

## CHAPTER I 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 weakened the distinction between organic and inorganic compounds, and this distinction was completely ended with the synthesis of acetic acid from its elements by Kolbe in 1845, and the synthesis of methane by Berthelot in 1856. A common belief appears to be that Wöhler's synthesis had little effect on the vital-force theory because it did not start with the elements. Wöhler had prepared his ammonium cyanate from ammonia and cyanic acid, both of which were of animal origin. Partington (1960), however, has pointed out that Priestley (1781) had obtained ammonia by reduction of nitric acid, which was later synthesised from its elements by Cavendish (1785). Also, potassium cyanide was obtained by Scheele (1783) by passing nitrogen over a strongly heated mixture of potassium carbonate and carbon, and since one form of carbon used was graphite, this reaction was therefore carried out with inorganic materials. Since potassium cyanide is readily converted into potassium cyanate, Wöhler's synthesis is one which starts from the elements.

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. Chromatography offers a means of concentrating a product that occurs naturally in great dilution, and is an extremely valuable method for the separation, isolation, purification and identification of the constituents of a mixture.

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. Some important exceptions are chloramphenicol (chlorine), Tyrian Purple (bromine) and thyroxine (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  $1120^{\circ}$ . 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. Improvements and new methods for analysis, however, are always being published; e.g., chlorine and sulphur may be determined by wrapping the sample of the compound in filter paper, igniting and lowering it into a flask filled with oxygen. The acid gases are absorbed in hydrogen peroxide; the sulphuric acid formed is titrated with standard alkali, and the chloride is determined by titrating the neutralised solution with mercuric nitrate (Mikl *et al.*, 1953). Fluorine, chlorine and nitrogen may be determined by decomposition in a nickel bomb (Brown *et al.*, 1955).

(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.

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  $\text{Ag}_2\text{A}$ .

$\therefore$  there is 216 g. silver in  $\frac{0.701 \times 216}{0.497}$  g. of  $\text{Ag}_2\text{A} = 304.7$  g.

*i.e.*, the M.Wt. of  $\text{Ag}_2\text{A}$  is 304.7.

$\therefore$  the M.Wt. of acid  $\text{H}_2\text{A}$  is  $(\text{Ag}_2\text{A} - 2\text{Ag} + 2\text{H}) = (304.7 - 216 + 2) = 90.7$ .

(ii) **Molecular weights of organic bases (method of chloroplatinate).** Organic bases combine with chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , 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  $\text{B}_2\text{H}_2\text{PtCl}_6$ ; if a "diacid" base,  $\text{BH}_2\text{PtCl}_6$ .

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  $\text{B}_2\text{H}_2\text{PtCl}_6$ , *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  $\text{B}_2\text{H}_2\text{PtCl}_6$ .

$\therefore$  there is 195 g. of platinum in  $\frac{0.800 \times 195}{0.262} = 595.4$  g. of  $\text{B}_2\text{H}_2\text{PtCl}_6$ .

*i.e.*, the M.Wt. of  $\text{B}_2\text{H}_2\text{PtCl}_6$  is 595.4.

$\therefore$  the M.Wt. of B is

$$\frac{\text{B}_2\text{H}_2\text{PtCl}_6 - \text{H}_2\text{PtCl}_6}{2} = \frac{595.4 - (2 + 195 + 213)}{2} = 92.7.$$

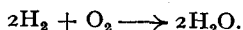
(iii) The *molecular formula* of any gaseous hydrocarbon (compound containing carbon and hydrogen only) may be determined by exploding a measured volume of the gas with a measured excess of oxygen, in a eudiometer tube.

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?

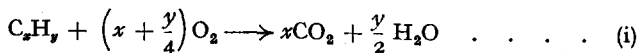
There are two ways of solving this problem:



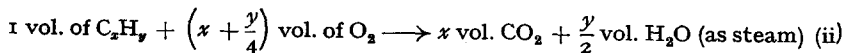
Thus one atom of carbon requires one molecule of oxygen.



Thus one atom of hydrogen requires  $\frac{1}{4}$  molecule of oxygen. Let the formula of the hydrocarbon be  $\text{C}_x\text{H}_y$ . Then  $x$  molecules of oxygen will be required to burn the carbon to carbon dioxide, and  $\frac{y}{4}$  molecules of oxygen to burn the hydrogen to water. Thus we have



From Avogadro's law, it follows that



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 =  $\left(1 + x + \frac{y}{4}\right) - x = \left(1 + \frac{y}{4}\right)$  vol.

After treatment with potassium hydroxide solution, the contraction will be vol. (*i.e.*, vol. of  $\text{CO}_2$ ).

From the figures of the experiment, we have

$$\text{First contraction} = 90 - 70 = 20 \text{ ml.}$$

$$\text{Second contraction} = 70 - 50 = 20 \text{ ml.}$$

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

∴  $y = 4$  and  $x = 2$ .

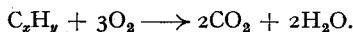
Hence the hydrocarbon is  $C_2H_4$ .

(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.  $C_2H_4 + 30$  ml.  $O_2 \longrightarrow 20$  ml.  $CO_2 + 20$  ml.  $H_2O$  (steam).

∴ from Avogadro's law



∴  $x = 2, y = 4$ ; 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.

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

(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, but it may also be used for liquids and gases. 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, and is applicable to gases, liquid and solids. It is, however, usually confined to gases or compounds in the vapour state.

(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.

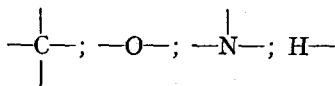
The term *complete synthesis* means the building up of a compound, step by step, *starting from its elements* (and any others that may be necessary). In either case (synthesis or complete synthesis), *the structure of each intermediate compound is taken as proved by its synthesis from the compound that 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. More recently, compounds containing bivalent carbon (*carbenes*) are believed to be formed as intermediates during certain reactions. 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.*,



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  $\text{C}_4\text{H}_{10}\text{O}$ . 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  $\text{C}_2\text{H}_6\text{O}$ ; its structural formula is

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

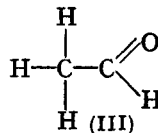
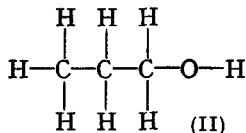
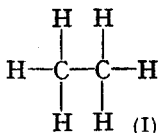
So far nothing has been said about the *spatial* disposition of the four valencies of carbon. Later (Ch. II) it will be shown that when carbon is joined to four univalent atoms or groups, the four valencies are directed towards the four corners of a tetrahedron. Thus the above plane-structural

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. Since the actual *spatial* arrangements of a given structure may differ, this gives rise to isomerism of the type known as *stereoisomerism*. *Stereoisomers* have different *configurations*, *i.e.*, the spatial arrangements are different but not their structures (see p. 399).

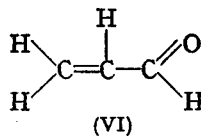
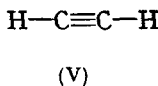
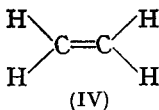
A structural formula is really a short-hand description of the properties of the compound. Hence the study of organic chemistry is facilitated by mastering the structural formula of every compound the reader meets. An organic molecule, however, is only completely described when the following facts are known: *structure* or *constitution* (this includes a knowledge of the electron distribution; see resonance, p. 17), *configuration* (p. 399), and *conformation* (p. 488).

#### 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,  $C_2H_6$  (I), *normal* propanol,  $C_3H_8O$  (II), acetaldehyde,  $C_2H_4O$  (III).



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,  $C_2H_4$  (IV); this compound contains a *double* bond. Acetylene,  $C_2H_2$  (V); this contains a *triple* bond. Acetaldehyde,  $C_2H_4O$  (VI); this contains a double bond. *The double bond between the carbon and oxygen atoms is not a sign of unsaturation (cf. acetaldehyde above).*



#### CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds are classified into three major groups:

- (1) (a) **Aliphatic, open-chain, or acyclic** compounds.
- (b) **Alicyclic** compounds. These are **carbocyclic** or **ring** compounds which resemble aliphatic compounds in many ways.
- (2) **Aromatic** compounds. These are carbocyclic or ring compounds *containing at least one benzene ring* (see also p. 509).
- (3) **Heterocyclic** compounds. These are cyclic (ring) compounds containing other elements besides carbon in the ring. In a few cases *no* carbon atom is in the ring.

#### READING REFERENCES

- Partington, *A Short History of Chemistry*, Macmillan (1957, 3rd ed.). Ch. X. The Beginnings of Organic Chemistry.
- Schorlemmer, *The Rise and Development of Organic Chemistry*, Macmillan (1894).



- Japp, Kekulé Memorial Lecture, *J.C.S.*, 1898, 73, 97.
- Mann and Saunders, *Practical Organic Chemistry*, Longmans, Green (1960, 4th ed.).  
Part IV. Quantitative Analysis.
- Belcher and Godbert, *Semi-Micro Quantitative Organic Analysis*, Longmans, Green (1954, 2nd ed.).
- Pregl, *Quantitative Organic Microanalysis*, Churchill (1937).
- Vogel, *Practical Organic Chemistry*, Longmans, Green (1956, 3rd ed.), Ch. 12. Semi-micro Technique.
- Ann. Reports (Chem. Soc.)*, 1955, 52, 353. Classical Organic Analysis.
- Ingram, The Rapid Micro-combustion Procedure, *Chem. and Ind.*, 1956, 103.

## CHAPTER II

### STRUCTURE OF THE ATOM

ACCORDING to modern theory, an atom consists of a *nucleus* which contains *protons* and *neutrons*, and which is surrounded by *electrons*. The mass of a proton is almost the same as that of a neutron, but whereas the proton carries a unit of *positive* charge, the neutron is electrically *neutral*. The electron has about  $\frac{1}{1850}$ th of the mass of a proton, and carries a unit of *negative* charge. The electrons are arranged in shells around the nucleus, each shell being able to contain up to a maximum number of electrons, this maximum depending on the number of the shell,  $n$ .  $n$  is known as the *principal quantum number*, and indicates the main energy level of the electrons in that shell.  $n$  has *whole* number values, 1, 2, 3, 4 . . . , the shells corresponding to which are also denoted by the letters *K, L, M, N* . . . respectively. In every principal quantum shell there are  $n$  energy sublevels, and these are indicated by  $l$ , the *orbital quantum number* (also known as the *azimuthal* or *serial* quantum number). Just as the principal quantum number  $n$  can have values 1, 2, 3 . . . , so can  $l$  have values 0, 1, 2, 3 . . . ,  $n - 1$ . The energy state corresponding to  $l = 0$  is called the *s* state;  $l = 1$ , the *p* state;  $l = 2$ , the *d* state; etc. As we shall see later (p. 23), these *s, p* and *d* states are subdivided into a number of *orbitals*. The total number of orbitals that a principal quantum shell can contain is given by  $n^2$ . Thus, when the principal quantum number is 1 (*i.e.*, the first or *K* shell), then  $l = 0$ , *i.e.*, there is a single orbital in this *K* shell and is of the *s* type and is known as the *1s* orbital. When  $n = 2$  (*i.e.*, the second or *L* shell), then  $l = 0$  or 1. This means there are *two* energy sublevels in the *L* shell. As pointed out above, the total number of orbitals in a given quantum shell is equal to  $n^2$ . Thus, when  $n = 2$ , there are four possible orbitals. When  $l = 0$ , this corresponds to the *2s* orbital. When  $l = 1$ , then there are *three equivalent* orbitals; these are the three *2p* orbitals. When  $n = 3$  (*i.e.*, the third or *M* shell), then the total number of possible orbitals is 9 ( $3^2$ ). These correspond to one *3s* orbital ( $l = 0$ ), three *3p* orbitals ( $l = 1$ ) and five *3d* orbitals ( $l = 2$ ). The existence of one *s* level, three *p*, five *d* and seven *f* levels of energy was used to explain the existence of spectral lines observed in the spectra of atoms and molecules. It should also be noted that the farther an electron is from the nucleus, the greater is its potential energy. Owing to the phenomenon of *penetration* of orbitals, *i.e.*, outer electrons can penetrate into the shell of inner electrons, the energy level of an electron is thus not completely determined by its principal quantum number, but also depends on the orbital quantum number (*i.e.*, on the *shape* of the orbital). Thus there is the following order of increasing energy: *1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p* . . . (see also p. 24).

In addition to the energy levels of an electron described by quantum numbers  $n$  and  $l$ , electrons have spin about their axis, some spinning in one direction and others in the opposite direction. This is indicated by the *spin quantum number* ( $s$ ), and can have values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Finally, an electron also has a *magnetic quantum number* ( $m$ ), and this gives the allowed orientations of the orbitals in an external magnetic field. Thus an electron is described by *four* quantum numbers,  $n, l, s$  and  $m$ .

By the fundamental *Pauli Exclusion Principle* (1925), no two electrons, in any system, can be assigned the same set of four quantum numbers. Hence there can be only *two* electrons in any one orbital, and these must be differentiated from each other by their spins, which *must* be *antiparallel*, *i.e.*, in the

opposite sense. Such electrons are said to be *paired*, and a pair of electrons with antiparallel spins in the same orbital is represented by the symbol  $\downarrow\uparrow$ . Since a moving charge is accompanied by a magnetic field, a spinning electron behaves as a small bar-magnet, and consequently two paired electrons will give a zero resultant magnetic field.

The hydrogen atom consists of one proton and one electron. When the hydrogen atom is in the "ground" state, *i.e.*, the state of lowest energy, its electron will be in the lowest energy level, *i.e.*, the 1s level, and is represented by (1s). When hydrogen is in an "excited" state, its electron will occupy a higher energy level, the actual level depending on the amount of "excitation".

Helium has two electrons; hence its electron configuration in the ground state is represented as (1s)<sup>2</sup>. Lithium has three electrons. Since the maximum number of electrons in the *K* shell ( $n = 1, l = 0$ ) is two, the third electron must start the *L* shell ( $n = 2, l = 0, 1$ ). Electrons occupy lowest energy levels first. Thus this third electron occupies the 2s orbital, and not the 2p, because the 2p is a higher energy level than the 2s. Hence the electron configuration of lithium is (1s)<sup>2</sup>(2s). Thus the *K* shell is filled first. Then the electrons enter the *L* shell until that is filled. In this shell the s level is filled before the p. In fitting electrons into shells containing orbitals of *equivalent* energy, Hund's rules are used to assign the electrons to their orbitals. These rules are: (i) electrons tend to avoid being in the same orbital as far as possible; (ii) two electrons, each singly occupying a given pair of *equivalent* orbitals, tend to have their spins parallel when the atom is in the ground state. Thus carbon, with six electrons, may be represented as (1s)<sup>2</sup>(2s)<sup>2</sup>(2p)<sup>2</sup>. The *K* shell is filled first; the *L* shell is filled next, the 2s orbital being doubly filled before a higher level is used; then singly two of the 2p orbitals. Nitrogen, with seven electrons, is (1s)<sup>2</sup>(2s)<sup>2</sup>(2p)<sup>3</sup>: all three 2p orbitals each contain one electron. Oxygen, with eight electrons, is (1s)<sup>2</sup>(2s)<sup>2</sup>(2p)<sup>4</sup>: here one of the 2p orbitals is doubly filled.

#### THE ELECTRONIC THEORY OF VALENCY

The electronic theory of valency starts with the assumption that valency involves the electrons in the outer shells: in some cases only those in the highest sublevel in the outermost shell; in other cases those in the highest and penultimate sublevels, even though the penultimate sublevel may be in a lower quantum shell. Lewis (1916) assumed that the electron configuration in the rare gases was particularly stable (since these gases are chemically inert), and that chemical combination between atoms took place by achieving this configuration. The outermost shell of the rare gases always contains an *octet* of two s and six p electrons. Since both the s and p sublevels are completely filled, the octet will be a stable configuration. In the case of helium, however, an octet is impossible; here the *stable* arrangement is the *duplet*, the two 1s electrons of which completely fill the first quantum shell.

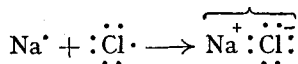
The octet rule applies only to atoms with 2s and 2p electrons, *i.e.*, to elements in the second period (Li—F). With the other elements, *d* orbitals may also be used in bond formation, and hence higher covalencies (*i.e.*, expansions beyond an octet) are possible, *e.g.*, PBr<sub>5</sub> (10 electrons), SF<sub>6</sub> (12 electrons) and IF<sub>7</sub> (14 electrons). Since elements in period 2 have only 2s and 2p orbitals, the maximum covalency they can exhibit is 4.

Lewis also suggested that there was a definite tendency for electrons in a molecule to form pairs. This rule of 2, as we have seen, became established by the developments of quantum mechanics. There are few molecules that contain an odd number of valency electrons: where such *odd electron*

*molecules* do exist, unusual properties are found to be associated with them (see free radicals).

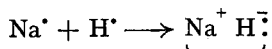
There are three general *extreme* types of chemical bonds: electrovalent, covalent and metallic bonds. In addition to these extreme types, there are also bonds of *intermediate* types.

