

A TEXT-BOOK OF ORGANIC CHEMISTRY

BY

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PREFACE

IN this edition the opportunity has been taken to revise and rewrite a number of sections, including those dealing with the heterocyclic compounds, and to give an account of recent work on such diverse topics as the parachor, Walden inversion, theory of the benzene ring, free radicals, irones, Roelen synthesis, aliphatic fluorine compounds, alkaloids of the indole group, etc. Space has also been found for Robinson's explanation of Lyndon Small's experimental data on phenyldihydrothebaine as illustrating the interesting and significant results which come from a combination of careful experimentation and ingenious interpretation. Finally, increased emphasis has been placed on the contribution of physical chemistry to the problems of organic chemistry.

To avoid increasing the size of the book unduly I have had to employ drastic methods of selection and compression, but I have at the same time tried to compensate for this by giving up-to-date references in the journals and reviews. It is perhaps opportune to mention a new comer to chemical literature, the *Quarterly Reviews of the Chemical Society*, which gives authoritative surveys of selected, important topics and which are deservedly enjoying great popularity with those chemists who are anxious to keep abreast with modern developments.

It is impossible to thank all those who have assisted in drafting the present edition, but special thanks are due to my wife for her invaluable help in preparing the manuscript, compiling the index, and proof-reading; Professors E. L. Hirst and J. N. Davidson, and Dr E. G. V. Percival for valuable suggestions and advice; Professor Schönberg and Mr L. A. Wiles for pointing out inaccuracies in the last edition; Dr W. W. Easton for his help with the text and diagrams; and those research students who helped so generously in the final stages.

Thanks are also due to the publishers for their never-failing courtesy and co-operation.

NEIL CAMPBELL

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LIST OF ABBREVIATIONS

ABBREVIATIONS

JOURNALS

Am. C. J.	American Chemical Journal.
Ann.	Liebig's Annalen der Chemie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Reports.	Annual Reports of the Chemical Society.
Ann. Rev. Biochem.	Annual Review of Biochemistry.
Arch. Pharm.	Archiv. der Pharmazie.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Biochem. J.	Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Biochem. Z.	Biochemische Zeitung.
Bull. Soc.	Bulletin de la Société Chimique à Paris.
C.	Chemisches Zentralblatt.
Chem. and Ind.	Chemistry and Industry.
Chem. Rev.	Chemical Reviews.
Ch. Zeit.	Chemiker-Zeitung.
C. r.	Comptes rendus de l'Académie des Sciences.
Gazz.	Gazzetta Chimica Italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Journal of Industrial and Engineering Chemistry.. Analytical Edition.
J.A.C.S.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry.
J.	Journal of the Chemical Society.
J. Chem. Ed.	Journal of Chemical Education.
J.C.S., A.	Abstracts of the Chemical Society.
J. Physiol.	Journal of Physiology.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Ch.	Journal für praktische Chemie.
J.S.C.I.	Journal of the Society of Chemical Industry.
Monats.	Monatshefte für Chemie.
Pogg. Ann.	Poggendorf's Annalen der Physik.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-bas.
Trans. Farad. Soc.	Transactions of the Faraday Society.
Z. anal. Ch.	Zeitschrift für analytische Chemie.
Z. ang. Ch.	Zeitschrift für angewandte Chemie.
Z. Ch.	Zeitschrift für Chemie.
Z. Elek.	Zeitschrift für Elektrochemie.
Z. Krist.	Zeitschrift für Kristallographie.
Z. phys. Ch.	Zeitschrift für physikalische Chemie.
Z. physiol. Ch.	Zeitschrift für physiologische Chemie.

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ORGANIC CHEMISTRY

Introduction

COMPARATIVELY early in the history of chemistry an interest began to be taken in the remarkable variety of carbon compounds which could be prepared from plant and animal sources. This led eventually to systematic investigations on their origin and the manner in which they could be transformed one into another. It was not until the eighteenth century, however, that the first results of importance were obtained at the hands of Lavoisier. The work was found to present peculiar difficulties and to require a special laboratory technique, hence at the beginning of the nineteenth century it was severed completely from inorganic chemistry and considered as a separate branch of chemical science. The name of *Organic Chemistry* originated in the belief that compounds of this type could not be prepared artificially in the laboratory, but were formed solely in living organisms under the influence of a mysterious agency termed Vital Force. Experimental evidence at first lent support to this theory, in so far that all attempts to build up such substances from materials not themselves obtained from living organisms were unsuccessful.

