ORGANIC
CHEMISTRY

By

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PREFACE TO SECOND EDITION

THE aim of this book has remained unchanged. Since I do not consider the chemistry of natural products fundamental chemistry but rather the application of fundamental principles, I have excluded almost completely the study of natural products. It is my hope, however, to write a companion volume in which I shall deal with further aspects of stereochemistry and also with the chemistry of many classes of natural products.

In this second edition, I have taken the opportunity to correct various errors in the text. I wish to thank those reviewers, correspondents and many of my students who brought these errors to my notice, and also made suggestions for improving the book.

In this edition I have used the alphabetical order of naming prefixes, and I have described the older method on p. 697. The principal additions include a more detailed account of molecular orbital theory, some further aspects of stereochemistry, various heterocyclic compounds, and a number of dyestuffs.

My original intention was to deal with molecular orbital theory in the future companion volume. I came to the conclusion, however, that the treatment of this subject is best dealt with in this book. I have therefore given an elementary account of molecular orbitals in Chapter II, and I have discussed their applications throughout the text alongside the resonance theory so that the student can gain some knowledge of both theories. In order to keep the size of this book within reasonable limits, I have used smaller type for much of the additional matter.

It is impossible to express my indebtedness to those authors of monographs, articles, etc., from which I have gained so much information. I can only hope that some measure of my gratitude is expressed by the references I have given to their works.

<div align="right">I. L. FINAR.</div>

1953

PREFACE

IN this book my aim has been to describe the fundamental principles of organic chemistry. Although the book has not been written with any particular examination in view, nevertheless the subject matter covers most of the organic chemistry required for the General Honours degree of the London University. It also covers a large amount of the organic chemistry of Part I of the Special Honours degree in chemistry of the London University, and a number of sections of this book should serve as an introduction to Part II.

To many beginners organic chemistry may seem to consist of a large variety of methods and reactions which appear to be isolated and, consequently, only to be learned by heart. After many years' experience of teaching organic chemistry to degree students, I have found that the best method of instruction is by the introduction of electronic theories as early as possible, with a constant application of their principles. These electronic theories give to organic chemistry a certain coherence that is soon appreciated by the beginner, and thus facilitate his study in this branch of chemistry. Stress has been laid on structural formulæ, properties of compounds, and reaction mechanisms. Special attention has been given to the systematic nomenclature of organic compounds. The alphabetical order of naming prefixes was adopted by the Chemical Society in April, 1950. This book was completed before this date and so this method has not been used. The reader, however, should have no difficulty in locating a compound in the index.

It is my experience that only a fairly detailed study of the subject matter enables the student to appreciate the problems involved. Too short an account usually leaves the impression that " everything works according to plan ". This is undesirable for those who are expected to acquire a certain amount of factual knowledge and at the same time learn to think for themselves. I have therefore included detailed discussions on developments of a straightforward nature and also of a controversial nature, in the hope of encouraging the student to weigh up the evidence for himself. This will also give him an idea of some of the problems being investigated at the present time, and will show him that many " facts " are subject to change. Controversial material and the more advanced sections have generally been printed in small type.

Only by reading original papers in which are described the " whys and wherefores " can the student hope to gain a more mature outlook. A selected number of reading references have therefore been given at the end of each chapter. Since summaries of various topics by workers in special fields are of great value in extending the student's knowledge, references of this type have also been included. An account of the literature of organic chemistry has been given in an appendix.

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In describing methods of preparation of various compounds, I have given, wherever possible, actual percentage yields (taken mainly from *Organic Syntheses*). The student will thus be enabled to assess the value of a particular method. Where general methods of preparation have been described, the yields have been indicated according to the following (arbitrary) scheme :

0–15% very poor (*v.p.*); 16–30% poor (*p.*); 31–45% fair (*f.*); 46–60% fairly good (*f.g.*); 61–75% good (*g.*); 76–90% very good (*v.g.*); 91–100% excellent (*ex.*).