1. **Electrovalency** is manifested by the *transfer* of electrons, and gives rise to the *ionic* bond. Consider sodium chloride. Sodium is  $(1s)^2(2s)^2(2p)^6(3s)^1$ ; chlorine is  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$ . Sodium has completed *K* and *L* shells, and is starting the *M* shell with one electron. This electron (the *3s* electron) is the valency electron of sodium. Chlorine has completed *K* and *L* shells, and has seven electrons in the *M* shell. These *M* electrons are the valency electrons of chlorine. If the sodium completely transfers its valency electron to the chlorine atom, then each atom will have eight electrons in its outermost shell, and this, as we have seen, is a stable arrangement. Since both atoms were originally electrically neutral, the sodium atom, in losing one electron, will now have a single positive charge, *i.e.*, the neutral atom has become a positive ion. Similarly, the neutral chlorine atom, in gaining one electron, has become a negative ion. In the sodium chloride crystal these ions are held together by electrostatic forces. If the symbol of an element is used to represent the nucleus of an atom and all the electrons other than the valency electrons, and dots are used to represent the valency electrons, then the combination of the sodium and chlorine atoms to form sodium chloride may be represented as follows:



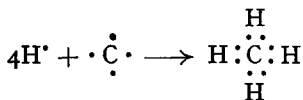
2. **Covalency.** This type of bonding involves a *sharing* of electrons in pairs, each atom contributing one electron to form a shared pair, each pair of electrons having their spins antiparallel. This method of completing an octet (or any of the other possible values) gives rise to the *covalent* bond.

**Hydrogen** is usually *univalent*: occasionally it is unielectrovalent, *e.g.*, in sodium hydride, hydrogen exists as the hydride anion, formed by accepting an electron from the sodium:



**Carbon** almost invariably forms covalent compounds. The electron configuration of carbon is  $(1s)^2(2s)^2(2p)^2$ . Since the two *2s* electrons are paired, it would appear that carbon is bivalent, only the two single *2p* electrons being involved in compound formation. As pointed out previously, carbon is almost always quadrivalent; thus the *2s* and *2p* electrons must be involved. Just how these four electrons readjust themselves to give quadrivalent carbon will be described later; at this stage we shall assume it done, and write quadrivalent carbon as  $\cdot\ddot{\text{C}}\cdot$ .

In methane the four hydrogen atoms each contribute one electron and the carbon atom four electrons towards the formation of four shared pairs:



Each hydrogen atom has its duplet (as in helium), and the carbon atom has an octet.

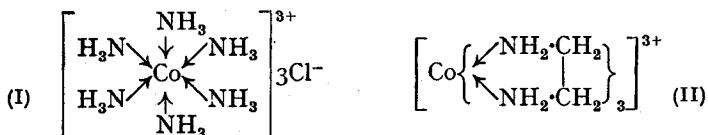


Once the co-ordinate bond has been formed, there may be no way of distinguishing it from any other covalent bond, but since one atom has supplied the pair of shared electrons, charges are produced in the molecule. When a covalent bond is formed, charges may also be produced in the molecule, giving rise to a dipole (*q.v.*). Hence the co-ordinate bond is effectively a covalent bond. The extent of the charge on each atom in a dative (or covalent) bond may be found as follows. Add the number of unshared electrons to one half of the shared electrons, and compare the result with the number of valency electrons of the neutral atom, *e.g.*, (i) methane,  $\text{CH}_4$ . Here there are 8 shared electrons;  $\frac{1}{2} \times 8 = 4 =$  number of electrons in the neutral carbon atom; therefore methane is uncharged. (ii)  $\text{H}_3\text{N} \rightarrow \text{BF}_3$ . For the nitrogen atom we have  $\frac{1}{2} \times 8 = 4$ ; but since the neutral nitrogen atom has 5 valency electrons, in the compound  $\text{H}_3\text{N} \rightarrow \text{BF}_3$  the nitrogen has a charge of +1. For boron we have  $\frac{1}{2} \times 8 = 4$ ; but since the neutral boron atom has 3 electrons, in this molecular compound the boron has a charge of -1.

Electrovalent compounds are good electrical conductors in the fused state or in solution. They are generally non-volatile, and are usually insoluble in hydrocarbons and allied solvents. Covalent compounds are non-electrical conductors, are generally volatile, and are usually soluble in hydrocarbons and allied solvents. Since the covalent bond is directional, *stereoisomerism* (space-isomerism) is possible (see p. 399). Co-ordinated compounds behave very much like covalent compounds, but they are usually less volatile than purely covalent compounds.

#### CHELATE COMPOUNDS

In the co-ordinated compounds discussed above, one donor atom has shared its lone pair with one acceptor atom. It is possible, however, for an acceptor atom to receive a number of shares in lone pairs, *e.g.*, cobalt-ammine chloride,  $[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$ . In this complex, the cobalt atom receives shares from six lone pairs, each ammonia molecule donating its nitrogen lone pair (I). Now let us consider ethylenediamine as the donating molecule. Its structure is  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ . In this molecule there

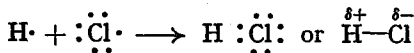


are two lone pairs, and it has been found that each nitrogen atom can act independently as a donor. Thus one ethylenediamine molecule can occupy two positions in the complex, producing the cation (II). This complex will, therefore, contain three rings. Compounds such as this are known as *chelate* compounds, *chelation* taking place when the donating molecule shares two lone pairs on different atoms within the molecule with a single acceptor atom, thereby producing a ring. Chelation may also take place *intramolecularly*, *i.e.*, between two atoms in the *same* molecule; but in these cases the chelate rings are formed, not by co-ordinate bonds, but by hydrogen bonds (see later).

#### DIPOLE MOMENTS

When a covalent bond is formed between two identical atoms, *e.g.*,  $\text{H}-\text{H}$ ,  $\text{Cl}-\text{Cl}$ , etc., the two electrons forming the covalent bond may be regarded as being symmetrically disposed between the two atoms. The centres of

gravity of the electrons and nuclei therefore coincide. With two *dissimilar* atoms the two electrons are no longer symmetrically disposed, because each atom has a different *electron-affinity* (*electronegativity*), *i.e.*, attraction for electrons. Chlorine has a much greater electron-affinity than hydrogen; so that when chlorine and hydrogen combine to form covalent hydrogen chloride, the electrons forming the covalent bond are displaced towards the chlorine atom without any separation of the nuclei:



The hydrogen atom will, therefore, be slightly positively charged, and the chlorine atom slightly negatively charged. Thus, owing to the greater electron-attracting power of the chlorine atom, the covalent bond in hydrogen chloride is characterised by the separation of small charges in the bond. A covalent bond such as this, in which one atom has a larger share of the electron-pair, is said to possess *partial ionic character*.

In analogy with a magnet, such a molecule is called a *dipole*, and the product of the electronic charge,  $e$ , and the distance  $d$ , between the charges (positive and negative centres) is called the *dipole moment*,  $\mu$ ; *i.e.*,  $\mu = e \times d$ .  $e$  is of the order of  $10^{-10}$  e.s.u.;  $d$ ,  $10^{-8}$  cm. Therefore  $\mu$  is of the order  $10^{-18}$  e.s.u., and this unit is known as the Debye (D), in honour of Debye, who did a large amount of work on dipole moments.

The dipole moment is a vector quantity, and its direction is often indicated by an arrow parallel to the line joining the points of charge, and pointing towards the negative end, *e.g.*,  $\overset{\rightarrow}{\text{H}-\text{Cl}}$ . The greater the value of the dipole moment, the greater is the *polarity* of the bond. The terms *polar* and *non-polar* are used to describe bonds, molecules and groups, and the reader is advised to make sure he appreciates how the terms are applied in each case under consideration.

The following points are useful in organic chemistry:

(i) In the bond  $\text{H}-\text{X}$ , where X is any atom other than hydrogen or carbon, the hydrogen atom is the positive end of the dipole, *i.e.*,  $\overset{\rightarrow}{\text{H}-\text{X}}$ .

(ii) In the bond  $\text{C}-\text{X}$ , where X is any atom other than carbon, the carbon atom is the positive end of the dipole, *i.e.*,  $\overset{\rightarrow}{\text{C}-\text{X}}$ . Earlier work appeared to show that in saturated compounds of carbon, the dipole for the  $\text{C}-\text{H}$  bond was  $\overset{\leftarrow}{\text{C}-\text{H}}$ . Work by Coulson (1942), however, indicates that the dipole is in the opposite direction, *i.e.*,  $\overset{\rightarrow}{\text{C}-\text{H}}$ , and that in methane the value is 0.30D. Both the direction and value, however, are not constant, but depend on the nature of the hybridisation (see p. 89).

(iii) When a molecule contains two or more polar bonds, the resultant dipole moment of the molecule is obtained by the vectorial addition of the constituent bond dipole moments (see also pp. 427, 513).

(iv) A symmetrical molecule is non-polar, although it may contain polar bonds.

#### ELECTRON DISPLACEMENTS IN A MOLECULE

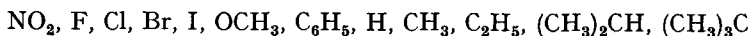
**1. Inductive effect.** Consider a carbon chain in which one terminal carbon atom is joined to a chlorine atom:  $-\text{C}_3-\text{C}_2-\text{C}_1-\text{Cl}$ . Chlorine has a greater electron-affinity than carbon; therefore the electron pair forming the covalent bond between the chlorine atom and  $\text{C}_1$  will be displaced towards the chlorine atom. This causes the chlorine atom to acquire a small negative charge, and  $\text{C}_1$  a small positive charge. Since  $\text{C}_1$  is positively charged, it will attract towards itself the electron pair forming the covalent

bond between  $C_1$  and  $C_2$ . This will cause  $C_2$  to acquire a small positive charge, but the charge will be smaller than that on  $C_1$  because the effect of the chlorine atom has been transmitted through  $C_1$  to  $C_2$ . Similarly,  $C_3$  acquires a positive charge which will be smaller than that on  $C_2$ . This type of electron displacement along a chain is known as the *inductive effect*; it is *permanent*, and decreases rapidly as the distance from the source increases. From the practical point of view, it may be ignored after the second carbon atom. It is important to note that the electron pairs, although permanently displaced, *remain in the same valency shells*.

This inductive effect is sometimes referred to as a *transmission effect*, since it takes place by a displacement of the intervening electrons in the molecule. There is also another effect possible, the *direct* or *field effect*, which results from the electrostatic interaction across space or through a solvent of two charged centres in the same molecule, *i.e.*, the direct effect takes place independently of the electronic system in the molecule (Ingold, 1934). Apparently it has not been possible to separate these two modes of inductive effect in practice.

The inductive effect may be represented in several ways. The following will be adopted in this book:  $-C \rightarrow -C \rightarrow -C \rightarrow -Cl$ .

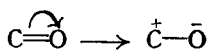
Inductive effects may be due to atoms or groups, and the following is the order of decreasing inductive effects:



For measurement of relative inductive effects, hydrogen is chosen as reference in the molecule  $CR_3-H$  as standard. If, when the H atom in this molecule is replaced by Z (an atom or group), the electron density in the  $CR_3$  part of the molecule is *less* in this part than in  $CR_3-H$ , then Z is said to have a  $-I$  effect (electron-attracting or electron-withdrawing). If the electron density in the  $CR_3$  part is *greater* than in  $CR_3-H$ , then Z is said to have a  $+I$  effect (electron-repelling or electron-releasing) *e.g.*, Br is  $-I$ ;  $C_2H_5$  is  $+I$ . This terminology is due to Ingold (1926); Robinson suggests the opposite signs for I, *i.e.*, Br is  $+I$ ;  $C_2H_5$ ,  $-I$ . Ingold's terminology will be used in this book.

2. **Electromeric effect.** This is a *temporary* effect involving the *complete transfer* of a shared pair of electrons to one or other atom joined by a multiple bond, *i.e.*, a double or triple bond. The electromeric effect is brought into play only at the requirements of the attacking reagent, and takes place almost instantaneously. Consider the following:  $C=O$  or  $C \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$ . At the moment of reaction the oxygen atom takes complete control of one of the shared electron pairs, the electronic structure becoming  $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}: \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$ . Since the carbon has lost its share in the electron pair, and the oxygen gained a share, the carbon acquires a positive charge and the oxygen a negative one. Removal of the attacking reagent causes the charged molecule to revert to its original electronic condition. It should be noted that the original condition of the molecule will have *small* charges on both the carbon and oxygen atoms (positive and negative, respectively), due to the inductive effect of the oxygen, which is more strongly electron-attracting than carbon. Another effect may also operate to give each atom a small charge (see resonance).

The electromeric effect is represented as follows:



The curved arrow shows the displacement of the shared electron pair, beginning at the position where the pair was originally, and ending where



the pair has migrated. It should be noted that the electromeric effect might have taken place:



However, this is most unlikely, since oxygen is strongly electron-attracting, and therefore "assists" the displacement towards itself, and "opposes" the displacement away from itself. This is an example of the electromeric and inductive effects aiding each other. It is possible, however, for them to oppose each other, and when they do so, the electromeric effect generally overcomes the inductive effect, but this happens only when the chain has conjugated double bonds (see *e.g.*, benzene).

The electromeric effect is represented by the symbol E, and is said to be +E when the displacement is *away* from the atom or group, and -E when *towards* the atom or group (*cf.* the I effect).

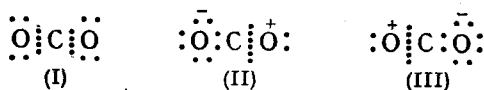
The displacement of the electron pair forming a covalent bond when a unit charge is brought up is a measure of the *polarisability* of that bond. It is not a permanent polarisation since, when the charge is removed, the electron displacement disappears.

**3. Mesomerism or Resonance.** The theory of mesomerism was developed on chemical grounds. It was found that no structural formula could satisfactorily explain all the properties of certain compounds, *e.g.*, benzene. This led to the idea that such compounds exist in a state which is some combination of two or more electronic structures, all of which seem equally capable of describing most of the properties of the compound, but none of describing *all* the properties. Ingold (1933) called this phenomenon *mesomerism* ("between the parts", *i.e.*, an intermediate structure). Heisenberg (1926), from quantum mechanics, supplied a theoretical background for mesomerism; he called it *resonance*, and this is the name which is widely used.

The chief conditions for resonance are:

- (i) The positions of the nuclei in each structure must be the same or nearly the same.
- (ii) The number of unpaired electrons in each structure must be the same.
- (iii) Each structure must have about the same internal energy, *i.e.*, the various structures have approximately the same stability.

Let us consider carbon dioxide as an example. The electronic structure of carbon dioxide may be represented by at least three possible electronic arrangements which satisfy the above conditions:



Structures (II) and (III) are identical *as a whole*, since both oxygen atoms are the same.\* Each structure, however, shows a given oxygen atom to be in a *different* state, *e.g.*, the oxygen atom on the left in (II) is negative, whereas in (III) it is positive. Although two (or more) of the electronic structures may be the same when the molecule is considered as a whole, each one must be treated as a separate individual which makes its own contribution to the resonance state. Structures (I), (II) and (III) are called the *resonating*, *unperturbed* or *canonical* structures of carbon dioxide, and carbon dioxide is said to be a *resonance hybrid* of these structures, or in the *mesomeric state*.

\* If the two oxygen atoms are not the same but one is isotope  $^{16}\text{O}$  and the other isotope  $^{18}\text{O}$ , then clearly structures (II) and (III) are different.

It is hoped that the following crude analogy will help the reader to grasp the concept of resonance. Most readers will be familiar with the rotating disc experiment that shows the composite nature of white light. When stationary, the disc is seen to be coloured with the seven colours of the rainbow. When rotating quickly, the disc appears to be white. The resonating structures of a resonance hybrid may be compared to the seven colours, and the actual state of the resonance hybrid to the "white"; *i.e.*, the resonating structures may be regarded as superimposed on one another, the final result being *one kind of molecule*. **In a resonance hybrid all the molecules are the same; a resonance hybrid cannot be expressed by any single structure.**

In a resonance hybrid the molecules have, to some extent, the properties of each resonating structure. The greater the contribution of any one structure, the more closely does the actual state approach to that structure. At the same time, however, a number of properties differ from those of any one structure. The observed heat of formation of carbon dioxide is greater than the calculated value by 31.6 kg. cal. In other words, carbon dioxide requires 31.6 kg. cal. more energy than expected to break it up into its elements, *i.e.*, carbon dioxide is more stable than anticipated on the structure  $O=C=O$ . How can this be explained? Arguments based on quantum mechanics show that a resonance hybrid would be more stable than any single resonating structure, *i.e.*, the internal energy of a resonance hybrid is less than that calculated for any one of the resonating structures. The difference between the heat of formation of the *actual* compound, *i.e.*, the *observed* value, and that of the resonating structure which has the *lowest* internal energy (obtained by *calculation*) is called the **resonance energy**. Thus the value of the resonance energy of any resonance hybrid is *not an absolute value*; it is a *relative* value, the resonating structure containing the least internal energy being chosen as the arbitrary standard for the resonance hybrid. The greater the resonance energy, the greater is the stabilisation due to resonance. The resonance energy is a maximum when the resonating structures have equal energy content, and the more resonating structures there are, the greater is the resonance energy. When the resonating structures are identical in energy content, and consequently the resonance energy is a maximum, the compound is said to be completely *degenerate*.

The resonance energy of a molecule is a property of the molecule in the ground state. Most measurements of resonance energies have been obtained from heats of combustion, but a few measurements have also been obtained from heats of hydrogenation; the latter method is more accurate than the former. The heat of combustion of the most stable classical structure (*i.e.*, the resonating structure with the lowest internal energy) is, as mentioned above, obtained by *calculation*. This presupposes that *accurate* values for bond-energies are known. If these values are *not* accurate, then one cannot expect to obtain accurate resonance energies. In practice, several different sets of bond-energies have been proposed, one set using bond-energies in isolation (*i.e.*, the bond between two atoms is assumed to be independent of other atoms in the molecule), and another set using bond-energies which depend on the environment (*i.e.*, takes into account other atoms in the molecule). Thus different resonance energies are usually obtained for any given molecule, and so, when these values are small (*i.e.*, the resonance energy is small), the value may be almost, if not completely, due to the use of inaccurate bond-energies and not actually due to stabilisation of the molecule by resonance.