The Vital Force theory was disproved by the syntheses of organic compounds from inorganic constituents. It is often stated that the theory was discarded as the result of Wöhler's discovery¹ in 1828 that urea, one of the most characteristic products of animal metabolism, could be prepared from the inorganic constituents cyanic acid and ammonia. It has been pointed out, however, that the cyanic acid was obtained from organic matter such as dried blood and therefore could not be termed inorganic.² Since that time a large number of organic compounds have been synthesised from purely inorganic materials, one of the earliest being that of Kolbe,³ who in 1845 prepared acetic acid from carbon disulphide.

Other syntheses followed, until it was proved beyond all doubt that the same chemical forces operated in the organic as in the inorganic world, and the assumption of a vital force responsible for the production of carbon compounds in the organism was therefore superfluous. Nevertheless there are many substances of plant and animal origin, including

¹ Wöhler, "Ueber kunstliche Bildung des Harnstoffs," *Pogg. Ann.*, 1828, 12.

² See J. Read, *Text-Book of Organic Chemistry*, p. 146; Douglas McKie, *Nature*, 1944, 153, 608.

³ *Ann.*, 1845, 54, 145.

the very widespread class of proteins, which have so far eluded artificial preparation. Various reasons may be put forward to explain this lack of success. Not only has the precise chemical composition of the proteins yet to be determined, but even the mode of union of the atoms in these compounds is still uncertain. Nor have we any clear conception of the physico-chemical conditions under which these substances are produced in the living organism.

Although we still speak of organic and inorganic chemistry, the terms are retained solely for convenience of reference. The peculiarities of organic compounds depend only on the nature of their principal constituent carbon, and the wide extent of organic chemistry is a direct consequence of the unique combining capacity of the carbon atom. No other element approaches carbon in its ability to unite with itself, atom by atom, to form open and closed chains, and as a result, the number of known carbon compounds, now well over 500,000, exceeds that of the compounds of all the other elements put together.

*Organic Chemistry is thus to be defined as the chemistry of carbon compounds.*¹

As the majority of organic compounds resulting from plant and animal activity consist only of carbon, hydrogen, oxygen and less frequently nitrogen, these elements have been termed organogenetic. Organic substances containing sulphur, phosphorus and more rarely other elements are also known to occur in nature, but their number is relatively small. On the other hand, by artificial means it is possible to prepare organic derivatives of any of the elements except the rare gases.

ANALYSIS OF ORGANIC COMPOUNDS

Relatively few organic compounds are distinguished by reactions sufficiently characteristic to serve as a basis for their qualitative identification. For the separation of organic substances from mixtures there is therefore no general procedure known comparable to the systematic analysis of inorganic chemistry.

In many cases the physical properties of a substance such as smell, crystalline form, melting-point, boiling-point, or optical rotation enable it to be identified. More often it is necessary to determine its composition, first qualitatively and then quantitatively.

Methods for the qualitative and quantitative determination of carbon, hydrogen, nitrogen, halogens, etc., will be found in books on practical organic chemistry. Microanalysis of organic compounds is now widely employed, a few milligrammes of a compound being sufficient for its complete analysis.²

¹ Carbon itself and a few of its simple compounds, such as carbon dioxide and carbonates which are of frequent occurrence in the mineral world, are usually described in text-books on inorganic chemistry and are not included here. ² F. Pregl, *Quantitative Organic Analysis*, translated by E. Fyfe (Churchill).

CALCULATION OF EMPIRICAL FORMULÆ

The formula of the substance is deduced from the percentage composition, as found by analysis, in the same way as with inorganic compounds. The percentage figures are first divided by the atomic weights of the elements to which they have reference; the quotients thus obtained show the relative proportions in which the atoms are combined together. On using the smallest of these quotients as a divisor for the others, values are arrived at which either approximate to whole numbers or do so after further simple multiplication. The formula finally deduced should be in accordance with the Law of Even Numbers.