At the end of each chapter there are questions designed to test the student's " book knowledge " and to test the application of his book knowledge. At the end of the book there are also fifty questions chosen from various examinations—B.Sc. General and Special Honours of the University of London, and the Associateship and Fellowship of The Royal Institute of Chemistry. I should here like to thank these Examining Boards for permission to reproduce these questions.

It is hoped that the method of presentation in this book will stimulate the reader's interest in organic chemistry and enable him to read with understanding original papers and monographs covering specialised fields.

I should like to acknowledge the valuable help given me by Mr. K. Merton in reading the manuscript and by Miss A. B. Simmonds, B.Sc., Ph.C., A.R.I.C., in reading the proofs.

I. L. FINAR.

July, 1950.

LIST OF JOURNAL ABBREVIATIONS

ABBREVIATIONS.	JOURNALS.
Ann. Reports (Chem. Soc.)	Annual Reports of the Progress of Chemistry (The Chemical Society, London).
Ber.	Berichte der Deutschen Chemischen Gesellschaft (name now changed to Chemische Berichte).
Chem. Eng. News	Chemical and Engineering News (American Chemical Society).
Chem. Reviews	Chemical Reviews.
Chem. and Ind.	Chemistry and Industry.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal. Ed.)	Industrial and Engineering Chemistry (Analytical Edition) [name now changed to Analytical Chemistry].
Ind. Eng. Chem. (News Ed.)	Industrial and Engineering Chemistry (News Edition).
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Educ.	Journal of Chemical Education.
J.C.S.	Journal of the Chemical Society.
J. Org. Chem.	Journal of Organic Chemistry.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
Nature	Nature.
Quart. Reviews (Chem. Soc.)	Quarterly Reviews of the Chemical Society (London).
Rec. trav. chim.	Recueil des Travaux Chimiques des Pays-Bas.
Trans. Faraday Soc.	Transactions of the Faraday Society.

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INTRODUCTION

HISTORICAL INTRODUCTION

ALTHOUGH organic substances such as sugar, starch, alcohol, resins, oils, indigo, etc., had been known from earliest times, very little progress in their chemistry was made until about the beginning of the eighteenth century. In 1675, Lemery published his famous *Cours de Chymie*, in which he divided compounds from natural sources into three classes : *mineral, vegetable* and *animal*. This classification was accepted very quickly, but it was Lavoisier who first showed, in 1784, that all compounds obtained from vegetable and animal sources always contained at least carbon and hydrogen, and frequently, nitrogen and phosphorus. Lavoisier, in spite of showing this close relationship between vegetable and animal products, still retained Lemery's classification. Lavoisier's analytical work, however, stimulated further research in this direction, and resulted in much-improved technique, due to which Lemery's classification had to be modified. Lemery had based his classification on the *origin* of the compound, but it was now found (undoubtedly due to the improved analytical methods) that in a number of cases the *same* compound could be obtained from both vegetable and animal sources. Thus no difference existed between these two classes of compounds, and hence it was no longer justifiable to consider them under separate headings. This led to the reclassification of substances into two groups : all those which could be obtained from vegetables or animals, *i.e.*, substances that were produced by the *living organism*, were classified as *organic* ; and all those substances which were not prepared from the living organism were classified as *inorganic*.

At this stage of the investigation of organic compounds it appeared that there were definite differences between organic and inorganic compounds, *e.g.*, complexity of composition and the combustibility of the former. Berzelius (1815) thought that organic compounds were produced from their elements by laws different from those governing the formation of inorganic compounds. This then led him to believe that organic compounds were produced under the influence of a *vital force*, and that they could not be prepared artificially.

In 1828, Wöhler converted ammonium cyanate into urea, a substance hitherto obtained only from animal sources. This synthesis, however, had very little effect on the belief in the vital force theory because it did not start from the elements. Wöhler had prepared his ammonium cyanate from ammonia and cyanic acid, both of which were of animal origin. Wöhler himself appreciated this point, but at that time no methods were known for obtaining ammonia and cyanic acid from their elements. Thus Wöhler's synthesis remained incomplete for the time being. It was not until 1845 that the complete synthesis of an organic compound was carried out. In that year Kolbe synthesised acetic acid from its elements (see p. 150). This synthesis was later followed by others, *e.g.*, in 1856 Berthelot synthesised methane (see p. 30), and so belief in a vital force disappeared.