Another property of the resonance hybrid which differs from that of any of the resonating structures is that of the bond length, *i.e.*, the distance between atoms joined by a covalent bond. The normal length of the car-

bonyl double bond ( $C=O$ ) in ketones is about 1.22 Å; the value found in carbon dioxide is 1.15 Å. For a given pair of atoms, the length of a single bond is greater than that of a double bond, which, in turn, is greater than that of a triple bond. Resonance, therefore, accounts for the carbonyl bond in carbon dioxide not being single, double or triple (see also butadiene, p. 87, and benzene, p. 507).

In a resonance hybrid, the electronic arrangement and bond lengths will be different from those of the resonating structures. Consequently the observed dipole moment may differ from that calculated for any one structure.

As we have seen above, in a resonance hybrid all the molecules have the same structure. A difficulty that arises with the resonance theory is the representation of a resonance hybrid. The molecules corresponding to the structures chosen as the resonating structures do not necessarily have an actual existence. Thus, if these resonating structures are fictitious, what fictitious structures are we to choose? The normal way of solving this problem is first to ascertain the structure of the molecule by the usual methods, and then describe it by means of the classical valency-bond formula. Let us consider again the case of carbon dioxide. The classical structure is (I) (see above). As we have also seen, it has been found that not all the properties of carbon dioxide are described by this classical formula. Thus the classical structure is an approximation, and it is in this sense that classical structures are fictitious. By *postulating* other electronic structures (II) and (III), wave functions can then also be obtained for these fictitious structures. By a linear combination of all three functions, a "structure" is obtained which describes the properties of carbon dioxide. This "structure" is called the resonance hybrid of the classical (I) and the two postulated electronic structures (II) and (III).

It is very important to note here that wave-mechanics offers a theoretical method of studying the electron distribution in a molecule, but starts with a knowledge of the relative positions of all the nuclei concerned, *i.e.*, with the "classical structure". Theoretically, it is possible to start from a molecular formula, and then solve the structure. The number of possibilities and mathematical difficulties, however, are far too great at present, and so it seems that the classical chemist, who arrives at the classical structures by classical methods, will still be "in business" for a long time to come. Since, however, by means of wave-mechanics one can calculate the density of electronic charge at all points in a molecule (of known classical structure), it is possible from this information to deduce charge distributions, bond lengths and bond angles, and consequently the size and shape of a molecule.

The question that now arises is: Starting with the classical structure, what other electronic structures are we justified in postulating? A very important point in this connection is that *resonance can occur only when all the atoms involved lie in the same plane (or nearly in the same plane)*. Thus any change in structure which prevents planarity will diminish or inhibit resonance. This phenomenon is known as *steric inhibition of resonance* (p. 688).

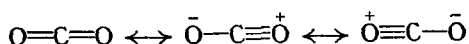
In practice, then, the conditions described above must be considered when choosing canonical structures. At the same time, the following observations will be a useful guide:

- (i) Elements of the first two rows never violate the octet rule (hydrogen, of course, can never have more than a duplet).
- (ii) The more stable a structure, then generally the larger will be its contribution to the resonance state. The stability of a molecule can be found from its bond energies. The bond energy is the amount of energy required

to dissociate a compound, say AB, in the gaseous state, into the neutral atoms A· and B·. Generally, the structure with the largest number of bonds is the most stable.

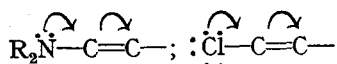
(iii) If the different resonating structures have the same number of bonds, but some structures are charged, then the charged molecules will be less stable than the uncharged. The high energy content of a charged molecule is due to the work put into the molecule to separate the charges, and the greater the distance of charge separation, the less stable is that structure. Even so, charged structures may make a considerable contribution to the resonance state, since resonance among a number of charged structures gives a resonance hybrid that is more stable than any one resonating structure.

The final problem is the method of representing a resonance hybrid. Various methods have been used, and the one used in this book is that introduced by Bury (1935). This consists of writing down the resonating structures with a double-headed arrow between each pair:

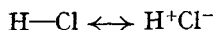


Inductive and resonance (mesomeric) effects are permanently operating in the "real" molecule; collectively they are known as the *polarisation effects*. On the other hand, there are also two temporary (time-variable) effects, the *electromeric effect* and the *inductomeric effect* (which operates by an inductive mechanism). Both of these are brought into play by the attacking reagent, and collectively they are known as the *polarisability effects*. Remick (1943) has suggested the use of subscripts *s* and *d* to represent the *static* (permanent) and *dynamic* (time-variable) effects. Thus the inductive effect may be represented by the symbol  $I_s$ , and the inductomeric effect by  $I_d$ . Since polarisability effects are brought into play only by the approach of the attacking reagent, they will therefore *aid* and never *inhibit* a reaction.

Strictly speaking, the term *resonance effect* (R) is not the same as the *mesomeric effect* (M). The mesomeric effect is a permanent polarisation, and the mechanism of electron transfer is the same as that in the electromeric effect, *i.e.*, the mesomeric effect is a permanent displacement of electron pairs which occurs in a system of the type  $Z-\text{C}=\text{C}$ ; *e.g.*,  $Z=\text{R}_2\text{N}$ ,  $\text{Cl}$ :



Thus the essential requirement for mesomerism is the presence of a *multiple* bond in the molecule. On the other hand, the resonance effect embraces *all* permanent electron displacements in the molecule in the ground state, *e.g.*, the hydrogen chloride molecule is a resonance hybrid of two resonating structures:



Since there is no multiple bond in this molecule, the mesomeric effect is not possible.

When the electronic displacement is *away* from the group the mesomeric (resonance) effect is said to be +M (+R), and when *towards* the group, -M (-R).

The mesomeric effect is particularly important in conjugated systems (p. 84), and the *combined* mesomeric and electromeric effects are known as the *conjugative effect*. This term is also used in the same sense as the resonance effect. Also, since this combined effect was first recognised in connection with tautomerism, it has also been called the *tautomeric effect* ( $\pm T$ ).

The possible polar influences of groups are shown in the following table:

Electronic mechanism	Polarisation effect (permanent)	Polarisability effect (temporary)
Inductive ( $\pm I$ )	Inductive (I or $I_s$ )	Inductomeric ( $I_d$ )
Conjugative (Tautomeric, $\pm T$ ; or Resonance, $\pm R$ )	Mesomeric (M) or Resonance (R)	Electromeric (E)
Fields in which operative	Physical properties. Reaction equilibria. Reaction rates.	— — Reaction rates only

As has been pointed out above, resonance describes *all* permanent electron displacements in the molecule in the ground state. It therefore follows that the I-effect can be described as due to resonance. Thus resonance is the combination of I- and M-effects. It is more convenient, however, from the point of view of the organic chemist, to consider a molecule with respect to its I-effect and "resonance" (mesomeric) effect separately. Hence from this point of view, resonance is the *additional permanent* electronic displacements to the I-effect, and it is customary to ignore the latter effect when discussing "resonance". In other words, resonance, in this context, is concerned only with the part of the molecule containing multiple bonds and is therefore, strictly speaking,  $\pi$ -electron resonance. This is the sense in which the term resonance will be used in this book.

**Effect of structure on reactivity.** The *type* of reaction of an organic compound is largely dependent on the nature of the functional group present (p. 48). It has been found that various structural changes, *e.g.*, the introduction of a given group into different positions in a molecule containing a given functional group, usually affect the rate of a given type of reaction and also the equilibrium position, and may even change the type of mechanism of the reaction. Much work has been done to try to correlate structure and reactivity (*i.e.*, rate of reaction), and as an outcome of this work, it appears that some sort of quantitative correlation can be made on the basis of consideration of independent contributions of inductive, resonance (mesomeric) and steric effects. When each effect has been assessed, then all three may be combined, and in this way there is obtained a relationship between structure and reactivity. In the text are discussed many cases of the effects on reaction rates and mechanism by polar (I and R) and steric effects.

Reactions in organic chemistry may be classified into the following main types: (i) substitution; (ii) replacement or displacement; (iii) addition; (iv) elimination; (v) isomerisation (rearrangement).

#### THE HYDROGEN BOND OR HYDROGEN BRIDGE

Compounds containing OH or NH groups often exhibit unexpected properties such as relatively high boiling points, and it was soon felt necessary to assume that the elements oxygen or nitrogen were linked by means of hydrogen, thereby producing the *hydrogen bond*. Detailed study has shown that the unexpected properties were exhibited only when the atoms participating in the bond had high electron-affinity—fluorine, oxygen and nitrogen (decreasing in this order), and to a less extent, chlorine and sulphur. Thus the hydrogen bond explained, for example, the existence of the  $\text{HF}_2^-$  ion, the association of hydroxylic compounds such as water, alcohols, etc., and the association of ammonia.

The exact nature of the hydrogen bond has been the subject of much discussion. Possibly a number of factors contribute, but it appears that the most important one is electrostatic. In bond  $Z-H$ , if  $Z$  has high electron-affinity, there will be a relatively large amount of polarity, *i.e.*, the state of affairs will be  $Z^{\delta-}-H^{\delta+}$ , where  $\delta+$  is relatively large. Since the hydrogen atom has a tiny volume, the H will exert a large electrostatic force and so can attract atoms with a relatively large  $\delta-$  charge, providing these atoms have a small atomic radius. Fluorine, oxygen and nitrogen are of this character. If the atom has a greater radius the electrostatic forces are weaker; thus chlorine, although it has about the same electron-affinity as nitrogen, forms very weak hydrogen bonds since its atomic radius is greater.

This theory of electrostatic union has much to support it. The hydrogen bond is very weak, and has more in common with the "van der Waals forces" (which are electrical in nature) than with anything else. Values obtained for the energy of the hydrogen bond are  $H-F\cdots H$ , 10 k.cal./mole;  $H-O\cdots H$ , 7;  $H-N\cdots H$ , 2.

Hydrogen bond formation *intramolecularly*, *i.e.*, involving one molecule only, gives rise to ring formation or chelation, and this usually when the formation of a 5-, 6- or 7-membered ring is possible. Hydrogen bonding *intermolecularly*, *i.e.*, between two or more molecules, gives rise to association. Many examples of hydrogen bonding will be found in the text, and this is represented by a dotted line between the hydrogen and other atom involved (as shown above).

Hydrogen bonding affects all physico-chemical properties such as m.p., b.p., solubility, spectra (infra-red and Raman shifts), etc., *e.g.*, association produces a higher boiling point than expected (*e.g.*, from the molecular weight of the compound). On the other hand, chelation usually produces a lower boiling point than expected, *e.g.*, a nitro-compound usually has a higher boiling point than its parent compound, but if chelation is possible in the nitro-compound, the boiling point is lowered (see, *e.g.*, nitrophenols, p. 626).

#### ATOMIC AND MOLECULAR ORBITALS

So far, we have discussed the structure of molecules in terms of valency bonds. There is an alternative method of investigating the structure of molecules, and to appreciate this approach—and to extend the other—it is necessary to consider the structure of matter from the point of view of wave-mechanics. Classical physics (*i.e.*, the laws of mechanics, etc.) is satisfactory when dealing with large masses. These laws are approximations, but deviations become significant only when dealing with very small particles such as electrons and nuclei. The behaviour of these small particles, however, may be satisfactorily studied by *wave (quantum) mechanics*. This uses the idea of the particle-wave duality of matter. It has already been pointed out that the electron may be regarded as a tiny mass carrying a negative charge. In 1923, de Broglie proposed that every moving particle has wave properties associated with it. This was first experimentally verified in the case of the electron (Davisson and Germer, 1927; G. P. Thomson, 1928). Thus an electron has a dual nature, particle and wave, but it behaves as one or the other according to the nature of the experiment; *it cannot at the same time behave as both*. According to wave-mechanics, a moving particle is represented by a wave function  $\psi$  such that  $\psi^2 dv$  is the *probability* of finding the particle in the element of volume  $dv$ . The greater the value of  $\psi^2$ , the greater is the probability of finding the electron in that volume  $dv$ . Theoretically,  $\psi$  has a finite value at a large distance (compared

with atomic dimensions) from the nucleus, but in practice there is very little probability of finding the electron beyond a distance of  $2-3\text{\AA}$ . It is therefore possible to map out regions or contours within which the probability of finding the electron is high, and outside which there is very little likelihood of finding the electron.

An alternative interpretation of the wave function  $\psi$  is to regard the electron as a cloud (*charge-cloud*), the density of the cloud at any point being proportional to  $\psi^2$ . Hence once again it is possible to draw contours within which almost all the electron charge is to be found. These regions (of probability or of density of charge-cloud) are known as *atomic orbitals* (A.O.s), and have characteristic shapes.

In 1926, Schrödinger developed the wave-equation, which connected the wave function  $\psi$  of an electron with its energy,  $E$ . This equation has an infinite number of solutions, but very few of these solutions describe the *known* behaviour of electrons. Thus only certain values for  $E$  are permissible, since certain conditions must be satisfied. The permitted solutions for  $\psi$  are called the *eigenfunctions*, and the corresponding values of  $E$  are called the *eigenvalues*. A number of eigenfunctions exist, the simplest being those which possess *spherical symmetry* ( $\psi_s$  function), and the next simplest being those which possess an *axis of symmetry* ( $\psi_p$  function). The eigenvalues (*i.e.*, the energy values) for the  $\psi_s$  functions are not, in general, the same as those for the  $\psi_p$  functions. Since  $\psi^2 dv$  measures the probability of finding the electron in the element of volume  $dv$ , we can therefore picture "probability regions" which will be generated by the expressions  $\psi_s^2$  and  $\psi_p^2$ . Such regions are those we have called *atomic orbitals*, and we can speak of the energy of an A.O. if we mean the eigenvalue (energy value) corresponding to that wave function  $\psi$ .

In addition to its wave function  $\psi$ , an electron also has spin. Two electrons can have the same wave function, *i.e.*, can occupy the same orbital *provided their spins are opposite* (Pauli exclusion principle). In this case the electrons are said to be paired.

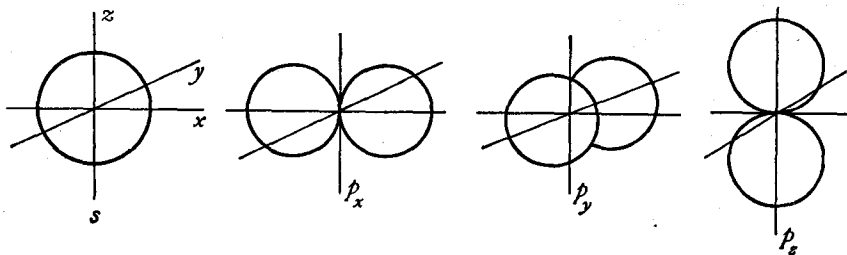


FIG. 2.1.

The various A.O.s are classified as  $s$ ,  $p$ ,  $d$ ,  $f$ , . . . orbitals. Only the  $s$  and  $p$  orbitals need concern us, and Fig. 1\* shows their shapes. The  $s$ -orbital is spherically symmetrical, which means that the region within which it is reasonable to expect to find the electron is a sphere having the nucleus as centre. The  $p$ -orbitals are dumb-bell in shape, and the two halves are separated by a *nodal plane*, over which the value of  $\psi$  is zero, *i.e.*, there is no likelihood of finding the electron in this plane. In these  $p$ -orbitals, the electron is confined to regions which have a marked directional character, each orbital having an axis at right angles to those of the other

\* Each diagram has been given two numbers, the first indicating the chapter, and the second the order in that chapter. Reference to a diagram in its *own* chapter will be indicated by the *second* number only.

two, and hence they are known as the  $p_x$ ,  $p_y$ ,  $p_z$  orbitals, respectively. These orbitals are entirely equivalent except for their directional property.

The order of orbital energies is  $1s < 2s < 2p < 3s < 3p < \dots$ . Since an electron must occupy some *particular* orbital, when the electron "jumps" from that orbital to another, it acquires the energy of the new orbital, absorbing or emitting the difference in a "discrete energy packet" or *quantum*. Not all transitions between different energy levels are allowable; a definite rule of selection exists, *e.g.*, permitted transitions are  $s \rightarrow p$ ,  $p \rightarrow s$  or  $d$ , etc.;  $s \rightarrow s$  is *not* permitted. When an electron absorbs a quantum of energy, it is driven into an (allowable) orbital of higher energy. The atom is then said to be "excited", and is more reactive. On returning to its normal orbital, the electron emits the quantum of energy at a definite wave-length, giving rise to a particular line in the emission spectrum (see p. 773). When all the electrons in an atom are in their normal orbitals, *i.e.*, orbitals of lowest energy, the atom is said to be in the "ground" state.

So far, we have dealt only with atoms, *i.e.*, with electrons associated with *one* nucleus. The wave-equations for molecules cannot be solved without making some approximations. Two types of approximations have been made, one set giving rise to the *valence-bond* method (V.B.); and the other set to the *molecular orbital* method (M.O.). The V.B. method—due mainly to the work of Heitler, London, Slater and Pauling—considers the molecule as being made up of atoms *with electrons in atomic orbitals on each atom*. Thus a molecule is treated as if it were composed of atoms which, to some extent, retain their individual character when linked to other atoms. The M.O. method—due mainly to the work of Hund, Lennard-Jones and Mulliken—treats a molecule in the same way as an atom, except that in the molecule an electron moves in the field of *more than one nucleus*, *i.e.*, *molecular orbitals* are *polycentric*. Thus each electron in a molecule is described by a certain wave function, the *molecular orbital*, for which contours can be drawn as for A.O.s, but differing in that the former are polycentric and the latter monocentric. In general, the greater the freedom (*i.e.*, the larger the region for movement) allowed to an electron, the lower will be its energy. Thus atoms combine to form a molecule because, owing to the overlap of the A.O.s when the atoms are brought together, the electrons acquire a greater freedom, and the energy of the system is lowered below that of the separate atoms. Energy would therefore have to be supplied to separate the atoms in the molecule, and the greater the amount of energy necessary, the stronger are the bonds formed between the various atoms.