Example.—The analysis of a substance consisting of carbon, hydrogen, nitrogen, chlorine and oxygen gave

	44.05% C,	7.31% H,	10.18% N,	26.19% Cl,	and by difference 12.20% O.
The divisions	$\frac{44.05}{12}$,	$\frac{7.31}{1}$,	$\frac{10.18}{14}$,	$\frac{26.19}{35.5}$,	$\frac{12.20}{16}$ yield the
figures	3.67,	7.31,	0.73,	0.74,	0.76
These divided by 0.73 give	5.02,	10.01,	1.0,	1.01,	1.04

From which the simplest formula is $C_5H_{10}ONCl$.

The simplest formula obtained in this way is termed the *empirical formula*, and does not always correspond to the real molecular weight, which may prove to be some higher multiple thereof.

After discovering the percentage composition of a substance and with it the proportions in which the atoms are united together, the next problem is to ascertain the true molecular weight.

DETERMINATION OF MOLECULAR WEIGHT—MOLECULAR FORMULA OF AN ORGANIC COMPOUND

It is frequently possible to deduce the probable molecular weight of a compound from the reactions by which it is formed. In other cases the information can be gained from a detailed chemical investigation of the nature of the substance. In most instances, however, the best results are given by physical methods.

Determination of Molecular Weight by Chemical Methods

It should be said at once that an absolutely sure method of determining molecular weights by purely chemical means is not available. It is only possible to eliminate certain of the values in question and to estimate with some probability the actual size of the molecule.

For this purpose derivatives of the substance must be prepared possessing an atom or radical capable of being quantitatively determined, from the proportion of which the molecular formula of the derivative may be calculated and hence that of the parent substance.

Salt-forming compounds, such as acids and bases, lend themselves best to this end. In the case of acids the determinations are carried out preferably with the silver salts, because these are usually of normal composition and easily analysed. In addition it is necessary to know the basicity of the acid, which may be ascertained from an examination of the esters or salts. As will be seen later (p. 73) the electrical conductivity also gives valuable information on this point.

For similar reasons the determination of the molecular weight of a base is carried out by means of its platinum salt, which is generally of the type of ammonium chloroplatinate, $(\text{NH}_3)_2\text{H}_2\text{PtCl}_6$, and thus contains 1 mol. of hydrochloroplatinic acid, H_2PtCl_6 , for each 2 mols. of a monacid or 1 mol. of a diacid base.

The proportion of platinum in the double salt is estimated by ignition, and from this is calculated the total weight of the other constituents associated with one atom of platinum (at. wt. 195.2). By subtracting the weights of six atoms of chlorine and two atoms of hydrogen from the number so obtained, and subsequent division by 2 (for a monacid base), the molecular weight of the base is found.

Under certain conditions the molecular weight of a base may also be determined by estimating the amount of hydrochloric acid in the hydrochloride.

Example I.—Acetic acid on analysis gives the empirical formula CH_3O . It is a monobasic acid, and in silver acetate one hydrogen atom of the acid is therefore replaced by one atom of silver. Hence in order to find the molecular weight of acetic acid we only require to estimate the amount of silver in the silver salt.

0.4120 gm. silver acetate leaves on ignition 0.2665 gm. metallic silver. The salt therefore contains 64.70 per cent. silver; or
100 parts of silver acetate consist of—

Organic residue	= 35.3
Silver	= 64.7

The molecular weight of the organic residue in silver acetate is therefore given by the equation

$$\begin{aligned} 64.7 : 35.3 &= 107.88^1 : x \\ x &= 59. \end{aligned}$$

Free acetic acid, however, contains in addition to these 59 parts of acetic acid residue a further atom of hydrogen. The molecular weight of the free acid is therefore 60. The simplest formula CH_3O arrived at through analysis, and corresponding to the mol. wt. 30, must accordingly be doubled, and the composition of acetic acid expressed by the formula $\text{C}_2\text{H}_4\text{O}_2$.

This is termed the *molecular formula* and indicates how many atoms of the elements composing the compound are contained in one molecule.

Example II.—Analysis of aniline shows it to consist of 77.42 per cent. C, 7.53 per cent. H, and 15.05 per cent. N: from which is derived the empirical formula $\text{C}_6\text{H}_7\text{N}$. As is well known, NH_3 combines with HCl to form ammonium chloride in the proportion of 17:36.4. Aniline also combines directly with hydrochloric acid to form a similar salt. The molecular weight of aniline may therefore be considered to be that amount

¹ Atomic weight of silver.

which combines with 36 + gms. HCl, and may be calculated from the chlorine content of aniline hydrochloride. On precipitation with silver nitrate, 0.2590 gm. of this salt gives 0.2870 gm. of silver chloride, which corresponds to 0.073 gm. of HCl. Consequently 0.259 gm. of the salt contains 0.073 gm. of HCl, and by difference 0.186 gm. of aniline. From this it follows from the equation

$$0.073 : 0.186 = 36.4 : x$$

that 93 parts by weight of aniline are united with 36.4 parts of HCl.