Since the supposed differences between the two classes of compounds have been disproved, the terms organic and inorganic would appear to be no longer necessary. Nevertheless, they have been retained, but it should be appreciated that they have lost their original meaning. The retention of the terms organic and inorganic may be ascribed to several reasons : (i) all

so-called organic compounds contain carbon ; (ii) the compounds of carbon are far more numerous (over 750,000) than the known compounds of *all* the other elements put together ; (iii) carbon has the power to combine with other carbon atoms to form long chains.   This property, known as *catenation*, is not shown to such an extent by any other element.

Hence organic chemistry is the chemistry of the carbon compounds.

This definition includes compounds such as carbon monoxide, carbon dioxide, carbonates, carbon disulphide, etc.   Since these occur chiefly in the inorganic kingdom (*original meaning*), they are usually described in text-books of inorganic chemistry.

ANALYSIS OF ORGANIC COMPOUNDS

The following is an outline of the methods used in the study of organic compounds.

(1) **Purification.**   Before the properties and structure of an organic compound can be completely investigated, the compound must be prepared in the pure state.   Common methods of purification are :

(i) Recrystallisation from suitable solvents.

(ii) Distillation : (*a*) at atmospheric pressure ; (*b*) under reduced pressure or *in vacuo* ; (*c*) under increased pressure.

(iii) Steam distillation.

(iv) Sublimation.

(v) Chromatography.   This method is based on the differential adsorption of the different components of a mixture on various adsorbents.   A widely used adsorbent is alumina.

It is surprising how much information has often been obtained about the properties and structure of a substance that has not been isolated in a pure state.   Even so, purification should always be attempted, since it is much simpler to investigate a pure substance than an impure one.

(2) **Qualitative analysis.**   The elements commonly found in organic substances are : carbon (always : by definition), hydrogen, oxygen, nitrogen, halogens, sulphur, phosphorus and metals.

(i) **Carbon and hydrogen.**   The compound is intimately mixed with dry cupric oxide and the mixture then heated in a tube.   Carbon is oxidised to carbon dioxide (detected by means of calcium hydroxide solution), and hydrogen is oxidised to water (detected by condensation on the cooler parts of the tube).

(ii) **Nitrogen, halogens and sulphur.**   These are all detected by the *Lassaigne method*.   The compound is fused with metallic sodium, whereby nitrogen is converted into sodium cyanide, halogen into sodium halide, and sulphur into sodium sulphide.   The presence of these sodium salts is then detected by inorganic qualitative methods.

(iii) **Phosphorus.**   The compound is heated with fusion mixture, whereby the phosphorus is converted into metallic phosphate, which is then detected by the usual inorganic tests.

(iv) **Metals.**   When organic compounds containing metals are strongly heated, the organic part usually burns away, leaving behind a residue.   This residue is usually the oxide of the metal, but in certain cases it may be the free metal, *e.g.*, silver, or the carbonate, *e.g.*, sodium carbonate.

As a rule, no attempt is made to carry out any test for oxygen ; its presence is usually inferred from the chemical properties of the compound.

The non-metallic elements which occur in *natural* organic compounds, in order of decreasing occurrence, are hydrogen, oxygen, nitrogen, sulphur, phosphorus, iodine, bromine and chlorine.   Halogen compounds are essentially synthetic compounds, and are not found to any extent naturally.   One important exception is thyroxin, which

contains iodine. In addition to these non-metallic elements, various metallic elements occur in combination with natural organic compounds, *e.g.*, sodium, potassium, calcium, iron, magnesium, copper.

(3) **Quantitative analysis.** The methods used in the determination of the composition by weight of an organic compound are based on simple principles.