Let us now consider the case of the hydrogen molecule. A hydrogen atom has one  $1s$  electron. When the bond is formed between two hydrogen atoms to form the hydrogen molecule, these two  $1s$  electrons become *paired* to form *molecular electrons*, *i.e.*, both occupy the same M.O., a state of affairs which is possible provided their spins are antiparallel. A very important principle for obtaining the M.O. is that the bond energy is greatest when the component A.O.s overlap one another as much as possible. To get the maximum amount of overlap of orbitals, the orbitals should be in the same plane. Thus the M.O. is considered as being a *linear combination of atomic orbitals with maximum overlap* (L.C.A.O.). Furthermore, according to L.C.A.O. theory, the binding energy is greater the more nearly equal are the energies of the component A.O.s. If these energies differ very much, then there will be no significant combination between the two atoms concerned.

Since the hydrogen molecule is composed of two identical atoms, the probability of finding both electrons simultaneously near the same nucleus is very small. Hence one might expect the M.O. to be symmetrical with respect



to the two hydrogen nuclei, *i.e.*, the M.O. in the hydrogen molecule will be "plum-shaped" (Fig. 2).

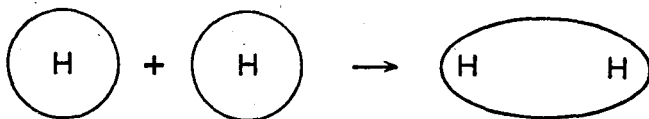
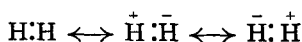


FIG. 2.2.

Although the probability of finding the two electrons simultaneously near the same nucleus is very small, nevertheless this probability exists, and gives rise to the two *ionic* structures  $\text{H}^+\text{H}^-$  and  $\text{H}^-\text{H}^+$ . Thus the hydrogen molecule will be a resonance hybrid of three resonating structures, one purely covalent (*i.e.*, the two electrons are *equally* shared), and two ionic (*i.e.*, the pair of electrons are associated with *one* nucleus all the time):



Calculation has shown that the ionic structures contribute very little to the actual state of the hydrogen molecule, and the bond between the two hydrogen atoms is described as a *covalent bond with partial ionic character*. It should here be noted that when the single bond is formed between the two hydrogen atoms, the probability of finding the electrons is greatest in the region *between* the two nuclei. It is this concentration of the negatively charged electrons between the two positive hydrogen nuclei that binds the nuclei together. Since electrons are negatively charged, they will repel each other and so tend to keep out of the region between the two nuclei. On the other hand, since the spins of the two electrons are antiparallel, this produces attraction between the two electrons, thereby tending to concentrate them in the internuclear region. The net result is that the electron density for *paired electrons* is greatest *between* the two nuclei. Such a bond is said to be a *localised* M.O., and preserves the idea of a bond connecting the two atoms. This localisation (in a covalent bond) gives rise to the properties of bond lengths, dipole moments, polarisability and force constants.

#### HYBRIDISATION OF BOND ORBITALS

The electron configuration of carbon is  $(1s)^2(2s)^2(2p_x, 2p_y)$ . It therefore appears to be bivalent. To be quadrivalent, the  $(2s)^2$  and the  $(2p_x, 2p_y)$  electrons must be involved. One way is to *uncouple* the paired  $2s$  electrons, and then *promote* one of them to the empty  $2p_z$  orbital. Should this be done, four valencies would be obtained, since each of the electrons could now be paired with an electron of another atom. The resulting bonds, however, would not all be equivalent, since we would now have the component A.O.s  $2s, 2p_x, 2p_y, 2p_z$ . All work on *saturated* carbon compounds indicates that the four valencies of carbon are equivalent (but see below). In order to get four equivalent valencies, the four "pure" A.O.s must be "mixed" or *hybridised*. It is possible, however, to hybridise these four "pure" A.O.s in a number of ways to give four valencies which may, or may not, be equivalent. Three methods of hybridisation are important: (i) *tetrahedral* ( $sp^3$  bond), (ii) *trigonal* ( $sp^2$  bond), (iii) *digonal* ( $sp$  bond).

(i) In **tetrahedral hybridisation**, the  $(2s)$  and  $(2p_x, 2p_y, 2p_z)$  electrons are *all* hybridised, resulting in **four equivalent orbitals arranged tetrahedrally**, *i.e.*, pointing towards the four corners of a *regular* tetrahedron (Fig. 3). The orbitals are greatly concentrated along these four directions (Fig. a shows

the shape along one of these directions). Then by linear combination with the  $1s$  orbitals of four hydrogen atoms, four equivalent M.O.s are obtained for methane. Because of the large amount of overlapping between the hybridised A.O.s of the carbon and the  $s$  A.O. of the hydrogen atom, there will be strong binding between the nuclei. As in the case of the hydrogen molecule, each M.O. is almost completely confined to the region between the two nuclei concerned, *i.e.*, in methane are four *localised* molecular orbitals. This scheme of localised M.O.s may be satisfactorily applied to all compounds containing single covalent bonds. Bond orbitals which are symmetrical about the line joining the two nuclei concerned are known as  $\sigma$ -bonds.

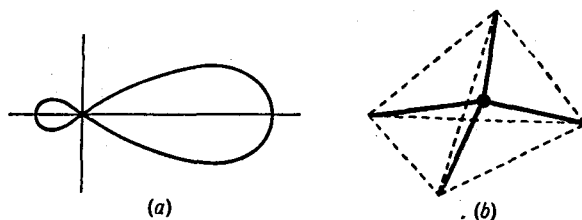


FIG. 2.3.

The above state of affairs holds good only so long as four *identical* groups are attached to the carbon atom, *e.g.*, in  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{C}(\text{CH}_3)_4$ , etc. When the groups are different, *e.g.*, in  $\text{CHCl}_3$ , the four bonds are no longer equivalent. The four carbon valencies are now hybridised in a *non-equivalent* fashion, pointing towards the four corners of an *irregular* tetrahedron. In  $\text{CHCl}_3$ , the three  $\text{Cl}-\text{C}-\text{Cl}$  angles are increased from the normal angle of  $109^\circ 28'$  to about  $111^\circ$ , and the three  $\text{Cl}-\text{C}-\text{H}$  angles decreased to about  $108^\circ$ .

(ii) In **trigonal hybridisation**, the  $2s$ ,  $2p_x$  and  $2p_y$  orbitals are hybridised,

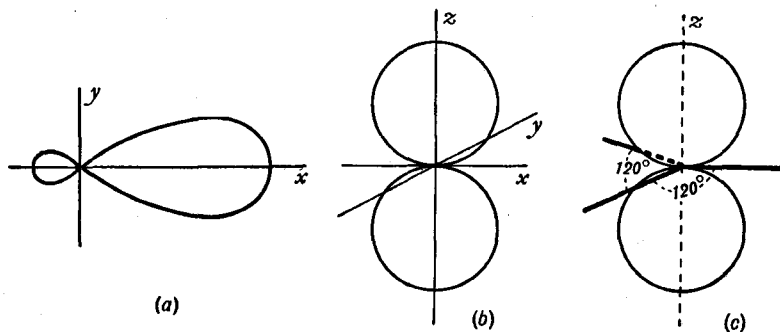


FIG. 2.4.

resulting in **three equivalent coplanar orbitals pointing at angles of  $120^\circ$  in the  $xy$  plane** (Fig. 4a). The remaining orbital is the undisturbed  $2p_z$  (Fig. b). Thus there will be three equivalent valencies in one plane and a fourth pointing at right angles to this plane (Fig. c). The three coplanar valencies form  $\sigma$ -bonds, and the  $2p_z$  valency forms the so-called  $\pi$ -bond. The  $2p_z$  electrons are known as  $\pi$ -electrons, *mobile* electrons, or *unsaturation* electrons when they form the  $\pi$ -bond. The trigonal arrangement occurs in compounds containing a *double* bond, which is regarded as being made up

of a strong bond ( $\sigma$ -bond) between two trigonal hybrid A.O.s of carbon, and a weaker bond ( $\pi$ -bond) due to the relatively small overlap of the two pure  $p_z$  orbitals in a plane at right angles to the trigonal hybrids. Fig. 5(a) shows the plan, and (b) the elevation of ethylene,  $\text{CH}_2=\text{CH}_2$  (see also p. 427).

The  $\text{H}-\text{C}-\text{H}$  angle in ethylene has been measured spectroscopically, and it has been found to be  $119^\circ 55'$  (Gallaway *et al.*, 1942). This is in agreement with the value expected for trigonal hybridisation.

*It is the  $\pi$ -electrons which are involved in the electromeric and resonance effects.*

When a compound contains two or more double bonds, the resulting

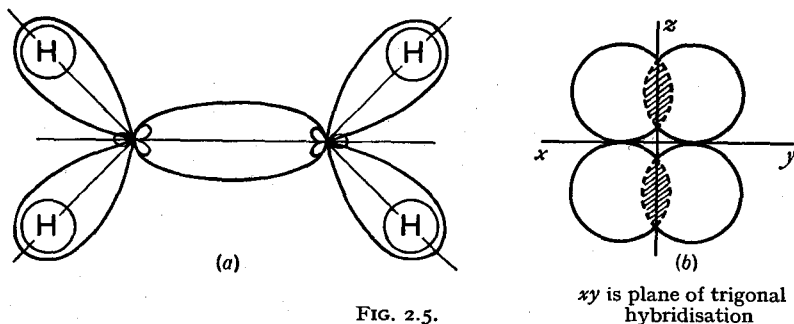


FIG. 2.5.

M.O.s depend on the positions of these bonds with respect to one another (see, *e.g.*, butadiene, p. 88, and benzene, p. 509).

(iii) In **digonal hybridisation**, only one  $2s$  electron and the  $2p_x$  electron are hybridised, resulting in **two equivalent collinear orbitals** (Fig. 6); the  $2p_y$  and  $2p_z$  electrons remain undisturbed. Thus we get two equivalent valencies (forming the  $\sigma$ -type of bond) pointing in opposite directions along a straight line, and two other valencies (each forming a  $\pi$ -type of bond), one concentrated along the  $y$ -axis (the  $2p_y$  orbital), and the other along the  $z$ -axis (the  $2p_z$  orbital). The digonal arrangement occurs in compounds containing a *triple* bond, *e.g.*, acetylene.

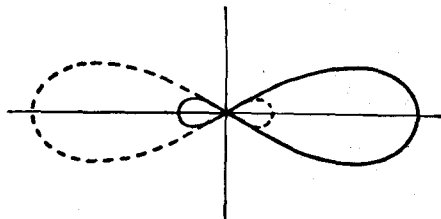


FIG. 2.6.

When the electrons of any atom have been placed in hybridised orbitals, that atom is said to be in a "valence state". The atom on its own cannot exist in a valence state; energy is required to promote the atom to this condition. This energy is obtained through the formation of bonds which are stronger with the hybridised orbitals than with the "pure" orbitals, *i.e.*, more energy is released with the former than with the latter.

In the foregoing account of carbon hybridisation, multiple bonds (double and triple) have been described in terms of  $\sigma$ -bonds and  $\pi$ -bonds. There is, however, an alternative approach to this problem of valency theory. The application of this theory makes use of the Pauli exclusion principle, and also takes into account the electrostatic repulsion between electrons. These principles lead to the conclusion that electrons with the same spin avoid each other. Thus, for example, Zimmerman *et al.* (1949) have shown, as a consequence of the exclusion principle, that the most probable arrangement of the four electrons of carbon ( $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ) is at the corners of a regular tetrahedron provided all the electrons have the same spin. This tetrahedral configuration, however, is achieved only if the four electrons are equivalent, *i.e.*, the electrons occupy orbitals which in carbon atoms are  $sp^3$  hybrid orbitals.

As we have seen, in *saturated* carbon compounds the four  $sp^3$  orbitals point towards the corners of a tetrahedron. In ethylene we have used  $sp^2$  trigonal hybridisation (one  $\sigma$ - and one  $\pi$ -bond) to describe the double bond. It is possible, however, to still use  $sp^3$  hybridisation to describe ethylene. In this case two electrons are in one orbital of "banana" shape ("bent" bond), and the other two electrons in a second "banana" orbital, equivalent to the first but the mirror image of it. Thus ethylene may be represented (Fig. 7; see also p. 488):

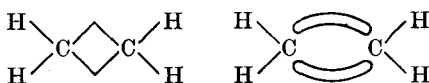


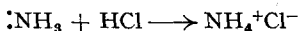
FIG. 2.7.

It is interesting to note that this "bent" bond method of representing ethylene is equivalent to Baeyer's description of a double bond (p. 487).

In the same way, the triple bond in acetylene (previously described in terms of one  $\sigma$ - and two  $\pi$ -bonds) may also be regarded as made up of three equivalent  $sp^3$  hybrids symmetrically disposed round the C—C axis.

Quantum mechanical arguments show that both methods of representing these multiple bonds are equal to each other, each method having certain advantages. The  $\sigma$ - $\pi$  bond method is more convenient for describing transitions from one state into another (*e.g.*, in electronic spectra), whereas the "bent" bond method is more convenient for describing electron distribution in a molecule.

Now let us consider molecules in which the central atom has lone pairs. Consider nitrogen, with electron configuration  $(1s)^2(2s)^2(2p)^3$ . This has three  $2p$  orbitals, and if each combines with a hydrogen atom, then the molecule of ammonia is  $\text{NH}_3$ . In this molecule there is a lone pair  $(2s)^2$ , and the three hydrogen atoms, bound by the overlap with  $2p$  orbitals, will therefore have a valency angle of  $90^\circ$ . The nitrogen atom is trivalent, and by virtue of its lone pair, can act as a donor to become quadrivalent uni-electrovalent, *e.g.*,



At first sight it might appear that the four hydrogen atoms in the ammonium ion are not equivalent; three bonds are formed from  $2p$  electrons, and one by the lone  $2s^2$ . However, the fact is that all four hydrogen atoms in  $\text{NH}_4^+$  are equivalent, and also the valency angle is about  $109.5^\circ$  (the tetrahedral value). Moreover, the valency angle in ammonia is about  $107^\circ$  and not  $90^\circ$  (the expected value from  $2p$  bonding).

Now consider oxygen  $(1s)^2(2s)^2(2p)^4$ . One  $2p$  orbital is doubly filled, and so, in water, one would expect that the two single  $2p$  electrons would combine with hydrogen to form water in which the bond angle HOH is  $90^\circ$ . Actually the bond angle is about  $104.5^\circ$ . Also, since the water molecule has two lone pairs, it can act as a donor to form the hydroxonium ion,  $\text{H}_3\text{O}^{+}$ , and it is found that all the three hydrogen atoms are equivalent. The valency angles are nearly those expected of tetrahedral configurations, and the difference from  $90^\circ$  is far too large to be accounted for by repulsion between hydrogen atoms. A satisfactory explanation is as follows. Sidgwick *et al.* (1940) assumed that lone pairs of electrons and bonding pairs were of equal importance, and that they arranged themselves symmetrically so as to minimise the repulsions between them. Thus pairs of electrons in a valency shell, whether a bonding pair or a lone pair, are always arranged in the *same* way, and this depends only on the total number of pairs. Thus two pairs are arranged linearly (*e.g.*,  $\text{HgCl}_2$ ), three pairs in the form of an equilateral triangle (*e.g.*,  $\text{BCl}_3$ ), four pairs tetrahedrally (*e.g.*,  $\text{CH}_4$ ), five pairs in the form of trigonal bipyramid and six pairs octahedrally. In all cases it is assumed that all the pairs of electrons occupy hybridised orbitals and only  $\sigma$ -bonds are present (see also p. 335).

Now let us consider ammonia and water from this point of view. In each of the valency shells of these central atoms there are four pairs of electrons (nitrogen with one lone pair, and oxygen with two lone pairs). If these four pairs occupy four tetrahedrally hybridised orbitals, then the valency angles should be about

$109.5^\circ$ . As we have seen above, in ammonia the angle is about  $107^\circ$ , and in water about  $104.5^\circ$ . The problem then is to account for these deviations from the anticipated "regular" shapes. This may be explained by assuming electrostatic repulsions between electron pairs in the valency shell (both bonding and lone pairs) are in the following order:

lone pair — lone pair > lone pair — bond pair > bond pair — bond pair.

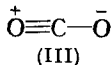
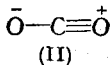
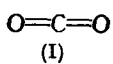
This order can be explained on the basis that lone pairs are more concentrated than bonding pairs (the latter are "stretched" in the formation of covalent bonds). Thus lone-pair electrons exert greater electrostatic repulsions on other lone pairs than on bonding pairs. Consequently, when lone pairs occupy the valency shell, bonding pairs are "forced together". In  $\text{CH}_4$  there are four bonding pairs, and so the distribution is symmetrical with a valency angle of  $109^\circ 28'$ . In  $\text{NH}_3$ , there are three bonding pairs and one lone pair, and since the latter has a bigger repulsive force, the bonding pairs are forced closer together (the bond angle is about  $107^\circ$ ). It should also be noted that the lone pair is also in a hybridised orbital, and so when the ammonia molecule is converted into the ammonium ion the four bonding pairs are in the same state of hybridisation, and consequently all four hydrogen atoms are equivalent.