The empirical formula C_6H_7N also gives 93 as the molecular weight and is therefore to be considered as the molecular formula of aniline.

Example III.—Caffeine, the physiologically active constituent of coffee and tea, gives on analysis the empirical formula $C_4H_5N_2O$.

It is a monacid base, and its platinum compound consists therefore of 2 mols. of caffeine combined with 2 mols. of hydrochloric acid and 1 mol. of platinum chloride. On ignition 100 parts by weight of this compound give 24.6 parts of metallic platinum; consequently the weight containing one atomic proportion (194.8) of platinum is

$$\frac{194.8 \times 100}{24.6} = 791.8.$$

These 791.8 parts of the platinum double salt consist however of 2 mols. of caffeine combined with $2HCl + PtCl_4$; the molecular weight of caffeine is therefore obtained from the equation

$$2x + (2 \times 36.4) + 336.3 = 791.8$$

$$x = 191.$$

The formula $C_4H_5N_2O$ quoted above, corresponding to the mol. wt. 97, must therefore be doubled, giving the molecular formula of caffeine as $C_8H_{10}N_4O_2$.

The majority of organic compounds are neither acids nor bases, and with indifferent substances such as these it is frequently impossible to determine the molecular weight by purely chemical methods. Sometimes a detailed study of the reactions of the substance leads to a definite conclusion.

Investigation may be made, for example, as to the manner in which the compound behaves on the substitution of hydrogen by chlorine, and the proportion of the total hydrogen which is replaceable in this way.

Example I.—Chloro-substituted carboxylic acids can be prepared by the direct action of chlorine on the acids. Acetic acid, with the empirical formula CH_3O , gives according to experimental conditions three different acids on treatment with chlorine, the final product of substitution having the formula $C_2HO_2Cl_3$. In acetic acid itself there are therefore three hydrogen atoms replaceable by chlorine, pointing to the molecular formula $C_2H_4O_2$ for acetic acid.

Example II.—The simplest formula for naphthalene as deduced from analytical data is C_8H_6 . Naphthalene reacts with chlorine, however, to give a substance, monochloronaphthalene, containing 73.8 per cent. C, 4.3 per cent. H and 21.9 per cent. Cl, from which the formula $C_{10}H_7Cl$ is derived. This compound is produced from naphthalene by the substitution of hydrogen by chlorine, so that at least one whole atom must have been replaced, since fractions are excluded. From the formula $C_{10}H_7Cl$, therefore, it is obvious that at least $\frac{1}{8}$ of the total hydrogen in the original compound has been replaced, and naphthalene contains in consequence 8, or 2×8 , or 3×8 , etc., hydrogen atoms, together with 10 (or a multiple of 10) carbon atoms. A multiple of 8 or 10 is, however, out of the question, since no derivatives have ever been obtained from naphthalene indicating the possibility of replacing, for example, $\frac{1}{8}$ or $\frac{1}{10}$ of the

total hydrogen. For these reasons the formula C_6H_4 is doubled, and the molecular formula $C_{10}H_8$ assumed for naphthalene.

In some cases an investigation of the additive compounds given with picric acid has been of service in determining the molecular weights of hydrocarbons.

Example III.—An illustration of the manner in which the chemical examination of even more complicated compounds may throw light upon the molecular weight is given in the case of fructose, which has the same percentage composition as acetic acid, and therefore the empirical formula CH_2O . This compound on reduction is converted into mannitol, which may be transformed back to fructose by oxidation. The molecular weight of mannitol is known, since it is a hexahydric alcohol $C_6H_8(OH)_6$, derived from hexane C_6H_{14} , and may be converted into this hydrocarbon. Consequently fructose similarly contains six atoms of carbon and has the molecular formula $C_6H_{12}O_6$.

Determination of Molecular Weight by Physical Methods¹

Of the many processes available for this purpose, those which have proved of greatest service to the organic chemist are the determination of vapour density by Victor Meyer's method, and the determinations of molecular weight by measuring the elevation of boiling-point or the depression of freezing-point of a solution. These are described in full detail in analytical text-books.