(i) **Carbon and hydrogen** are estimated by burning a known weight of the substance in a current of dry oxygen, and weighing the carbon dioxide and water formed. If elements (non-metallic) other than carbon, hydrogen and oxygen are present, special precautions must be taken to prevent their interfering with the estimation of the carbon and hydrogen.

(ii) **Nitrogen** may be estimated in several ways, but only two are commonly used.

(*a*) **Dumas' method.** This consists in oxidising the compound with copper oxide, and measuring the volume of nitrogen formed. This method is applicable to all organic compounds containing nitrogen.

(*b*) **Kjeldahl's method.** This depends on the fact that when organic compounds containing nitrogen are heated with concentrated sulphuric acid, the organic nitrogen is converted into ammonium sulphate. This method, however, has certain limitations.

(iii) **Halogens** may be estimated in several ways. One is the classical method of *Carius*. The substance is heated in a sealed tube with fuming nitric acid in the presence of silver nitrate. Silver halide is formed, and this is estimated gravimetrically.

A simpler method for *non-volatile* compounds is to fuse the substance with sodium peroxide in a nickel crucible, whereupon the halogen is converted into sodium halide, which is then estimated as before.

(iv) **Sulphur** may be estimated by the methods used for the halogens. In the Carius method for sulphur, no silver nitrate is used. Organic sulphur is converted into sulphuric acid (Carius method) or sodium sulphate (sodium peroxide fusion). In both cases the sulphate is precipitated as barium sulphate and weighed.

(v) **Phosphorus** may be estimated by heating the compound with fusion mixture and weighing the phosphate as magnesium pyrophosphate.

The Carius determination (no silver nitrate used, *cf.* sulphur) invariably gives low results for phosphorus. Olivier (1940) found that exact results were obtained by heating the organic compound mixed with calcium oxide in a stream of oxygen. The phosphate was then estimated as above.

(vi) **Oxygen** is usually estimated by difference. All direct methods are still not completely satisfactory, but recently Aluise and co-workers (1947) claim to have evolved a satisfactory technique. The organic compound is subjected to pyrolysis in a stream of nitrogen, and all the oxygen in the pyrolysis products is converted into carbon monoxide by passage over carbon heated at 1120°. The carbon monoxide is then passed over iodine pentoxide, and the iodine liberated is estimated titrimetrically.

Quantitative analysis falls into three groups according to the amount of material used for the estimation :

(i) **Macro-methods** which require about 0·1–0·5 g. of material (actual amount depends on the element being estimated).

(ii) **Semi-micro methods** which require 20–50 mg. of material.

(iii) **Micro-methods** which require 3–5 mg. of material.

Nowadays the tendency is to use method (ii) or (iii). Although all the methods are simple in theory, their successful application (particularly when using micro- or semi-micro-methods) requires a great deal of technical skill. These methods have become standardised, and are described in detail in many books on practical organic chemistry.

(4) **Empirical formula determination.** The empirical formula indicates the *relative numbers* of each kind of atom in the molecule, and is calculated from the percentage composition of the compound.

(5) **Molecular weight determination.** The molecular formula—this gives the *actual* number of atoms of each kind in the molecule—is obtained by multiplying the empirical formula by some whole number which is obtained from consideration of the molecular weight of the compound. In many cases this whole number is *one*.

The methods used for the determination of molecular weights fall into two main groups: physical and chemical. The standard physical methods are the determination of: (i) vapour density; (ii) elevation of boiling point: (iii) depression of freezing point. These methods are described fully in text-books of physical chemistry. In addition to these standard methods, which are used mainly for relatively simple molecules, there are also other physical methods used for compounds having high molecular weights, *e.g.*, rate of diffusion, rate of sedimentation, viscosity of the solution, osmotic pressure, etc. (see p. 399).

The chemical methods, since they are only useful in organic work, will be here described in detail.