In the water molecule (bond angle  $104.5^\circ$ ), there are two lone pairs, and consequently the bonding pairs are "closed up" more than in ammonia.

Other factors also play a part in deciding the values of the bond angles: the electronegativity of the central atom and the electronegativities of the attached atoms.

Let us now consider the hydrogen chloride molecule,  $\text{H}:\ddot{\text{Cl}}:$ . Here again the four pairs of electrons of the chlorine atom (one bonding pair and three lone pairs) each occupy each  $sp^3$  hybrid orbital. In this molecule, however, since chlorine is more strongly electron-attracting than hydrogen, the electrons are more likely to be simultaneously near the former atom than the latter. Thus, although the electrons will be found with great probability in the region between the atoms, *i.e.*, we have a localised M.O., nevertheless the region near the chlorine atom will tend to be occupied more than that near the hydrogen atom. In other words, in addition to the covalent structure  $\text{H}-\text{Cl}$ , there will also be a significant contribution of the ionic structure  $\text{H}^+\text{Cl}^-$ , the contribution of  $\text{H}-\text{Cl}^+$  being negligible. Thus we may say that hydrogen chloride is a resonance hybrid of the two resonating structures  $\text{H}-\text{Cl}$  and  $\text{H}^+\text{Cl}^-$ . The actual hydrogen chloride molecule will therefore have a dipole moment  $\text{H}-\overset{\rightarrow}{\text{Cl}}$ .

In general, when two dissimilar atoms are linked, the contribution of the two ionic structures,  $\text{A}^+\text{B}^-$  and  $\text{A}^-\text{B}^+$ , will *not* be equally important. The greater the electron-affinity of B with respect to A, the greater will be the contribution of  $\text{A}^+\text{B}^-$  to the actual state of the molecule. The problem is then to decide what are the weights of the contributions of the resonating structures. The importance of this problem is readily seen from a consideration of carbon dioxide.



Suppose these three structures are described by the wave functions  $\psi_1$ ,  $\psi_2$  and  $\psi_3$ . Then the actual molecule will be represented by a wave function which is a linear combination of the three structures:

$$\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3$$

The best approximation is given by values for the coefficients  $a_1$ ,  $a_2$  and  $a_3$  that give the *lowest energy* to the resonance hybrid, *i.e.*, coefficients  $a_1$ ,  $a_2$

and  $a_3$  are a measure of the weights of the resonating structures. This may be done by calculation. On the other hand, in *qualitative* resonance arguments, it is usual to assume that the weight of a resonating structure is directly related to its energy content. This, however, appears to be satisfactory only when two structures are involved, but often leads to erroneous results when three or more are involved.

Now let us consider the problem of ionic character of a bond, and for this purpose let us examine the hydrogen chloride molecule. There are two important structures for this molecule, one purely covalent and the other purely ionic:  $\text{H}-\text{Cl}$  and  $\text{H}^+\text{Cl}^-$ . The wave function of the resonance hybrid is:

$$\psi = \psi_{\text{covalent}} + a\psi_{\text{ionic}}$$

When the value of  $a$  is such that minimum energy is obtained, then  $(a^2/1 + a^2) \times 100$  is called the *per cent. ionic character* of the bond. This may be calculated from a knowledge of the dipole moment of the bond. The following values have been found for the hydrogen halides:

HF, 60; HCl, 17; HBr, 11; HI, 5.

Thus HF is largely ionic, and HI is mainly covalent.

We have already discussed the problem of the ground and excited states of an atom. Now let us consider the analogous position of molecules. Suppose we are dealing with a diatomic molecule in which each atom has supplied one electron to form the bond. By means of the L.C.A.O. theory, the solution for the M.O. is found by ultimately solving a *quadratic* equation derived from the combination of the two wave functions (A.O.s). Two *real* roots are obtained, *i.e.*, two M.O.s of different energy levels are possible when two A.O.s are combined. Now it is possible for both electrons to occupy either M.O., or for one electron to be in the M.O. of the lower energy level and the other in the higher energy level. When both electrons occupy the lower M.O., the molecule is in the *ground* state, and when one or both electrons occupy the higher M.O., the molecule is in an *excited* state. Suppose  $E_1$  and  $E_2$  (where  $E_1 < E_2$ ) are the energies of the two contributing A.O.s and  $\mathcal{E}_1$  and  $\mathcal{E}_2$  (where  $\mathcal{E}_1 < \mathcal{E}_2$ ) are the energies of the two resulting M.O.s. On comparing these energies, it will be found that  $\mathcal{E}_1 < E_1$  and  $\mathcal{E}_2 > E_2$ , *i.e.*, one M.O. has lower energy than the lower of its components (this is the *ground* state), and the other M.O. has a higher energy than the higher of its components (this is an *excited* state). In general, if  $n$  A.O.s are combined, then there are  $n$  resultant M.O.s, and any two consecutive M.O.s embrace one of the contributing A.O.s (see Fig. 8).

It can now be seen that when two atoms combine to form a bond, two types of bonding are possible. In one M.O., the energy level is lower than either of its component A.O.s. In this M.O., the electron charge is concentrated in the region *between* the two nuclei, resulting in strong bonding between the atoms. This type of M.O. is called a *bonding orbital* or  $\sigma_b$  bond (Fig. 9a). As we have seen, a bonding orbital is formed by two electrons with their spins antiparallel. In the other M.O., the energy level is higher than either of its component A.O.s. In this M.O., the charge is pushed *away* from the region between the two nuclei, resulting in a nodal plane midway between A and B. In this condition A and B repel each other, and this M.O. is said to be *anti-bonding* or a  $\sigma_u$  bond (Fig. 9b). In an anti-bonding orbital, the two electrons have the *same* spin, and since negatively charged electrons repel each other, and since electrons with the same spin tend to keep as far away from each other as possible, the concentration of two such electrons in the internuclear region is reduced to such a great extent that there is no bonding between the two nuclei; the result is thus an anti-bond.

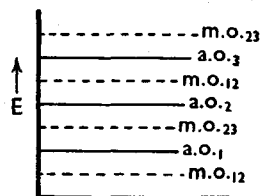


FIG. 2.8.

Any two A.O.s can be combined provided their energies are approximately the same. In the above example of bonding and anti-bonding orbitals, A and B were atoms with  $s$  electrons. Combination of two  $2p$  electrons also gives one bonding and one anti-bonding orbital (Fig. 10a and b). In the bonding orbital, a  $\pi_u$ -bond, there is *one* nodal plane (which contains the molecular axis), but in the anti-bonding orbital, a  $\pi_g$ -bond, there are *two* nodal planes (one containing the

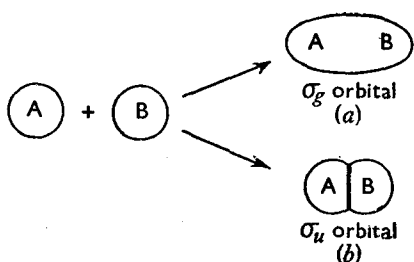


FIG. 2.9.

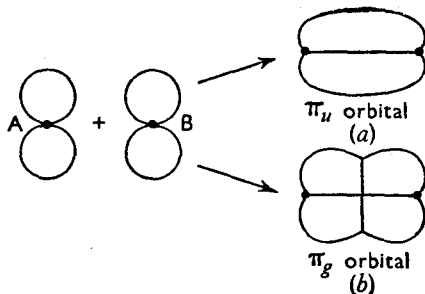


FIG. 2.10.

molecular axis, and the other perpendicular to it). It should here be noted that as the number of nodes in a bond increases, the energy level rises, and consequently the bond becomes weaker. When a molecule undergoes transitions from one energy level to another (with emission or absorption of light), a  $g$  state must go to a  $u$  state, or vice-versa. Transitions from one  $g$  state to another  $g$  state, and from one  $u$  state to another  $u$  state, are forbidden.

An important difference between V.B. and M.O. theories is that when dealing with energy levels of electrons in *molecules*, in the V.B. method, electrons are dealt with in *pairs*, whereas in the M.O. method, electrons can be dealt with individually (see also p. 777).

#### THE GENERAL NATURE OF ORGANIC REACTIONS

Much work has been done on reaction mechanisms, *i.e.*, the actual steps by which a reaction takes place. A chemical equation indicates the initial and final products of a reaction; rarely does it indicate *how* the reaction proceeds. Many reactions take place via intermediates which may or may not have been isolated. When the products of a reaction are formed by a single collision of the reactant molecules, *i.e.*, the reaction proceeds without any intermediates, the reaction is said to be a *one-step* (or *elementary*) reaction. Most reactions, however, are *complex*, *i.e.*, they occur via a number of reaction steps. The rate of the *overall* reaction is controlled by the slowest step; this is known as the *rate-determining step*.

There is, in general, no one method that is satisfactory for the determination of mechanisms of reactions, but the use of a number of methods may lead to an acceptable answer. It should be borne in mind that mechanisms are, in general, theories that have been devised to explain the facts which have been obtained experimentally. Some of the commoner methods used for elucidating mechanisms are:

- (1) Kinetics. Kinetic studies are concerned with rates of reactions and provide the most general method for determining reaction mechanisms.
- (2) The identification of *all* the products of a reaction.
- (3) The detection, or better still (if it is possible), the isolation of intermediates.
- (4) The effect on reaction rates of changing the structure of the reactants.
- (5) The effect on reaction rates of changing the solvent.

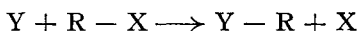
(6) Stereochemical evidence. This type of approach can only be used when dealing with optically active compounds.

(7) The use of isotopes. This method is particularly useful for tracing the part played by a particular atom in a reaction.

Applications of these methods are discussed in the text, but before ending this discussion, there are two other points of interest. One is the *principle of microscopic reversibility*. According to this principle, the mechanism of any reaction, under a given set of conditions, is identical in microscopic detail to that of the reverse reaction under the same conditions, except that it proceeds in the opposite way. With this principle it has been possible to deduce mechanisms where the forward or backward reactions do not lend themselves to kinetic studies (see, *e.g.*, p. 70).

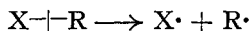
The other point is that when the various possible products of a reaction are *not* interconvertible under the conditions of the reaction, then the product formed most rapidly will be the one that predominates in the products. This most rapidly formed product is known as the *kinetically controlled* product. If, however, the possible products of the reaction are interconvertible under the reaction conditions, then the most stable product will predominate in the final products. This most stable product is known as the *thermodynamically controlled* product (see, *e.g.*, p. 87).

Now let us examine in more detail what happens when molecules containing *covalent* bonds undergo chemical reaction. Consider the reaction

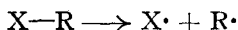


where RX and RY are both covalent molecules. It can be seen that in this reaction, bond R—X has been broken and the new bond Y—R has been formed. The mechanism of the reaction depends on the way in which these bonds are broken. There are three possible ways in which this may occur, and the result of much work has shown that the actual way in which the break occurs depends on the nature of R, X and Y, and the experimental conditions.

(i) Each atom (forming the X—R bond) retains one electron of the shared pair, *i.e.*,



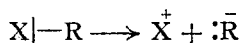
This equation is usually written:



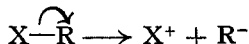
This gives rise to *free radicals*, and the breaking of the bond in this manner is known as *homolytic fission* (*homolysis*). Free radicals are *odd electron molecules*, *e.g.*, methyl radical  $\text{CH}_3\cdot$ ; triphenylmethyl radical  $(\text{C}_6\text{H}_5)_3\text{C}\cdot$ ; etc. The majority are electrically neutral (a few free radical ions are known). All possess addition properties, and are extremely reactive; when a free radical is stable, its stability is believed to be due to resonance. Free radicals are *paramagnetic*, *i.e.*, possess a small permanent magnetic moment, due to the presence of the odd (unpaired) electron. This property is used to detect the presence of free radicals. Diradicals are also known; these have an even number of electrons, but *two are unpaired* (see, *e.g.*, methylene, anthracene). In general, free-radical reactions are catalysed or initiated by compounds which generate free radicals on decomposition, or by heat or light. Furthermore, a reaction which proceeds by a free-radical mechanism can be inhibited by the presence of compounds that are known to combine with free radicals. Another important characteristic is that a free-radical mechanism leads to abnormal orientation in aromatic substitution.



(ii) Atom (or group) R retains the shared pair. This may be represented as:

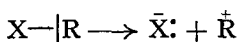


This equation is now usually written:

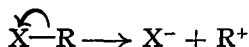


This is known as *heterolytic fission (heterolysis)*, and Y is said to be an *electrophilic* (electron-seeking) or *cationoid* reagent, since it *gains* a share in the two electrons retained by R. Obviously an electrophilic reagent attacks a molecule at the point of *high* electron density. When an electrophilic reagent is involved in a *substitution* or a *replacement* reaction, that reaction is represented by  $S_E$  (S referring to substitution, and E to the electrophilic reagent). When  $\bar{R}:$  is a negative group in which the carbon atom carries the negative charge, *i.e.*, has an unshared pair of electrons, the group is known as a **carbanion**.

(iii) Atom (or group) R loses the shared pair, *i.e.*, the shared pair remains with X. This may be represented as:



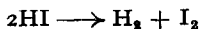
or



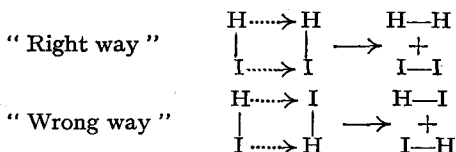
This also is heterolytic fission (heterolysis), and Y is said to be a *nucleophilic* (nucleus-seeking) or *anionoid* reagent, since it *supplies* the electron pair. Obviously a nucleophilic reagent attacks a molecule at the point of *low* electron density. When a nucleophilic reagent is involved in a substitution or a replacement reaction, that reaction is represented by  $S_N$ . When  $R^+$  is a positive group in which the carbon atom carries the positive charge, *i.e.*, lacks a pair of electrons in its valency shell, the group is known as a **carbonium ion**, and is in a trigonal state of hybridisation. Furthermore, such a carbonium ion is said to have a "classical" structure. There are, however, various cases where the ion is better represented as a *bridged carbonium ion*, and in these cases the ions are said to have a "non-classical" structure (see, *e.g.*, p. 101).

Because of their positive charge, carbonium ions are very unstable, but they may be stabilised by delocalisation (*i.e.*, by spreading) of the charge by means of solvation. Alternatively, the ion may be stabilised by delocalisation of the charge *within* the molecule by inductive and/or resonance effects. In certain cases, delocalisation may be the result of hyperconjugation (see p. 269).

**Transition state theory of reactions.** According to the *collision theory* of reactions, before molecules can enter into chemical reaction, they must collide and they must be activated, *i.e.*, they must attain a certain amount of energy ( $E$ ) above the average value. However, the rate of a reaction depends not only on the frequency of collisions in which the energy of activation is exceeded but also on whether the colliding molecules are suitably oriented with respect to each other for effective reaction to occur. This limitation is known as the *probability* or *steric factor*, and depends, for a given type of reaction, on the geometry of the reacting molecules. A simple example of the steric factor is that in the reaction

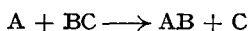


If hydrogen iodide decomposes on collision, then activated molecules can collide in one of two ways, the "right" way leading to decomposition, and the "wrong" way leading to merely a "change in partners".

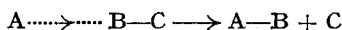


One can expect that when various paths are possible for a given reaction under given conditions, then the path actually followed will be the one requiring the lowest energy of activation. The problem therefore is to try to work out the path that requires the minimum energy of activation.

The *transition state theory* of reactions does not use the simple idea of collision, but considers how the potential energy of a system of atoms and/or molecules varies as the molecules are brought together. Consider the reaction



This is known as a *three-centre reaction*. London (1929), by making certain approximations, showed that the minimum energy required in a three-centre reaction is when the reaction proceeds by an *end-on approach*, i.e., in the above reaction, the approach of A to BC requiring the minimum activation energy is for A to approach BC along the bonding line of BC and on the side remote from C:

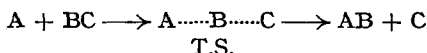


In this three-centre reaction, the value of the activation energy depends on four factors: (i) The strength of the B—C bond. The stronger this is, the greater will be  $E$ . (ii) The repulsion between A and BC. The greater this repulsion, the greater will be  $E$ . (iii) The repulsion between AB and C. The greater this repulsion, the greater will be  $E$ . (iv) The strength of the A—B bond. The greater the strength of this bond, the lower be  $E$ .

Since most reactions are carried out in solution, another factor affecting the value of  $E$  is solvation of molecules and ions.

When we consider the mechanism of activation of this three-centre reaction, we can imagine that there are two extreme cases possible: (i) A is forced up against the repulsion of BC until it is close enough to compete with B on equal terms with C, which is finally expelled. (ii) BC acquires so much energy that the bond B—C is broken, and then A and C combine without any opposition.

Polanyi *et al.* (1931-1938) amplified London's ideas into the *transition state theory*. These authors showed by mathematical treatment that the lowest value of  $E$  is obtained when the reaction proceeds through a compromise between the two extremes (i) and (ii) mentioned above. A approaches BC along the bonding line of BC remote from C, and is forced against the repulsion of BC, and at the same time bond BC stretches until A and C can compete on equal terms for B. Thus a point is reached when the distances A—B and B—C are such that the forces between each pair are the same. This condition is the *transition state (activated complex)*; in this state neither molecule AB nor BC exists independently. The system can now proceed in either direction to form A and BC or AB and C. This sequence of events may be represented by the following equation (T.S. = transition state):



It should be noted that the *new* bond is formed on the side opposite to that of the *original* bond (which was broken). Thus the original molecule is turned "inside out", i.e., *inverted* when the new molecule is formed. This inversion may be observed if B contains an asymmetric carbon atom (see the Walden inversion, p. 413).