Polymerism

It is seen from the foregoing pages that compounds of the same percentage composition may possess different molecular weights and therefore different properties. Such compounds are said to be **polymers** or **polymerides**. The number of organic compounds exhibiting this relationship is very large, familiar examples being cyanic acid, $HCNO$, and cyanuric acid, $(HCNO)_3$; formaldehyde, CH_2O , and fructose, $C_6H_{12}O_6$.

Molecular Structure and Isomerism

Even supposing the composition and molecular weight of a substance to have been determined by means of the methods indicated in the previous chapter, the molecular formula arrived at from these data is not yet sufficiently characteristic to obviate the possibility of confusion with other substances. There are numerous organic compounds of the same percentage composition and molecular weight which nevertheless differ in their physical and chemical properties. Such substances are called **isomers**, or **isomerides**.

For example, five different compounds are known having the composition and molecular formula C_3H_8O , and ethylamine and dimethylamine of the same molecular formula C_2H_7N show considerable differences in their chemical and physical behaviour.

¹ Two simple micro-methods of determining molecular weights have been described by G. Barger (*J.*, 1904, 85, 286; see also K. Rast, *Ber.*, 1921, 54, 1979) and by K. Rast *Ber.*, 1922, 55, 1051.

The reason for such differences must be sought in the internal structure of the molecules, which are assumed to contain a dissimilar *arrangement* of atoms. This difference of arrangement may refer :—

(a) To the manner in which the atoms are linked together, without reference to their positions in space. These are cases of **structural isomerism**, and are treated in detail under the theory of structure.

(b) To the relative position of the atoms in space. These are cases of **stereoisomerism** and are discussed under stereochemistry.

It is a point of interest that the development of these two branches, which together comprise the theory of molecular structure, originated solely in the sphere of organic chemistry.¹

I.—STRUCTURE

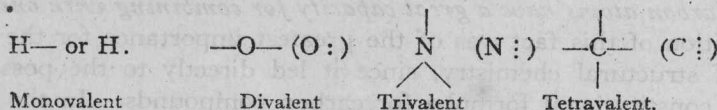
The theory of the structure of organic compounds deals with the manner in which the atoms are connected one with another, and is based on the conception of valency.

(a) Outline of the Theory of Valency

In the year 1858 Kekulé advanced two hypotheses which form the foundation of modern views on the structure of carbon compounds. They postulated that carbon is a tetravalent element and that its atoms have the power to combine one with another.² Somewhat later Couper³ published similar views, which gave rise to the idea of atomic linkings.⁴

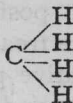
Whereas at first it was assumed that the different atoms forming a molecule were held together in such a manner that one attracted all or a certain number of the others, and these themselves exerted a reciprocal attraction on the first, thus holding it in position, it was realised later that this mutual influence extended only from atom to atom. Graphically expressed, the atoms are conceived as strung into a chain, each member being linked to those adjacent to it; if one be removed and not replaced by another, the chain breaks and the compound decomposes. Such chains may be built up from a variety of atoms which need not be of the same valency. A monovalent atom such as hydrogen, however, has only the one opportunity of union, whilst one which is divalent has two, and so on.

The power of union or valency of an atom is indicated by placing small lines or points close to the symbols of the elements, in such a way that each line or point expresses a unit of valency :



¹ The phenomenon of isomerism is comparatively rare in inorganic chemistry. ² *Ann.*, 1858, 106, 151. ³ *Ann. chim. phys.*, 1858 (3), 53, 469. ⁴ It should be noted that Kekulé and Couper are not the actual founders of the theory of valency. This honour belonged to Frankland and Kolbe. The former investigators have, however, rendered the great service of expanding the ideas of Frankland and Kolbe, and of applying them to organic chemistry.

Assuming that in the formation of a compound these valencies are mutually used up, it follows that those elements which combine with hydrogen according to the formula $X-H$ must, like hydrogen, be monovalent. The elements which combine according to the formulæ

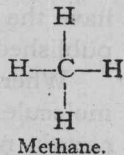


are then di-, tri- and tetravalent respectively.