(i) **Molecular weights of organic acids (method of silver salt).** If the basicity of the acid is known, then the molecular weight of that acid may be determined from the analysis of its silver salt. The silver salt is chosen because: (*a*) Most silver salts are insoluble in water, and hence they are readily prepared. (*b*) Most silver salts are anhydrous; this is a definite advantage, since it does not introduce a possible source of error (*i.e.*, the determination of water of crystallisation). (*c*) All silver salts are readily decomposed on ignition, leaving a residue of metallic silver.

The method of calculation is shown in the following example : 0·701 g. of the silver salt of a dibasic acid on ignition yielded 0·497 g. of metallic silver. Calculate the M.Wt. of the acid, given that the A.Wt. of silver is 108.

Since the acid is dibasic, its molecule can be represented by the formula H_2A, where A is that part of the molecule other than replaceable hydrogen atoms. Hence the silver salt will be Ag_2A, *i.e.*, one gram molecule of it contains 216 g. of silver.

There is 0·497 g. silver in 0·701 g. of Ag_2A

$\therefore$ there is 216 g. silver in $\dfrac{0·701 \times 216}{0·497}$ g. of Ag_2A = 304·7 g.

i.e., the M.Wt. of Ag_2A is 304·7.

$\therefore$ the M.Wt. of acid H_2A is $(Ag_2A - 2Ag + 2H) = (304·7 - 216 + 2) = 90·7$.

(ii) **Molecular weights of organic bases (method of chloroplatinate).** Organic bases combine with chloroplatinic acid, H_2PtCl_6, to form insoluble, anhydrous chloroplatinates (platinichlorides) which, on ignition, leave a residue of metallic platinum. Let B represent one molecule of the base. If it is a " monoacid " base, the formula of its chloroplatinate will be $B_2H_2PtCl_6$; if a " diacid " base, BH_2PtCl_6.

EXAMPLE. 0·800 g. of the chloroplatinate of a " monoacid " base on ignition gave 0·262 g. of platinum. Calculate the M.Wt. of the base, given that the A.Wt. of platinum is 195.

Since the base is " monoacid ", the formula of its chloroplatinate will be $B_2H_2PtCl_6$, *i.e.*, one gram molecule of the chloroplatinate contains 195 g. of platinum.

There is 0·262 g. of platinum in 0·800 g. of $B_2H_2PtCl_6$.

∴ there is 195 g. of platinum $\dfrac{0\cdot800 \times 195}{0\cdot262} = 595\cdot4$ g. of $B_2H_2PtCl_6$.

i.e., the M.Wt. of $B_2H_2PtCl_6$ is 595·4.

∴ the M.Wt. of B is $\dfrac{B_2H_2PtCl_6 - H_2PtCl_6}{2} = \dfrac{595\cdot4 - (2 + 195 + 213)}{2} = 92\cdot7$.

(iii) The *molecular formula* of any *gaseous hydrocarbon* (compound containing carbon and hydrogen only) may be determined by exploding a measured volume of the gas with a measured excess of oxygen, in a eudiometer tube.

EXAMPLE. 10 ml. of a gaseous hydrocarbon was mixed with 80 ml. of oxygen and the mixture exploded. 70 ml. of gas remained (after cooling to room temperature), and this was reduced to 50 ml. (of oxygen) after treatment with potassium hydroxide solution. What is the formula of the hydrocarbon?
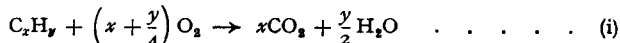There are two ways of solving this problem :

(*a*) $$C + O_2 \rightarrow CO_2$$

Thus one atom of carbon requires one molecule of oxygen.

$$2H_2 + O_2 \rightarrow 2H_2O.$$
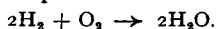
Thus one atom of hydrogen requires $\frac{1}{4}$ molecule of oxygen. Let the formula of the hydrocarbon be C_xH_y. Then x molecules of oxygen will be required to burn the carbon to carbon dioxide, and $\dfrac{y}{4}$ molecules of oxygen to burn the hydrogen to water. Thus we have