The above sequence of events may also be represented graphically by means of an *energy profile diagram* (Fig. 11). This diagram is obtained by plotting the potential energy (P.E.) of the system against the reaction co-ordinates (the various distances between the nuclei of A, B and C).

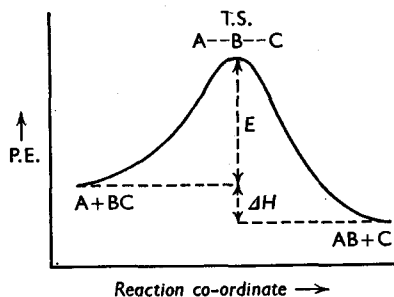


FIG. 2.11.

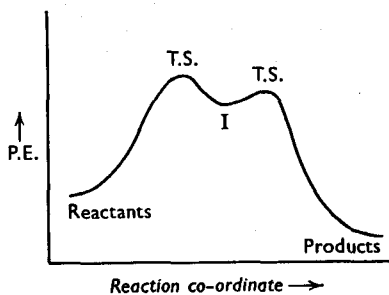


FIG. 2.12.

$E$  is the activation energy, and  $\Delta H$  is the heat of reaction at constant pressure. It is assumed that the reaction rate is given by the rate at which the reactant molecules pass through the transition state. For a given shaped "hump", the lower it lies (*i.e.*, the lower the *energy barrier* is), the easier it is for the reactant molecules to enter the transition state. Also, the wider the hump for a given height, the easier it is for the reactant molecules to enter the transition state, since there is now a wider latitude in nuclei positions for the activated complex.

The activated complex is *not* a true molecule; it contains *partial bonds*, and the energy content of the system is a maximum. Its life is extremely short, and hence it cannot be isolated; it is always decomposing into reactants or products. The reaction, however, if complex, will proceed through true intermediates which possess some measure of stability, and if this is great enough, the intermediates may be isolated. If the reaction proceeds through a true intermediate (I) (Fig. 12), there will be a minimum in the energy profile diagram. The greater the dip, the more stable will be the intermediate, and conversely, the shallower the dip, the less stable will be the intermediate. In the extreme case, the dip may be so shallow that the intermediate is indistinguishable from the transition state. It should be noted here that each intermediate has its own transition state, and it appears that it is usual to assume that the structure of the transition state closely resembles the structure of the intermediate (*i.e.*, the product of that step). There is, however, evidence to show that in some cases the transition state may be closer to the parent system than to the intermediate (or product).

**Use of isotopes in organic chemistry.** In recent years the use of isotopes has been extremely helpful in the study of reaction mechanisms and rearrangements, in the elucidation of structures, and also in quantitative analysis. The application of isotopes in biochemistry has also been particularly fruitful, since they offer a means of identifying intermediates and the "brickwork" of the final products. The common isotopes that have been used in organic chemistry are: deuterium ( $^2\text{H}$ , D; stable), tritium ( $^3\text{H}$ , T; radioactive),  $^{13}\text{C}$  (stable),  $^{14}\text{C}$  (radioactive),  $^{15}\text{N}$  (stable),  $^{18}\text{O}$  (stable),  $^{32}\text{P}$  (radioactive),  $^{35}\text{S}$  (radioactive),  $^{37}\text{Cl}$  (stable),  $^{82}\text{Br}$  (radioactive),  $^{131}\text{I}$  (radioactive).

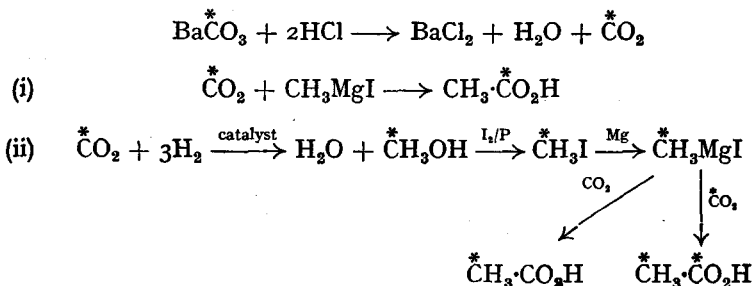
Various methods of analysis are used. Radioactive isotopes are usually analysed with the Geiger-Müller counter, and the stable isotopes by means of the mass spectrograph. Deuterium is often determined by means of infrared spectroscopy; and there are also the older methods for deuterium and  $^{18}\text{O}$  of density, or refractive index measurements (of the water produced after combustion of the compound). A new method is that of nuclear

magnetic resonance, this technique being applicable only to those isotopes having nuclear magnetic moments, *e.g.*, D, T,  $^{13}\text{C}$  and  $^{15}\text{N}$ .

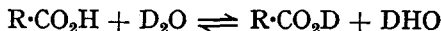
Isotopes are usually used as *tracers*, *i.e.*, the starting material is labelled at some particular position, and after reaction the labelled atom is then located in the product. This does not mean that labelled compounds contain 100 per cent. of the isotope, but that they usually contain an abnormal amount of the isotope. Many examples of the use of isotopic indicators will be found in the text (see Index, Isotopic indicators).

The use of isotopes, stable or radioactive, is based on the fact that the chemical behaviour of any particular isotope is the same as that of the other atoms isotopic with it (the chemical properties of an element depend on the nuclear positive charge and the number of electrons surrounding the nucleus, and not on the number of neutrons in the nucleus). This identity in chemical behaviour is essentially true for the heavy atoms, but in the case of the lightest elements, reactions involving heavier isotopes are slower, but so long as identical paths are followed, the final result is unaffected. This difference in rates of reaction of isotopes is known as the *kinetic isotope effect*, and the magnitude of such effects depends on the weight ratio of the isotopes involved. Thus the kinetic isotope effect is greatest with H and D (and T). The kinetic effect has been widely used to study reaction mechanisms, since this difference in rate is significant when the bond attaching the isotopic atom is stretched in the activated state, *e.g.*, a protonated molecule may react about seven times as fast as the corresponding deuterium compound.

Ion accelerators and nuclear reactors produce, as by-products, artificial isotopes, particularly those which are radioactive. These isotopes are then supplied in the form of some compound from which a labelled compound can be synthesised, *e.g.*,  $^{14}\text{C}$  is usually supplied as  $\text{Ba}^{14}\text{CO}_3$ ,  $^{15}\text{N}$  as  $^{15}\text{NH}_4\text{Cl}$ , etc. A simple example of the synthesis of a labelled compound is that of acetic acid (in the following equations, which involve a Grignard reagent, C is  $^{14}\text{C}$ ; this is a common method of representing a tracer atom, provided its nature has been specified).



In a number of cases, an exchange reaction is a very simple means of preparing a labelled compound, *e.g.*, dissolving a fatty acid in water enriched with deuterium.



Because of the possibility of this exchange reaction, it is often necessary to carry out control experiments.

Isotopes are also very useful in the analysis of mixtures, particularly for the determination of the yield of products in a chemical reaction when isolation is difficult. A simple method is that of *isotopic dilution*. The labelled compound is prepared, and a known amount is then added to the mixture to be analysed. A portion of the substance is now taken and

analysed for its isotopic content. From a knowledge of the isotopic content of the labelled compound added and recovered, and the weight of the labelled compound added, it is thus possible to calculate the weight of the labelled compound in the mixture. This method can only be used as long as there is no isotopic exchange during the isolation.

## READING REFERENCES \*

- Sidgwick, *Electronic Theory of Valency*, Oxford Press (1927).  
 Watson, *Modern Theories of Organic Chemistry*, Oxford Press (1941, 2nd ed.).  
 Remick, *Electronic Interpretations of Organic Chemistry*, Wiley (1943).  
 Pauling, *The Nature of the Chemical Bond*, Cornell University Press (1960, 3rd ed.).  
 Hammett, *Physical Organic Chemistry*, McGraw-Hill (1940).  
 Branch and Calvin, *The Theory of Organic Chemistry (An Advanced Course)*, Prentice-Hall (1941).  
 Dewar, *The Electronic Theory of Organic Chemistry*, Oxford Press (1949).  
 Walsh, Remarks on the Strengths of Bonds, *Trans. Faraday Soc.*, 1947, 43, 60 (also pp. 158, 342).  
 Coulson, Representation of Simple Molecules by Molecular Orbitals, *Quart. Reviews (Chem. Soc.)*, 1947, 1, 144.  
 Coulson, *Valence*, Oxford Press (1961, 2nd ed.).  
 Wheland, *Resonance in Organic Chemistry*, Wiley (1955).  
 Wheland, *Advanced Organic Chemistry*, Wiley (1960, 3rd ed.).  
 Ferguson, *Electronic Structures of Organic Molecules*, Prentice-Hall (1952).  
 Hermans, *Theoretical Organic Chemistry*, Elsevier (1954).  
 Ingold, *Structure and Mechanism in Organic Chemistry*, Bell and Sons (1953).  
 Cartmell and Fowles, *Valency and Molecular Structure*, Butterworths (1956).  
 Hine, *Physical Organic Chemistry*, McGraw-Hill (1962, 2nd ed.).  
 Gould, *Mechanism and Structure in Organic Chemistry*, Holt and Co. (1959).  
 Pimental and McClellan, *The Hydrogen Bond*, Freeman and Co. (1960).  
 Leffler, *The Reactive Intermediates of Organic Chemistry*, Interscience (1956).  
 Dickens and Linnett, Electron Correlation and Chemical Consequences, *Quart. Reviews (Chem. Soc.)*, 1957, 11, 291.  
 Gillespie and Nyholm, Inorganic Stereochemistry, *Quart. Reviews (Chem. Soc.)*, 1957, 11, 339.  
 Bent, Distribution of Atomic s Character in Molecules and its Chemical Implications, *J. Chem. Educ.*, 1960, 37, 616.  
 Sanderson, Principles of Chemical Bonding, *J. Chem. Educ.*, 1961, 38, 382.  
 Orville-Thomas, Nuclear Quadruple Coupling and Chemical Bonding, *Quart. Reviews (Chem. Soc.)*, 1957, 11, 162.  
 Pople, The Molecular-Orbital and Equivalent Orbital Approach to Molecular Structure, *ibid.*, 1957, 11, 273.  
 Arnstein and Bentley, Isotopic Tracer Technique, *ibid.*, 1950, 4, 172.  
 Thomas and Turner, The Syntheses of Isotopically Labelled Organic Compounds, *ibid.*, 1953, 7, 407.  
 Gold and Satchell, The Principles of Hydrogen Isotope Exchange Reactions in Solution, *ibid.*, 1955, 9, 51.  
 Semenow and Roberts, Uses of Isotopes in Organic Chemistry, *J. Chem. Educ.*, 1956, 33, 2.  
 Popjak, Chemistry, Biochemistry, and Isotopic Tracer Technique, Lectures, Monographs and Reports of the Royal Institute of Chemistry, 1955, No. 2.

\* Books which deal with the electronic theories of organic chemistry will not be given as reading references in subsequent chapters in this book. The reader should always be prepared to refer to them on any matter dealing with mechanisms.

CHAPTER III  
ALIPHATIC COMPOUNDS

PARAFFINS

ALIPHATIC compounds are *open-chain* or *acyclic* compounds, and the name aliphatic arises from the fact that the first compounds of this class to be studied were the fatty acids (Greek: *aliphos*, fat).

Carbon forms a large number of compounds with hydrogen only and these are known collectively as *hydrocarbons*. There are two groups of hydrocarbons: (i) *saturated* hydrocarbons; (ii) *unsaturated* hydrocarbons.

The paraffin hydrocarbons or the *paraffins* are the saturated hydrocarbons. Many occur naturally, and the chief source of the paraffins is *mineral oil* or *petroleum*, which occurs in many parts of the world.

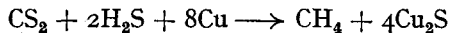
The simplest paraffin is **methane**,  $\text{CH}_4$ , which occurs in "natural gas" (*q.v.*) and the gases from oil-wells. Methane is the principal product of organic decay in swamps and marshes, the gas being set free by the action of bacteria; this method of formation in nature has given rise to the name "marsh-gas" for methane. Sewage sludge which has been fermented by bacteria yields a gas containing about 70 per cent. methane, and this is used as a liquid fuel. Methane also forms about 40 per cent. by volume of coal-gas.

Methane may be synthesised as follows:

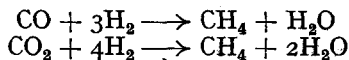
(i) By striking an electric arc between carbon electrodes in an atmosphere of hydrogen. Only a very small amount of methane is obtained in this way.

(ii) A mixture of carbon and reduced nickel is heated at  $475^\circ$  in the presence of hydrogen.

(iii) The first synthesis of methane was carried out by Berthelot in 1856, who passed a mixture of carbon disulphide and hydrogen sulphide over heated copper:



(iv) A mixture of carbon monoxide or dioxide and hydrogen is passed over finely divided nickel heated at about  $300^\circ$ :



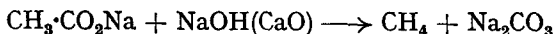
This synthesis is due to Sabatier and Senderens (1897). Until recently the nickel catalyst was usually prepared by reducing with hydrogen nickel oxide deposited on a suitable inert, porous support, *e.g.*, kieselguhr. The support is impregnated with a nickel salt, treated with sodium hydroxide, washed and dried, and the resulting nickel oxide reduced with hydrogen at  $300\text{--}450^\circ$ . Many organic compounds may be reduced by passing their vapours mixed with hydrogen over nickel heated at  $200\text{--}300^\circ$ . Any reduction that is carried out in this manner is referred to as the *Sabatier-Senderens reduction*, in honour of the workers who first introduced this method. It is quite a common feature in organic chemistry to name a reaction after its discoverer or, in certain cases, after a worker who investigated the reaction and extended its application. The reader should always make himself familiar with the reaction *associated* with a particular name.

The most common nickel catalyst used to-day is that prepared by the method introduced by Raney (1927). An alloy containing equal amounts of nickel and aluminium is digested with sodium hydroxide; the aluminium

is dissolved away, and the residual very finely divided nickel is washed and stored under water, ethanol, or any other suitable liquid. Raney nickel is more reactive than the supported nickel catalyst, and is usually effective at lower temperatures, often at room temperature.

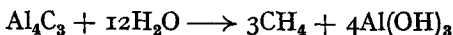
None of the syntheses described above is of any *practical* importance as a method of preparing methane in quantity. The following methods are those which may be used in the laboratory, *i.e.*, convenient methods of preparing methane in reasonable quantities. The degree of purity of the product depends on the particular method used. Quite often it is the purification of the crude product which causes an appreciable loss of material, and the more we aim at getting the "pure" compound, the smaller is the final yield.

1. The most convenient method is to heat a mixture of anhydrous sodium acetate and soda-lime:



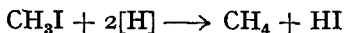
In chemical reactions soda-lime behaves as sodium hydroxide (or calcium hydroxide); it is not deliquescent and does not attack glass, and is therefore more convenient to use than solid sodium hydroxide.

2. By boiling aluminium carbide with water:



The methane is impure; it contains hydrogen.

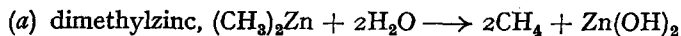
3. Almost pure methane (it contains traces of hydrogen) is obtained by the reduction of methyl iodide with nascent hydrogen:



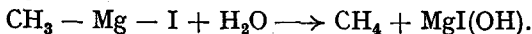
A common method for generating hydrogen uses zinc and acetic acid saturated with hydrogen chloride, or hydrochloric acid alone, or with aqueous sodium hydroxide. Another useful method is by the action of a zinc-copper couple on ethanol.

Lithium aluminium hydride or lithium hydride may also be used for reducing alkyl bromides.

4. By the action of water on:



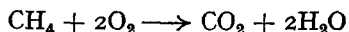
(b) Methylmagnesium iodide,



Method (b) is far more convenient than (a). Methylmagnesium iodide is a member of a group of compounds known as the *Grignard reagents* (p. 348).

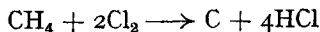
Methane is obtained in vast quantities from natural gas, gas from the oil-wells, and from cracked petroleum (*q.v.*).

**Properties of methane.** Methane is a colourless, odourless, non-poisonous gas; its b.p. is  $-164^\circ/760$  mm., and m.p.  $-184^\circ$ . It is somewhat soluble in water, 100 ml. of water dissolving about 5 ml. of methane at  $20^\circ$ ; but is quite soluble in ethanol and ether. It burns with a non-luminous flame in air or oxygen, forming carbon dioxide and water:

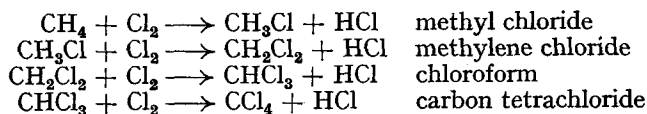


It explodes violently when mixed with air (or oxygen) and ignited, and this is believed to be the cause of explosions in coal-mines, where methane is known as *fire-damp*. Methane may be *catalytically* oxidised to methanol and formaldehyde.