The further development of the theory of valency in inorganic chemistry is complicated by the fact that elements do not always exhibit the same valency; thus copper is mono- or divalent according to whether it is present in a cuprous or a cupric compound. In organic chemistry the conditions are simpler, since the elements H, O, and C, of which the majority of important carbon compounds are composed, show with comparatively few exceptions a constant valency. In other words, hydrogen is monovalent, oxygen generally divalent¹ and carbon tetravalent.

The manner in which the atoms are linked up within the molecule indicates the constitution or structure of the compound, and is expressed by means of constitutional or structural formulæ. These are built up according to the following rules, based on experience:—

1. *The carbon atom is usually tetravalent*, in agreement with its position in the periodic classification. A carbon atom may thus combine with a maximum of four monovalent atoms or groups. This is illustrated by one of the simplest organic compounds, marsh gas or methane, in which one atom of carbon is combined with four atoms of hydrogen.



In a few compounds such as carbon monoxide, $C=O$, fulminic acid, $HO-N=C$ and others, carbon plays the part of a divalent element. It may also exist in the trivalent state in triphenylmethyl, and other compounds.

2. *The four valencies of carbon are equivalent to one another*, since the replacement of any one of the four hydrogen atoms in methane by the same monovalent atom, or group of atoms, always yields the same monosubstitution product.

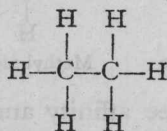
The equivalence of the four carbon valencies is established by the fact that compounds such as CCl_4 possess zero dipole moment (see p. 74).

3. *Carbon atoms have a great capacity for combining with one another*. Recognition of this fact was of the greatest importance for the development of structural chemistry, since it led directly to the possibility of writing constitutional formulæ for carbon compounds. In the union of carbon atoms it is supposed that each atom is bound by a valency, or several valencies, to a neighbouring atom; the remaining valencies can

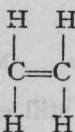
¹ It should be borne in mind that oxygen in organic compounds may under special conditions be tetravalent (see Collie and Tickle, *J.*, 1899, 75, 710; and Baeyer and Villiger, *Ber.*, 1901, 34, 2685) and carbon possibly trivalent.

then be saturated by hydrogen, or other simple or complex groups. Two carbon atoms may thus be linked together with one, two, or three valencies, these being termed single, double, or triple bonds respectively, e.g. $C-C$, $C=C$, $C\equiv C$.

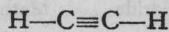
Those substances in which, as in I, only singly bound carbon atoms occur, are called saturated carbon compounds, whereas those, as in II and III, containing double or triple bonds are known as unsaturated.



I. Ethane

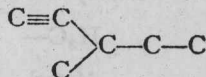
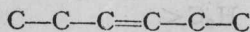
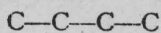


II. Ethylene

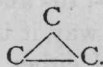
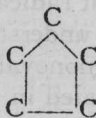
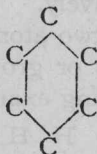


III. Acetylene.

In a similar way it is possible for three, four, or any larger number of carbon atoms to combine together. The final product may be an open chain such as

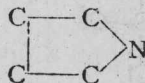
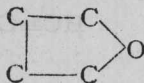


or closed chains or rings of the type



A number of important open chain carbon compounds are found in animal and vegetable fats. Consequently that section of organic chemistry which treats of open chain compounds is known as the fatty series, and a substance belonging to this class as a *fatty* or *aliphatic compound*.

On the other hand, those containing closed chains come under the heading of *cyclic compounds*. If the rings consist entirely of carbon atoms, as in the above examples, they are termed *carbocyclic*; if in addition to carbon we have elements such as oxygen, sulphur or nitrogen, taking part in the formation of rings of the type



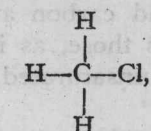
the compounds are termed *heterocyclic*.

Among the carbocyclic rings, the one containing six carbon atoms with six free valencies possesses a special interest. From it are derived substances classed as *aromatic compounds* or *benzene derivatives*.

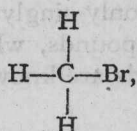
(b) Substitution, Radicals, Isomerism

Under suitable conditions the elements in organic compounds may be replaced, or substituted, in equivalent proportions by other elements.

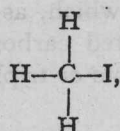
Once again considering the simplest compound of carbon, methane, it is possible for one of its hydrogen atoms to be replaced by one atom of chlorine, bromine or iodine, or by a group of atoms, such as .OH, having one free bond :—



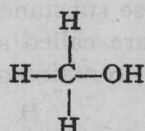
Methyl chloride



Methyl bromide



Methyl iodide



Methyl alcohol.

