, tubes. The process employed for the decomposition of organic substances by high temperatures is termed *dry distillation*; in this way new compounds are formed which are more stable at high temperatures than the original substances.

The nature of the reaction differs according to the original substance and the temperature. Sometimes the changes are tolerably simple, but usually they are exceedingly complex. As a rule the heat acts in such a way that hydrogen, oxygen, or carbon are split off in the form of water, carbon monoxide, or carbon dioxide:

$$\underset{\text{Succinic acid}}{C_4H_6O_4} = \underset{\text{Succinic anhydride}}{C_4H_4O_3} + H_2O$$

$$\underset{\text{Malonic acid}}{C_3H_4O_4} = \underset{\text{Acetic acid}}{C_2H_4O_2} + CO_2.$$

As oxygen is first split off, the compounds formed in greatest quantity are hydrocarbons, water and the oxides of carbon being left out of account. The hydrocarbons are not direct products of analytical processes, they are produced by the combination of hydrocarbon residues, such as CH_3, CH_2, CH :—

$$CH_3 + CH_3 = C_2H_6$$
$$CH_2 + CH_2 = C_2H_4$$
$$CH + CH = C_2H_2.$$

From these simple hydrocarbons more complicated ones are formed, partly by direct combination, partly by the mutual splitting off of hydrogen :—

$$3\,C_2H_2 = C_6H_6$$
$$2\,C_6H_6 = \underset{\text{Diphenyl}}{C_{12}H_{10}} + H_2$$
$$C_6H_6 + 2C_2H_2 = \underset{\text{Naphthalene}}{C_{10}H_8} + H_2$$
$$C_{10}H_8 + 2C_2H_2 = \underset{\text{Anthracene}}{C_{14}H_{10}} + H_2.$$

If the vapour of hydrocarbons be passed through red-hot tubes, a number of hydrocarbons richer in carbon are actually formed by synthesis or condensation.

As a rule the products of dry distillation form an extremely complicated mixture of different compounds: this is caused by so many processes of change taking place simultaneously. Wood consists chiefly of cellulose, the composition of which is expressed by the formula $(C_6H_{10}O_5)x$; by dry distillation gaseous and liquid products are obtained, and a residue of carbon remains behind in the retort. The gases contain hydrocarbons such as CH_4, C_2H_4, C_2H_2, &c., together with CO, CO_2, and other substances. The liquid distillate consists of two layers: the one contains methyl alcohol, acetic acid, acetone, &c., dissolved in water; the second layer, which is tarry and semi-fluid, contains a large number of compounds such as the hydrocarbons benzene C_6H_6, toluene C_7H_8, naphthaline $C_{10}H_8$; bodies containing oxygen such as phenol C_6H_6O, cresol C_7H_8O, &c. The composition of tar obtained by dry distillation is of course very variable; the nature and amount of its constituents are dependent upon the raw material, and the temperature at which the distillation is effected.

The tar of substances free from nitrogen has often a sour reaction; that containing nitrogen, especially *animal tar*, is alkaline on account of the formation of ammonia and other basic bodies such as aniline, pyridine bases, &c.

The *coal tar*, obtained as a bye-product in the manufacture of coal gas, forms an important raw material for the preparation of numerous aromatic compounds.

Carbohydrates, which form the chief constituents of plants, have always six, or an even multiple of six, atoms of carbon in the molecule, and it is worthy of note that the products obtained by the dry distillation of plants, and of fossil coals formed from them, chiefly consist of substances containing at least six carbon atoms in the molecule (aromatic bodies), although the linking of the carbon atoms in aromatic substances is quite different from what it is in the carbohydrates.

CHAPTER XXIX

DECAY AND FERMENTATION

Many organic substances, especially the complicated nitrogen and sulphur compounds which occur in the organisms of plants and animals (albumen, glue, &c.), suffer complete decomposition on exposure to air, without entering into chemical reaction with other substances. This process is termed *decay*, and is caused by microscopic organisms, the seeds and spores of which are always to be found in the air. The development and life process of these germs is the primary cause of decay. Organic substances may be made to decay by simple admixture with some body which is already decaying. Cellulose, the chief constituent of wood, is, in the pure state, not subject to decay, but in presence of decaying albuminous substances which are found in wood, it decomposes in a manner analogous to albumen itself.

Once decay has commenced, the presence of air is no longer necessary. Air loses the property of inducing decay if the germs which it contains be taken away or destroyed; this may be effected by passing the air through red-hot tubes, or filtering it through cotton wool. Decay is also prevented by *antiseptic* agents which kill the organisms and their germs. The best temperature for decay is 20°–30°—it cannot take place under 0° or over 100°; the presence of water is also essential—perfectly dry substances do not decay.

No sharp distinction can be drawn between the terms decaying and mouldering; it is usual however to apply the second of these expressions to processes where, together with the decomposition, a tolerably energetic oxidation at the cost of the oxygen of the air takes place. The final products of decay and mouldering are carbon dioxide, water, and ammonia; the process ends only with the complete disappearance of the organic substance; as intermediate products a number of bodies are formed which possess an extremely offensive smell, and which have been little investigated. The phenomena of *fermentation* are closely allied to those of decay, and this process is also brought about by the action of certain primitive organisms called *ferments*. Substances subjected to the working of these ferments are quickly decomposed. The phenomena of fermentation are not so complicated as those of decay; the decomposition products are relatively fewer in number. Fermenting substances are converted into other compounds without any action of the oxygen of the air, but wholly at the cost of the elements originally present.