**Substitution reactions of methane.** Chlorine has no action on methane in the dark. In bright sunlight the reaction is explosive, and hydrogen chloride and carbon are formed:



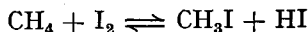
In diffused sunlight no explosion occurs, but a series of reactions takes place whereby the four hydrogen atoms in methane are successively replaced by chlorine atoms:



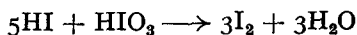
In methane the four carbon valencies are satisfied by combination with four hydrogen atoms. Carbon never exhibits a valency of more than four, and so cannot combine with more than four hydrogen atoms or four other univalent atoms or groups. Hence in the reaction with chlorine, the hydrogen atoms are displaced, and chlorine atoms take their place. This type of reaction is known as *substitution*, and is the *direct replacement of hydrogen* by some other atom or group. The products so formed are known as *substitution products*. The atom or group that has replaced the hydrogen atom is called the *substituent*, and when a substituent atom or group is replaced by some other atom or group, the reaction is referred to as a *replacement* (or *displacement*) reaction. It should be noted that in substitution or replacement reactions there is *no change in structure*. The *spatial arrangement* of the molecule, however, may have changed (see p. 413).

In the substitution reaction between methane and chlorine, all four substitution products are obtained, since it is impossible to stop the reaction at any particular stage. It has been found possible, however, to control the reaction so as to obtain mainly methyl chloride (*q.v.*).

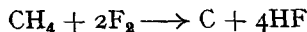
Methane also undergoes substitution with bromine, but the reaction is less vigorous than that with chlorine. With iodine the reaction is reversible:



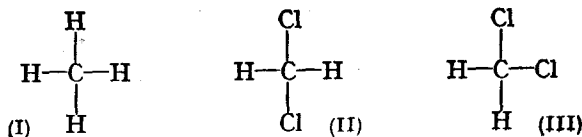
The equilibrium lies almost completely on the left, and consequently the yield of methyl iodide is negligible. On the other hand, in the presence of an oxidising agent, *e.g.*, iodic acid, nitric acid, mercuric oxide, etc., the reaction proceeds to the right, since the equilibrium is upset by the removal of the hydrogen iodide which is oxidised, *e.g.*,



Methane reacts explosively with gaseous fluorine. The initial reaction is possibly:

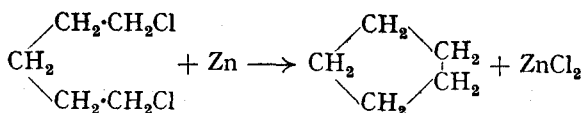


**Structure of methane.** The molecular formula of methane is  $\text{CH}_4$ . Assuming the quadrivalency of carbon and the univalency of hydrogen, we find that there is only one structure possible for methane, *viz.*, (I). Study of the reactions of methane shows that all four hydrogen atoms are equivalent,



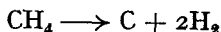


*e.g.*, methylene chloride,  $\text{CH}_2\text{Cl}_2$ , prepared by totally different methods, is always the same. Thus (II) and (III) are different ways of writing the *same* structure. At first sight it may appear that these two structural formulæ are different. They *are* different if the molecule is two-dimensional, but, as we have seen (p. 25), in saturated compounds the four valencies of carbon are arranged tetrahedrally. Examination of the two structures as tetrahedral figures shows that they are identical.\* The chief disadvantage of the plane-structural formula is that it does not show the spatial arrangement of the atoms. On the other hand, the three-dimensional structural formula is cumbersome, and for many complicated molecules cannot easily be drawn on paper. Hence we usually adopt the plane-formulæ when dealing with compounds from the point of view of their structure; only when we wish to stress the spatial arrangement of the atoms or groups in a molecule do we resort to solid diagrams (see, *e.g.*, Ch. XVII). How we show the relative positions of the various atoms or groups in the plane-structural formula of a given compound usually depends on ourselves, but where possible the simplest method of writing the structure should be chosen. Consider 1:5-dichloropentane,  $\text{C}_5\text{H}_{10}\text{Cl}_2$ . This is a "straight" chain compound, and its structural formula is usually written  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ . Now, 1:5-dichloropentane gives cyclopentane when treated with zinc. *cyclo*Pentane is a ring compound, and to show its formation from 1:5-dichloropentane, we write the structure of the latter as follows:



Thus "straight" chains may be "bent" to stress a particular point we may have in mind.

**Uses of methane.** (i) When heated at  $1000^\circ$ , methane is decomposed into carbon and hydrogen:



The carbon is formed in a very finely divided state, and is known as *carbon black*. This is used in making printers' ink and paints; it is also used in the rubber industry for motor tyres, etc.

(ii) Methane is used as a source of hydrogen (for synthetic ammonia and for synthesis gas). Methane is mixed with steam and passed over nickel supported on alumina heated at  $725^\circ$ :



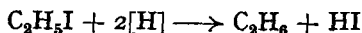
(iii) For the technical preparation of methyl chloride and methylene chloride (*q.v.*).

(iv) For the technical preparation of methanol and formaldehyde (*q.v.*).

(v) As a liquid fuel.

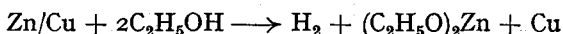
**Ethane**,  $\text{C}_2\text{H}_6$ , occurs with methane in natural gas and the gases from the oil-wells. It is formed to a slight extent when an electric arc is struck between carbon rods in an atmosphere of hydrogen. It may be *prepared* by any of the following methods:

1. By reduction of ethyl iodide with nascent hydrogen using, for example, the zinc-copper couple and ethanol:

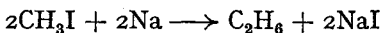


\* "Atomic models" are very useful to the organic chemist. Sets of these models may be bought; alternatively the reader can build his models from plasticine and matchsticks, which provide crude but usually satisfactory models.

The ethane is contaminated with traces of hydrogen:



2. By treating a dry ethereal solution of methyl iodide with sodium:



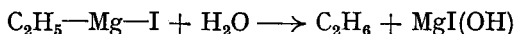
This is an example of the *Wurtz* reaction. It is not so straightforward as the equation indicates; other products are obtained in addition to ethane (see p. 51).

3. By the electrolysis of a concentrated solution of sodium or potassium acetate. A mixture of ethane and carbon dioxide is evolved at the anode, and hydrogen is evolved at the cathode:

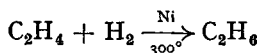


This means of preparation is an example of *Kolbe's electrolytic method*. The ethane may be freed from carbon dioxide by washing the mixture with aqueous sodium hydroxide, but still contains other impurities (see p. 52).

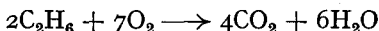
4. Pure ethane may be obtained by the action of water on ethylmagnesium iodide (a Grignard reagent):



5. The best way of preparing pure ethane in large quantity is by the catalytic hydrogenation of ethylene:



**Properties of ethane.** Ethane is a colourless gas, b.p.  $-89^\circ$ , sparingly soluble in water but readily soluble in ethanol. It burns in air or oxygen to form carbon dioxide and water:

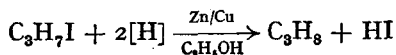


It reacts with halogens in a similar manner to methane to form substitution products, but a much greater number of products are possible due, firstly to the presence of six hydrogen atoms in ethane compared with four in methane, and secondly, to the fact that isomerism is possible in the substitution products of ethane, and not in those of methane. Thus, for example, two dichloroethanes are possible:  $\text{CH}_3\cdot\text{CHCl}_2$  and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$  (see later).

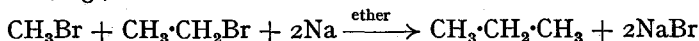
**Structure of ethane.** The molecular formula of ethane is  $\text{C}_2\text{H}_6$ . Assuming the quadrivalency of carbon and the univalency of hydrogen, the only possible structure for ethane is (I). This structure agrees with all the known properties of ethane. Writing the structural formula of ethane in the bond-diagram way uses up a lot of space. Hence it has become customary to use a "contracted" structural formula:  $\text{CH}_3\text{—CH}_3$  or  $\text{CH}_3\cdot\text{CH}_3$  or  $\text{CH}_3\text{CH}_3$ . The reader should make himself familiar with these different ways of writing structural formulæ as soon as possible.

**Propane.**  $\text{C}_3\text{H}_8$  is a constituent of natural gas and gas from the oilwells. It may be prepared by the following methods:

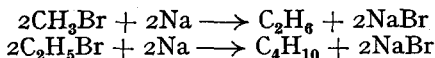
1. By reduction of propyl iodide with nascent hydrogen:



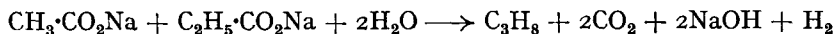
2. By the Wurtz reaction, using a mixture of methyl and ethyl halides, *e.g.*,



The yield of propane is poor, since ethane and butane,  $\text{C}_4\text{H}_{10}$  (as well as other compounds), are obtained as by-products:

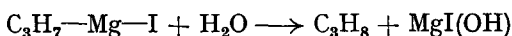


3. By Kolbe's electrolytic method, using a mixture of sodium acetate and sodium propionate:



Apart from other products, ethane and butane are obtained in relatively large quantities, resulting in a poor yield of propane (*cf.* 2 above).

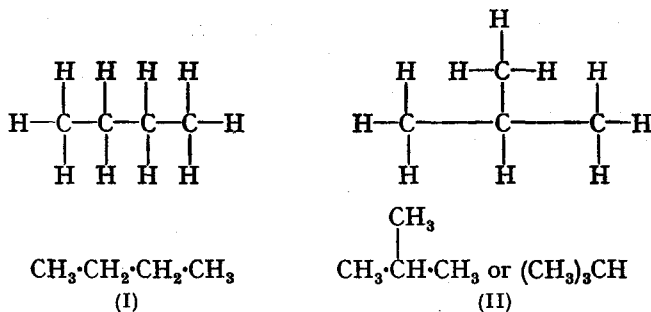
4. By the action of water on propylmagnesium iodide:



**Properties of propane.** Propane is a colourless gas, b.p.  $-44.5^\circ$ . It resembles methane and ethane in many of its chemical properties.

**Structure of propane.** The molecular formula of propane is  $\text{C}_3\text{H}_8$ . Assuming the quadrivalency of carbon and univalency of hydrogen, the only possible structure for propane is  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$ . This structure agrees with all the known properties of propane.

**Butanes,  $\text{C}_4\text{H}_{10}$ .** Theoretical consideration of this formula shows that two structures are possible:



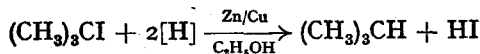
(I) has a *straight* chain, and (II) a *branched* chain. Both isomers are known, and thus "butane" is the first paraffin to exhibit structural isomerism. This is an example of *chain* or *nuclear* isomerism, and is characterised by the manner of linking of the *carbon chain*. (I) is known as *normal* butane, and (II) as *isobutane*. Both occur in natural gas and in petroleum gas, and they may be separated by fractional distillation under pressure.

*normal* Butane may be prepared by the Wurtz reaction using ethyl iodide:



It is a colourless gas, b.p.  $-0.5^\circ$ .

*iso*Butane may be prepared by reducing tertiary *butyl iodide* with nascent hydrogen:



It is a colourless gas, b.p.  $-10.2^\circ$ .

Examination of the two butane structures shows that all the carbon atoms are not equivalent, and also that all the hydrogen atoms are not equivalent. A *primary* carbon atom is one that is joined to *one* other carbon atom; a *secondary* carbon atom to *two* other carbon atoms; and a *tertiary* carbon atom to *three* other carbon atoms. Hydrogen atoms joined to primary, secondary and tertiary carbon atoms are known as primary, secondary, or tertiary hydrogen atoms, respectively. Thus *normal* butane contains two primary carbon atoms, two secondary carbon atoms, six primary and four secondary hydrogen atoms. *iso*Butane contains three primary carbon atoms, one tertiary carbon atom, nine primary hydrogen atoms, and one tertiary hydrogen atom. As we shall see later, the behaviour of these various types of hydrogen atoms differs considerably.

**Pentanes, C<sub>5</sub>H<sub>12</sub>.** Three pentanes are possible theoretically, and all are known.

Structure.	Name.	b.p.
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	<i>normal</i> pentane	36°
$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$	<i>isopentane</i>	28°
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	<i>neopentane</i>	9.4°

All the pentanes occur in natural gas and petroleum gas. *neo*Pentane contains a *quaternary* carbon atom, *i.e.*, a carbon atom joined to *four* other carbon atoms.

As the number of carbon atoms in the paraffin increases, the number of possible isomers increases rapidly, *e.g.*, the paraffin C<sub>15</sub>H<sub>32</sub> can exist in 4347 isomeric forms. The number of isomers of a given paraffin may be calculated by means of mathematical formulæ; in most cases very few have actually been prepared.

### Nomenclature of the Paraffins

Whenever a new branch of knowledge is opened up, there is always the problem of introducing a system of nomenclature. The early chemists usually named a compound on the basis of its history, *e.g.*, methane. This is the parent hydrocarbon of methyl alcohol, CH<sub>3</sub>OH. Methyl alcohol was originally obtained by the destructive distillation of wood, and was named "wood-spirit". From this arose the word methyl, which is a combination of two Greek words, *methu* (wine) and *hule* (wood). Other examples of this way of naming compounds are acetic acid, which is the chief constituent of vinegar (Latin: *acetum*, vinegar); malic acid, which was first isolated from apples (Latin: *malum*, apple), and so on. Thus grew up a system of *common* or *trivial* names, and in many cases the origin of the name has been forgotten. One advantage of the trivial system is that the names are usually short and easily remembered, but a disadvantage is that a particular compound may have a number of names.

As the number of known organic compounds increased, it became apparent that it was necessary to systematise the method of nomenclature. The most satisfactory system is one which indicates the structure of the compound. This task was originally begun in 1892 by an international committee of chemists at Geneva, and hence is referred to as the *Geneva system of nomenclature*. The work was carried on by the *International Union of Chemists* (I.U.C.) by a committee appointed in 1922, and in 1931 these

drew up a report which is often referred to as the I.U.C. system. Nomenclature is always undergoing revision, and the latest rules are those recommended in 1957 by the Commission on the Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry (I.U.P.A.C.). Various changes have been made, but two that have *not* been incorporated into this book are: (i) Numbers indicating the positions of substituents are to be separated by commas (not by colons as used in this book). (ii) Prefixes are to be italicised when they define the positions of named substituents or which are used to define stereoisomers (see p. 46). The reader should always consult the *Chemical Society Handbook* if he wishes to publish work in the *Journal*, and any mistakes he makes in nomenclature will soon be put right by the Editors!

Dyson (1946) has developed "a new notation for organic chemistry". This scheme does not provide a new means of *naming* compounds, but shows how it is possible to portray the structure of an organic compound irrespective of its complexity, and how it may be used for indexing.

There are at least three systems in use for naming paraffins, and in all three the *class-suffix*, *i.e.*, the ending of the name which indicates the particular homologous series (see later), is *-ane*.

i. In the **trivial system** of nomenclature the straight-chain compounds are always designated as *normal* compounds, and the word *normal* is usually abbreviated to *n-*. If the compound contains the grouping  $(\text{CH}_3)_2\text{C}-\text{H}$ , it is known as the *iso*-compound; if it contains a quaternary carbon atom, the compound is known as the *neo*-compound. It is impossible to name many of the more complex paraffins by the trivial system (see later for examples of the trivial system).

The first four paraffins have special names (related to their history); from the fifth member onwards, Latin or Greek numerals are used to indicate the number of carbon atoms in the molecule.

<i>Name.</i>	<i>Formula.</i>	<i>Name.</i>	<i>Formula.</i>
methane . . . . .	$\text{CH}_4$	hexadecane . . . . .	$\text{C}_{16}\text{H}_{34}$
ethane . . . . .	$\text{C}_2\text{H}_6$	heptadecane . . . . .	$\text{C}_{17}\text{H}_{36}$
propane . . . . .	$\text{C}_3\text{H}_8$	octadecane . . . . .	$\text{C}_{18}\text{H}_{38}$
butane . . . . .	$\text{C}_4\text{H}_{10}$	nonadecane . . . . .	$\text{C}_{19}\text{H}_{40}$
pentane . . . . .	$\text{C}_5\text{H}_{12}$	eicosane . . . . .	$\text{C}_{20}\text{H}_{42}$
hexane . . . . .	$\text{C}_6\text{H}_{14}$	heneicosane . . . . .	$\text{C}_{21}\text{H}_{44}$
heptane . . . . .	$\text{C}_7\text{H}_{16}$	docosane . . . . .	$\text{C}_{22}\text{H}_{46}$
octane . . . . .	$\text{C}_8\text{H}_{18}$	tricosane, etc. . . . .	$\text{C}_{23}\text{H}_{48}$ , etc.
nonane . . . . .	$\text{C}_9\text{H}_{20}$	triacontane . . . . .	$\text{C}_{30}\text{H}_{62}$
decane . . . . .	$\text{C}_{10}\text{H}_{22}$	hexatriacontane . . . . .	$\text{C}_{36}\text{H}_{74}$
undecane } . . . . .	$\text{C}_{11}\text{H}_{24}$	tetracontane . . . . .	$\text{C}_{40}\text{H}_{82}$
hendecane } . . . . .	$\text{C}_{11}\text{H}_{24}$	pentacontane . . . . .	$\text{C}_{50}\text{H}_{102}$
dodecane . . . . .	$\text{C}_{12}\text{H}_{26}$	hexacontane . . . . .	$\text{C}_{60}\text{H}_{122}$
tridecane . . . . .	$\text{C}_{13}\text{H}_{28}$	heptacontane . . . . .	$\text{C}_{70}\text{H}_{142}$
tetradecane . . . . .	$\text{C}_{14}\text{H}_{30}$	octacontane . . . . .	$\text{C}_{80}\text{H}_{162}$
pentadecane . . . . .	$\text{C}_{15}\text{H}_{32}$		

Univalent radicals that are formed by the removal of one hydrogen atom from a paraffin are known as *alkyl* or *aliphyl* radicals or groups. The name of each individual radical is obtained by changing the suffix *-ane* of the parent hydrocarbon into *-yl*. The first five alkyl radicals are often represented by a shorthand notation.