Such groups of atoms, which still exhibit free affinity and therefore are not stable in the free state, are often transferable as such from one compound to another, and are termed **radicals** or **groups**. The group OH is known as hydroxyl, and since it possesses only one free affinity is monovalent. By the removal of successive atoms of hydrogen from methane we may derive the following :



Methyl



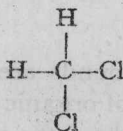
Methylene



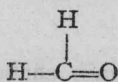
Methenyl or methine.

which are mono-, di- and trivalent radicals respectively.

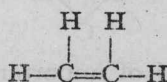
In the same way it is easy to understand that two atoms of hydrogen may be replaced either by two monovalent atoms or groups, or by one divalent atom or group, as illustrated in the following examples :



Methylene chloride

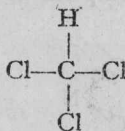


Formaldehyde

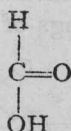


Ethylene.

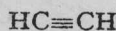
Similarly three hydrogen atoms of methane may be substituted by three monovalent atoms or radicals, by one monovalent and one divalent atom (or radical), or by a trivalent atom (or radical), as in the following compounds :



Chloroform

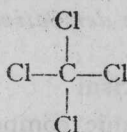


Formic acid

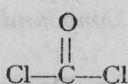


Acetylene.

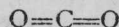
Finally, all four hydrogen atoms may be replaced by four monovalent atoms or radicals, etc., as in—



Carbon tetrachloride

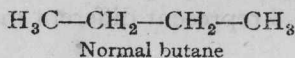


Phosgene

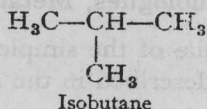


Carbon dioxide.

The substitution of hydrogen in methane by the radical CH_3 will be considered in more detail. When an atom of hydrogen in CH_4 is exchanged for the monovalent radical CH_3 , the hydrocarbon ethane, $\text{H}_3\text{C}-\text{CH}_3$, is produced. If in this compound H is again replaced by CH_3 , we obtain $\text{CH}_3-\text{CH}_2-\text{CH}_3$, propane. Obviously there is only one ethane or propane possible, since it is immaterial which hydrogen atom in methane or ethane is substituted. If, however, a hydrogen atom in propane is once again exchanged for CH_3 , two isomeric compounds may be formed, according to whether the H replaced is situated in one of the two CH_3 groups or in the CH_2 . In the first case normal butane is obtained



and in the second isobutane,

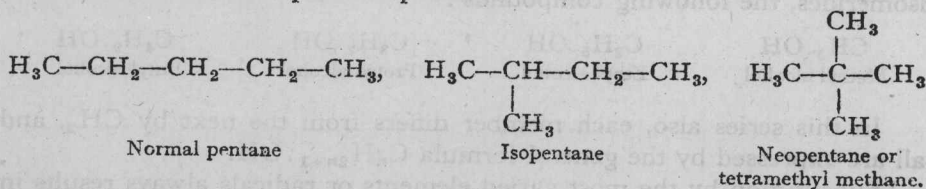


both of the composition C_4H_{10} .

As in numerous other cases, the cause of isomerism in the butanes is the different constitution of the carbon chains. Normal butane contains a straight carbon chain, whereas isobutane has a branched chain.

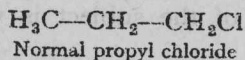
Isomerism of this type involving a different structure, or manner of linking, of the carbon chain or nucleus is termed **chain or nuclear isomerism**.

It is seen from the foregoing that there are two ways of linking up four carbon atoms; and if in a similar manner we derive from the formulæ of the two butanes the corresponding compounds with five carbon atoms, we find there are three possible pentanes—



With an increasing number of carbon atoms, the number of different modes of linking, and therefore the possible number of isomers, increases with extraordinary rapidity. There are five hexanes, C_6H_{14} , nine heptanes, C_7H_{16} , and eighteen octanes, C_8H_{18} , theoretically possible.

It is also possible for hydrogen atoms in all these hydrocarbons to be replaced by other elements or radicals. This gives rise to a different kind of isomerism from that discussed above. For example, different chlorine compounds may be derived from propane, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$, according as the halogen replaces hydrogen in the CH_2 or one of the CH_3 groups—



and