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad \cdots \cdots \text{(i)}$$

From Avogadro's law, it follows that

1 vol. of $C_xH_y + \left(x + \dfrac{y}{4}\right)$ vol. of $O_2 \rightarrow x$ vol. $CO_2 + \dfrac{y}{2}$ vol. H_2O (as steam) (ii)
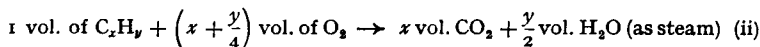
Since measurements of volume are carried out at room temperature, the water will be present as liquid, the volume of which may be ignored. Therefore, contraction after sparking $= \left(1 + x + \dfrac{y}{4}\right) - x = \left(1 + \dfrac{y}{4}\right)$ vol.

After treatment with potassium hydroxide solution, the contraction will be x vol. (*i.e.*, vol. of CO_2).

From the figures of the experiment, we have

First contraction $= 90 - 70 = 20$ ml.
Second contraction $= 70 - 50 = 20$ ml.

∴ since 10 ml. of C_xH_y is to be taken as 1 vol. (from equation ii), then $1 + \dfrac{y}{4} = 2$.

∴ $y = 4$ and $x = 2$.

Hence the hydrocarbon is C_2H_4.

(*b*) Total amount of oxygen used $= 80 - 50 = 30$ ml.

Of this, 20 ml. was required for burning the carbon (vol. of CO_2 is equal to vol. of O_2 used). Hence 10 ml. was required for the hydrogen which gives 20 ml. of steam.

∴ 10 ml. $C_xH_y + 30$ ml. $O_2 \rightarrow 20$ ml. $CO_2 + 20$ ml. H_2O (steam).

∴ from Avogadro's law

$$C_xH_y + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
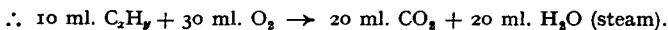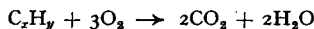
∴ $x = 2$, $y = 4$; and the hydrocarbon is C_2H_4.

(6) **Determination of structure**, *i.e.*, the manner in which the atoms are arranged in the molecule. The usual procedure for elucidating the structure of an unknown compound is to make a detailed study of its chemical reactions. This procedure is known as the *analytical method*, and includes breaking down (*degrading*) the compound into smaller molecules of *known* structure.

In addition to the purely chemical means, there are also various physical properties which are used to elucidate structure, *e.g.*:

(i) *Dipole moment.* This gives information on the spatial arrangement of atoms in a molecule, and so offers a means of distinguishing between alternative arrangements (see, *e.g.*, p. 367).

(ii) *Refractive index.* This may be used to distinguish between two types of structure, *e.g.*, between a keto and an enol form (p. 180).

(iii) *Parachor.* This has been used to distinguish between alternative structures.

(iv) *X-Ray analysis.* This offers a means of studying the arrangement of atoms in crystalline solids. Since most organic compounds are complex from the point of view of structure, X-ray analysis has mainly been used to " round off " information obtained by purely chemical means. Bond lengths may be measured by X-ray analysis, and deviations from " normal " values give information on structure.

(v) *Electron diffraction.* This has been used in the same way as X-ray analysis, but is applicable to gases, liquids and solids.

(vi) *Absorption spectra.* All organic compounds absorb light, which may be in one or more of the following regions : infra-red, visible or ultra-violet. Many bands are associated with particular groups, and it is therefore possible to ascertain the presence of these various groups in a new compound. In general, compounds possessing similar structures show similar absorption spectra. Hence the structure of a new compound may be elucidated by comparing its absorption spectrum with known spectra.

The *Raman effect* also is characteristic of a particular group, and has been widely used to ascertain the nature of the groups present in a compound.

When sufficient evidence has been accumulated, a tentative structure which best fits the facts is accepted. Sometimes two (or even more) structures fit the facts almost equally well, and it has been shown in certain cases that the compound exists in both forms which are in equilibrium. This phenomenon is known as *tautomerism.* Where tautomerism has not been shown to be present, one must accept (with reserve) the structure that has been chosen (see also next section).