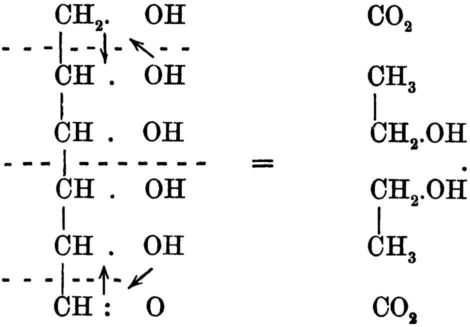
By the action of ferments, single cell organisms of the family *saccharomyces*, &c., grape and other fermentable sugars are decomposed, chiefly into alcohol and carbon dioxide (*alcohol fermentation*):—

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

Combination with water accompanies the fermentation of the saccharoses (cane sugar &c.):—

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

The process consists in a partial reduction and oxidation of the carbon atoms in the molecule:—



$$\begin{array}{lcl} CH_2 . OH & & CO_2 \\ CH . OH & & CH_3 \\ | & & | \\ CH . OH & & CH_2.OH \\ & = & \\ CH . OH & & CH_2.OH \\ | & & | \\ CH . OH & & CH_3 \\ CH : O & & CO_2 \end{array}$$

In addition to alcohol, succinic acid, glycerine, and other substances are always formed, though only in small quantities (about 5–6% of the weight of the sugar).

The concentration and temperature of the sugar solution exert an important influence upon alcohol fermentation. The temperature limits for the process are 5°–50°, but fermentation takes place most rapidly between 25°–40°. As regards the concentration of the solution, it should not at the most contain more than 35 parts of sugar to every 100 parts of water; the best strength is 10–15%.

The cause of the decomposition of sugar by the action of these organisms is not yet clearly known. It has been supposed that as the action of yeast proceeds best with a limited supply of air, it consists in the manifestation of some vital process, which is brought about by the latent force of the fermentable substance rich in oxygen (Pasteur). Another theory seeks to explain the process in a purely chemical way; it is presumed that the yeast cells separate a substance which is capable of transferring the oxygen of the sugar from one part of the molecule to another, thus causing its decomposition (Traube, Hoppe-Seyler). Nägeli a short time since proposed a molecular-physical theory. According to this fermentation consists in a transference of the internal motion possessed by certain of the substances contained in protoplasm to the fermentable body, the equilibrium of which is thereby destroyed, and its molecule decomposed.

Another organised ferment (rod-shaped bacteria) causes the conversion of certain kinds of sugars, particularly milk-sugar, into lactic acid as chief product (*lactic acid fermentation*):—

$$C_6H_{12}O_6 = 2C_3H_6O_3.$$

The best temperature for the lactic acid fermentation lies between 30° and 50°.

The formation of butyric acid from sugar is also accomplished by a microscopic ferment (*butyric acid fermentation*):—

$$C_6H_{12}O_6 = 2CO_2 + C_4H_8O_2 + 2H_2.$$

It is probable that the sugar is first converted into lactic acid, which then decomposes according to the above equation.

The term *acetic acid fermentation* is used to denote the conversion of alcohol into acetic acid by the action of a special organism (mother of vinegar). The process is not a fermentation in the ordinary sense, but a simple oxidation.

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

Many organic substances which contain nitrogen, but are not organised, may act as ferments, for example, diastase, myrosin, emulsine, ptyaline, pepsin, &c.; they are all products of vegetable or animal life, and cannot be prepared artificially; it is even uncertain whether they are distinct chemical compounds. They are called 'chemical ferments' in order to distinguish them from organised ferments. These substances are capable of causing the decomposition of certain complicated compounds into simpler ones. It is only anhydrides which are acted upon in this way, and the process is always accompanied by a combination with water.

Diastase, which occurs in seeds, converts starch into dextrose and maltose:—

$$^{*}\underset{\text{Starch}}{C_{36}H_{62}O_{31}} + 3H_2O = \underset{\text{Dextrose}}{2C_6H_{10}O_5} + \underset{\text{Maltose}}{2(C_{12}H_{22}O_{11}} + H_2O).$$

By the action of emulsine (the ferment of benzaldehyde) amygdalin is split up into grape sugar, benzaldehyde, and hydrocyanic acid:—

$$C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_7H_6O + HCN.$$

Potassium myronate, the glucoside which occurs in black mustard seeds, is decomposed by the accompanying

---

* The molecular weight of starch is probably greater than this.

ferment myrosin, into grape sugar, mustard oil, and potassium hydrosulphate :—

$$C_{10}H_{18}NKS_2O_{10} = C_6H_{12}O_6 + C_4H_5NS + KHSO_4.$$
$$(C_{10}H_{16}NKS_2O_9 + H_2O)?$$

Organised ferments may produce chemical ferments. Yeast gives one which is termed invertin, and has the power of converting cane sugar into grape and fruit sugars (Inversion) :—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

The action of invertin is entirely unconnected with the life of the yeast cell. The invertin continues to act after the cell is dead and the fermentation has ceased.

Chemical ferments are widely distributed both in vegetable and animal life, and they play an important part in the metamorphoses of bodies. Each ferment has its own special action, which ceases if the solution which contains it be heated to a high temperature.

CHAPTER XXX

SYNTHETICAL FORMATION OF ORGANIC SUBSTANCES

It has already been mentioned in the foregoing pages that organic substances can be built up directly or indirectly from their elements. The most important of these simple synthetical processes are the following:—

(1) The hydrocarbon *acetylene* is formed by passing a current of electricity between carbon poles in an atmosphere of hydrogen. $C_2 + H_2 = C_2H_2$.

(2) If a mixture of carbon disulphide and sulphuretted hydrogen be passed over red-hot copper the hydrocarbon *methane* is obtained:—

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

The same hydrocarbon is produced by treating carbon tetrachloride with nascent hydrogen:—

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

Trichlormethylsulphonic chloride $CCl_3.SO_2Cl$ is formed by the action of moist chlorine upon carbon disulphide; on treating with potassium hydrate and then with sodium amalgam, methyl sulphonic acid is obtained.

(3) A whole series of *hydrocarbons*, chiefly of the formula C_nH_{2n+2}, are produced by the action of boiling water upon carbon combined with iron (Cloëz).

(4) *Potassium formate* is formed by passing carbon monoxide over heated potassium hydrate (Berthelot):—

$$CO + KOH = HCO_2K.$$

(5) Carbon monoxide and potassium at high temperatures give *potassium carboxide* (Nietzki and Benckiser):—

$$6CO + 6K = C_6O_6K_6.$$

In this manner a benzene derivative is produced by direct synthesis from the simplest of all carbon compounds.

(6) *Formic acid* is obtained by the reduction of carbon dioxide with hydrogen. If moist carbon dioxide act upon metallic potassium, a mixture of potassium formate and carbonate is formed (Kolbe):—

$$3CO_2 + H_2O + 4K = K_2CO_3 + 2CHO_2K.$$

(7) If a mixture of charcoal and metallic potassium be heated in an atmosphere of nitrogen, *potassium cyanide* is produced:—

$$K_2 + C_2 + N_2 = 2KCN.$$

Complicated organic compounds may be built up from the simple organic bodies acetylene, methane, formic and hydrocyanic acids.

Organic substances occurring in nature are formed by methods of a different kind from the above.

The natural synthetical formation of organic bodies only takes place in plant cells containing chlorophyll.[1]

Little is known of the chemistry of the production of these substances. The foods of plants, the raw materials from which they are built up, are carbon dioxide, water, and nitrates or ammonia. The formation of the substance of plants from the above simple compounds proceeds only in sunlight, and in presence of certain inorganic salts which occur in the earth, and which contain phosphorus, sulphur, potassium, iron, &c. The action is on the whole one of reduction, but the actual stages are not known. *Starch* is the first organic substance which can be clearly detected in the chlorophyll cells; it is however probable that the formation of *sugar* precedes that of starch.

Sugar may be supposed to be produced from carbon dioxide and water according to the following equation:

$$6CO_2 + 6H_2O = \underset{\text{Sugar}}{C_6H_{12}O_6} + 6O_2.$$

Starch is then formed from the sugar by simple splitting off of water:—

$$xC_6H_{12}O_6 = (C_6H_{10}O_5)_x + xH_2O.$$

It has been supposed that by the reduction of carbon dioxide an aldehyde or similar substance is first

---

[1] The hydrocarbons which occur in nature, such as petroleum, are probably produced by the action of water upon red-hot carbonised iron in the interior of the earth, and it is possible that this process is still continuing. The formation of these hydrocarbons however is quite distinct from the reactions of organic substances in living nature.

formed, which then gives sugar or starch by condensation :—

$$CO_2 + H_2O - O_2 = \underset{\text{Formic aldehyde.}}{CH_2O}$$

$$6CH_2O = \underset{\text{Sugar.}}{C_6H_{12}O_6}$$

As a matter of fact a substance (methylenitan) resembling the carbohydrates, and possessing the formula $C_6H_{10}O_5$, has been prepared from formic aldehyde, and from the researches of Bokorny it has been proved that plants can form starch from formic aldehyde, or rather from the methylether of this aldehyde.

The other substances which occur in plants are secondary products of starch or sugar.

Animals and plants containing no chlorophyll are not capable of producing organic substances; their nourishment consists of organic material in the finished state derived directly or indirectly from the vegetable kingdom.

Organic substances being formed originally by the reduction of carbon dioxide and water, always contain less oxygen than these compounds; it is on this fact that their *combustibility* depends. Organic bodies readily combine with oxygen to form the simple oxidation products of carbon and hydrogen from which they were first produced; this takes place during the processes of combustion, decay, or mouldering, which all organic substances in nature must sooner or later undergo.

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