(7) **Synthesis of the compound.** The term *synthesis* means the building up of a compound, step by step, from a simpler substance of *known* structure. The term *complete synthesis* means the building up of a compound, step by step, *starting from its elements* (and any others that may be necessary). In either case (synthesis or complete synthesis), *the structure of each intermediate compound is taken as proved by its synthesis from the compound that preceded it.*

The synthesis of a compound is necessary to establish its structure beyond doubt. There is always the possibility of one or more steps not proceeding " according to plan ". Hence the larger the number of syntheses of a compound by *different* routes, the more reliable will be the structure assigned to that compound.

STRUCTURAL FORMULÆ AND ISOMERISM

In 1857, Kekulé postulated the *constant* quadrivalency (tetravalency) of carbon. From 1900 onwards, however, compounds containing *tervalent* carbon have been prepared, and their number is increasing rapidly. These compounds usually require special methods of preparation, and many have a very short life (see text). Since their properties are different from those compounds containing quadrivalent carbon, they are fairly easily recognised. Hence, unless there is definite evidence to the contrary, carbon is always assumed to be quadrivalent.

If " valency units " or " valency bonds " (see Ch. II) are represented by lines, then the number of lines drawn from the symbol shows the valency of that atom, *e.g.*,

$$-\overset{|}{\underset{|}{C}}-; \quad -O-; \quad -\overset{|}{N}-; \quad H-$$
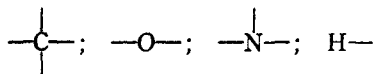
The molecular formula shows the number of each kind of atom present in the molecule, but does not indicate their arrangement. In organic chemistry there are many cases where a given formula represents two or more compounds that differ in physical and chemical properties, *e.g.*, there are at least seven compounds having the same molecular formula $C_4H_{10}O$. Such compounds, having the same molecular formula, but differing in physical and chemical properties, are known as *isomers* or *isomerides*, the phenomenon itself being known as *isomerism*. The existence of isomerism may be explained by assuming that the atoms are arranged in a definite manner in a molecule, and that there is a different arrangement in each isomer, *i.e.*, the isomers differ in *structure* or *constitution*. This type of isomerism is known as *structural isomerism*.

Obviously, then, from what has been said above, it is always desirable to show the arrangement (if known) of the atoms in the molecule, and this is done by means of *structural formulæ* or *bond-diagrams*; *e.g.*, the molecular

formula of ethanol is C_2H_6O; its structural formula is

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-H.$$

So far nothing has been said about the *spatial* disposition of the four valencies of carbon. Later (Ch. II) it will be shown that when carbon is joined to four univalent atoms or groups, the four valencies are directed towards the four corners of a tetrahedron. Thus the above plane-structural formula does not show the disposition of the atoms in space; a three-dimensional formula is necessary for this. Usually the plane-formula is satisfactory.

A structural formula is really a short-hand description of the properties of the compound. Hence the study of organic chemistry is facilitated by mastering the structural formula of every compound the reader meets.

SATURATED AND UNSATURATED COMPOUNDS

If, in an organic compound containing two or more carbon atoms, there are only *single* bonds linking any two adjacent carbon atoms, then that compound is said to be *saturated*, *e.g.*, ethane, C_2H_6 or

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H;$$

normal propanol, C_3H_8O or

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

acetaldehyde, C_2H_4O or

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=O.$$

On the other hand, if the compound contains at least one pair of adjacent carbon atoms linked by a *multiple* bond, then that compound is said to be *unsaturated*, *e.g.*, ethylene, C_2H_4 or

$$\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}.$$

This compound contains a *double* bond. Acetylene, C_2H_2 or $H-C{\equiv}C-H$; this contains a *triple* bond. Acraldehyde, C_3H_4O or

$$\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}=O;$$

this contains a double bond. *The double*