The radical derived from pentane has, in the past, been usually named *amyl*. This name is now abandoned and *pentyl* and *isopentyl* are to be used.

The paraffins are also known as the *alkanes*, since an alkyl radical plus one hydrogen atom gives a paraffin, *i.e.*, *alkyl* + H = *alkane*.

In chemical equations, if we are dealing with alkyl compounds as a group

<i>Paraffin.</i>	<i>Radical.</i>	<i>Short-hand notation.</i>
methane . . . . .	methyl $\text{CH}_3-$	Me
ethane . . . . .	ethyl $\text{C}_2\text{H}_5-$	Et
propane . . . . .	$n$ -propyl $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2-$	$n$ -Pr, Pr $\alpha$ , or Pr
	isopropyl $\text{CH}_2\cdot\overset{\text{CH}_3}{\underset{ }{\text{C}}}\cdot\text{CH}_3$	isoPr, Pr $\beta$ , or Pr $\dagger$
butane . . . . .	$n$ -butyl $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2-$	$n$ -Bu, Bu $\alpha$ , or Bu
	sec.-butyl $\text{CH}_3\cdot\text{CH}_2\cdot\overset{\text{CH}_3}{\underset{ }{\text{C}}}\cdot\text{CH}_3$	sec.-Bu, Bu $\beta$ , Bu $\dagger$ , or $s$ -Bu
	iso-butyl $(\text{CH}_3)_2\overset{\text{CH}_3}{\underset{ }{\text{C}}}\cdot\text{CH}_2-$	isoBu or Bu $\dagger$
pentane . . . . .	tert.-butyl $(\text{CH}_3)_3\text{C}-$	tert.-Bu, Bu $\dagger$ , or $t$ -Bu
	amyl $\text{CH}_3\cdot(\text{CH}_2)_4\cdot\text{CH}_2-$	$n$ -Am
	isoamyl $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2-$	isoAm or Am $\dagger$

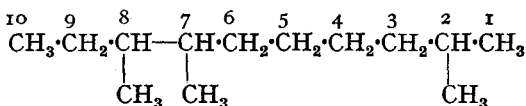
and we do not wish to specify any particular member, we use the symbol R to represent the unspecified alkyl radical, *e.g.*, RCl represents *any* alkyl chloride.

2. In this system of nomenclature the hydrocarbon, except the  $n$ -compound, is regarded as a substitution product of methane. The most highly branched carbon atom in the compound is named as the methane nucleus, and the alkyl groups attached to this carbon atom are named in order of increasing molecular weight of the groups (or in alphabetical order). If two groups have the same molecular weight, the simpler is named before the more complex, *e.g.*, propyl before isopropyl. Hydrogen atoms, if joined to the carbon atom chosen as the methane nucleus, are not named. Since April, 1950, however, the *Chemical Society* has adopted an alphabetical order for prefixes denoting substituents. This order follows in general that adopted in *Chemical Abstracts* except for differences in nomenclature, spelling, italicising, or punctuation. *Italicised prefixes* are neglected when assembling substituents, *e.g.*, isobutyl will be named before ethyl. Isomeric substituents, however, are arranged in alphabetical order of the italicised prefixes, except that *iso* follows directly after  $n$ , *e.g.*,  $n$ -butyl, isobutyl, sec.-butyl, tert.-butyl.

In the I.U.P.A.C. rules, however, the prefixes  $n$ , *iso*, *sec.*, *tert.*, *neo*, *cyclo*, *epi*, *allo*, etc., are no longer to be italicised, *i.e.*, they are to be written  $n$ , iso, s, t, neo, cyclo, epi, allo, etc. Also, the alphabetical order of prefixes follows the first roman letter, *e.g.*, ethyl, isobutyl, etc. (see appendix for further information on nomenclature).

This system of nomenclature is fairly good, since the name indicates the structure of the compound. It is impossible, however, to name the complex paraffins by this system.

3. In the I.U.P.A.C. system of nomenclature the longest chain possible is chosen, and the compound is named as a derivative of this  $n$ -hydrocarbon. The carbon chain is numbered from one end to the other by arabic numerals, and the positions of *side-chains* are indicated by numbers, the direction of numbering being so chosen as to give the lowest numbers possible to the side-chains. When series of locants containing the same number of terms are compared term by term, that series is "lowest" which contains the lowest number on occasion of the first difference, and this principle is used irrespective of the nature of the substituents, *e.g.*,



This is named 2:7:8-trimethyldecane and *not* 3:4:9-trimethyldecane; the first set is "lower" than the second set because at the first difference 2 is less than 3. When two sets of numbers are equally possible, then the

order of the prefixes in the name decides which shall be used, *e.g.*, 1-bromo-3-chloropropane and *not* 3-bromo-1-chloropropane. It should also be noted that the names of prefixes are arranged alphabetically, regardless of the number of each, *e.g.*, 5-ethyl-2 : 3-dimethyloctane.

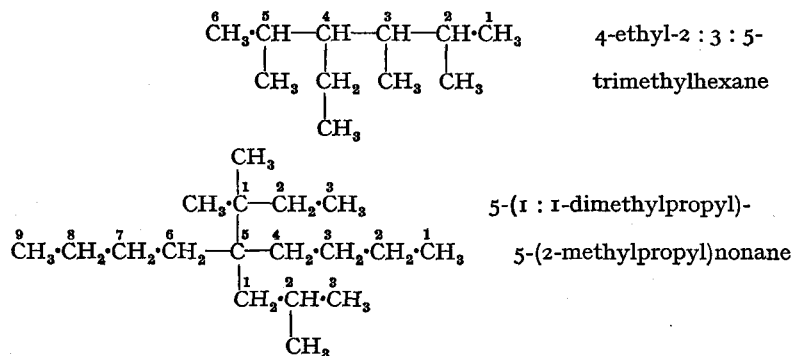
The I.U.P.A.C. system of nomenclature is undoubtedly superior to the other two, since it permits the naming of any paraffin on sight.

The following are examples of the three systems of nomenclature:

$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1.	2.	3.
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{CH}_2} \cdot \overset{4}{\text{CH}_2} \cdot \overset{5}{\text{CH}_3} \end{array}$	<i>n</i> -butane	<i>n</i> -butane	<i>n</i> -butane
	isopentane	ethyl dimethyl- methane	isopentane
		( <sup>2</sup> C is most highly branched)	
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \cdot \overset{2}{\text{C}} \cdot \overset{3}{\text{CH}_2} \cdot \overset{4}{\text{CH}_2} \cdot \overset{5}{\text{CH}_3} \\   \\ \text{CH}_3 \end{array}$	<i>neo</i> hexane	ethyl trimethyl- methane	2 : 2-dimethyl- butane
		( <sup>2</sup> C is most highly branched)	
$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \overset{5}{\text{CH}} \cdot \overset{6}{\text{CH}_2} \cdot \overset{7}{\text{CH}_2} \cdot \overset{8}{\text{CH}_2} \cdot \overset{9}{\text{CH}_3} \\   \\ \text{CH}_2 \\   \\ \text{CH} - \text{CH}_3 \\   \\ \text{CH} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	—	—	5-ethyl-2 : 3- dimethyloctane

*N.B.* The following names are retained for *unsubstituted hydrocarbons only*: isobutane, isopentane, neopentane, isohexane.

When several chains are of equal length, that chain chosen goes in series to: (a) the chain which has the greatest number of side-chains; (b) the chain whose side-chains have the lowest-numbered locants; (c) the chain having the greatest number of carbon atoms in the smaller side-chains; (d) the chain having the least-branched side-chains. Also, where there is a side-chain within a side-chain, the latter is also numbered, and the name of the complex radical is considered to begin with the *first* letter of its complete name, *e.g.*,



### Homologous Series

If we examine the formulæ of the various paraffins we find that the formula of each individual differs from that of its "neighbour" by  $\text{CH}_2$ , *e.g.*,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ , . . . A set of compounds, such as

the paraffins, in which the members differ in composition from one another by  $\text{CH}_2$ , is known as an *homologous series*, the individual members being known as *homologues*.

Throughout organic chemistry we find homologous series, each series being characterised by the presence of a *functional group*. The functional group is an atom or a group of atoms that causes a compound to behave in a particular way, *i.e.*, it is the functional group that gives rise to homologous series. Some of the more important functional groups and the classes of compounds to which they give rise are shown in Table I.

It is also possible for a compound to contain two (or more) identical or different functional groups, and this gives rise to *polyfunctional* compounds (see text).

If we examine the formulæ of the various paraffins, we find that the formula  $\text{C}_n\text{H}_{2n+2}$  will represent any particular homologue when  $n$  is given the appropriate value, *e.g.*, for pentane  $n$  is 5; therefore the formula of pentane is  $\text{C}_5\text{H}_{12}$ . The formula  $\text{C}_n\text{H}_{2n+2}$  is known as the *general formula* of the paraffins. The composition of any homologous series can be expressed by means of a general formula.

When we study the methods of preparation of the different paraffins, we find that several methods are common to all, *i.e.*, similar methods may be used for the preparation of all the homologues. This gives rise to the *general methods of preparation* of a particular homologous series.

TABLE I

Class of Compound.	Functional Group.	
	Formula.	Name.*
Alcohols . . . . .	$-\text{OH}$	Hydroxyl group
Aldehydes and ketones . . . . .	$\begin{array}{c} > \text{C}=\text{O} \\ > \end{array}$	Carbonyl group
Carboxylic acids . . . . .	$\begin{array}{c} > \text{C}=\text{O} \\ > \text{OH} \end{array}$	Carboxyl group
Cyanides . . . . .	$-\text{C}\equiv\text{N}$	Cyano group
Nitro-compounds . . . . .	$-\text{NO}_2$	Nitro group
Amines . . . . .	$-\text{NH}_2$	Amino group
Mercaptans . . . . .	$-\text{SH}$	Mercapto group
Sulphonic acids . . . . .	$-\text{SO}_3\text{H}$	Sulphonic acid group

\* Many functional groups are known by more than one name. Nomenclature is dealt with in each homologous series described in the text.

Examination of the properties of the paraffins shows that many properties are, more or less, common to all the paraffin homologues. This gives rise to the *general properties* of an homologous series.

The occurrence of homologous series facilitates the study of organic chemistry, since it groups together compounds having many resemblances. If we know the properties of several of the lower homologues, we can obtain a fair idea of the properties of higher homologues, *i.e.*, we can forecast (within limits) the properties of a compound that we have not yet prepared. The reader, however, must never be too hasty in predicting the properties of an unknown homologue. The idea of homologous series should be used as a guide, not as a hard-and-fast rule.

In view of what has been said above, we can see that in studying organic chemistry it is advantageous to describe first the general methods of preparation of an homologous series, and then the general properties of that series. It is also usual to describe the more important members individually, and

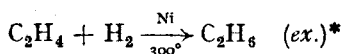


to indicate, at this stage, any *special* methods of preparation and any *special* properties. This is the way (wherever possible) in which we shall deal with organic chemistry throughout this book, and we shall start by reconsidering the paraffins from this point of view.

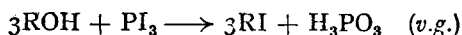
The general methods of preparation of the paraffins fall into three groups.

#### A. From compounds containing the same number of carbon atoms.

1. By the catalytic reduction of unsaturated hydrocarbons, *e.g.*, reduction of ethylene:



2. (a) An alcohol, ROH, is converted into its corresponding alkyl iodide using, *e.g.*, phosphorus triiodide (see alkyl halides):

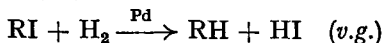


The alkyl iodide may then be converted into the paraffin by various means:

(i) Reduction with nascent hydrogen:



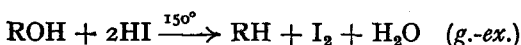
(ii) Catalytic reduction using palladium as catalyst (see p. 65 for the preparation of this catalyst):



(iii) Reduction by heating with concentrated hydriodic acid at  $150^\circ$ . This high temperature necessitates heating under pressure, since the maximum boiling point of hydriodic acid (57 per cent. HI) is  $126^\circ$ . High-pressure work is carried out in *autoclaves*, but where the pressure is not excessive, sealed, thick-walled glass tubes may be used. Reductions with hydriodic acid under pressure are carried out in sealed tubes:

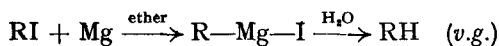


The reduction can be performed directly on the alcohol, using excess of hydriodic acid:

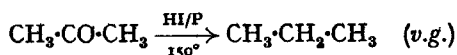


Reduction with concentrated hydriodic acid is usually carried out in the presence of a small amount of red phosphorus which regenerates the hydriodic acid from the iodine formed. The hydriodic acid-red phosphorus mixture is one of the most powerful reducing agents used in organic chemistry.

Instead of reduction, the alkyl iodide may be converted into the corresponding Grignard reagent, which is then decomposed by water to form the paraffin:



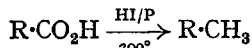
(b) By the reduction of a carbonyl compound with concentrated hydriodic acid and red phosphorus, heated under pressure at  $150^\circ$ , *e.g.*, acetone is converted into propane:



\* See preface for the significance of these terms in parentheses.

Alternatively, the carbonyl compound can be reduced to the corresponding alcohol, which is then reduced by HI/P (*cf.* above). On the other hand, ketones may be converted into the corresponding paraffins by the *Clemmensen* (see p. 150) and *Wolff-Kishner* (see p. 153) reductions.

(c) By the reduction of fatty acids,  $R\cdot CO_2H$ , with HI/P in a sealed tube at  $200^\circ$ :



The yields are very good for the higher paraffins, and may even be improved by heating the fatty acids with hydrogen under pressure in the presence of a nickel catalyst.

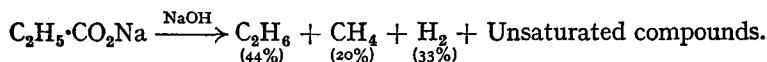
## B. From compounds containing a larger number of carbon atoms.

1. By heating a mixture of the sodium salt of a fatty acid and soda-lime:



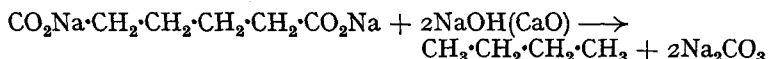
This process of eliminating carbon dioxide from a carboxylic acid is known as *decarboxylation*. Soda-lime is a very useful reagent for this process, but various other reagents may also be used.

Oakwood *et al.* (1950) have shown that only sodium acetate decomposes according to the equation given above. In all of the other cases tested—propionate, butyrate and caproate—various products were obtained, *e.g.*, with sodium propionate:



This method, therefore, is not suitable for the preparation of simple paraffins since, apart from the low yield of the desired product, it is very difficult to separate the mixtures obtained.

2. By heating a mixture of the disodium salt of a dicarboxylic acid and soda-lime, *e.g.*, sodium adipate gives *n*-butane:



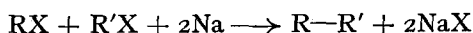
The reader may well ask: why not use tricarboxylic acids, etc.? When dealing with a preparation, there are at least three important points that must be considered: (i) the yield of crude product; (ii) the yield of pure product; (iii) the *accessibility* of the starting materials. In certain cases the yield of crude material is high, but the nature of the impurities is such that purification causes a large loss of material, resulting in a poor yield of pure product. On the other hand, it often happens that the product of one reaction is to be used as the starting material for some other compound which can readily be freed (*i.e.*, purified with very little loss) from the original impurity. Provided, then, that this impurity does not interfere with the second reaction, the crude material of the first step can be used as the starting material for the second. Thus the yield alone of a particular reaction cannot decide the usefulness of that method of preparation; the subsequent history of the product must also be taken into consideration. Furthermore, all things being equal, the more accessible materials, *i.e.*, readily prepared or purchased, are used as the starting materials.

With respect to the decarboxylation of acids as a means of preparing paraffins, the reader will find that tricarboxylic acids, etc., are not readily accessible; in fact, they are less accessible than the paraffins that can be

prepared from them. It would, therefore, be useless, from the practical point of view, to use these acids as starting materials for paraffins. From the point of view of learning the subject, however, some useful purpose is served in carrying out "paper reactions" with inaccessible materials, since the reader may then master reactions of practical value.

### C. From compounds containing fewer carbon atoms.

1. By the **Wurtz reaction** (1854). An ethereal solution of an alkyl halide (preferably the bromide or iodide) is treated with sodium, *e.g.*,



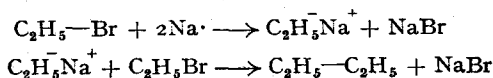
As previously pointed out, when we do not wish to specify a particular alkyl radical, we use the symbol R. When we deal with two unspecified alkyl radicals which may, or may not, be the same, we can indicate this by R and R': also, when dealing with compounds containing a halogen atom, and we do not wish to specify the halogen, we can indicate the presence of the unspecified halogen atom by means of X.

Consideration of the equation given above shows that in addition to the desired paraffin R—R', there will also be present the paraffins R—R and R'—R'. Unsaturated hydrocarbons are also obtained. Obviously, then, the best yield of a paraffin will be obtained when R and R' are the same, *i.e.*, when the paraffin contains an even number of carbon atoms and is symmetrical. It has been found that the Wurtz reaction gives good yields only for "even carbon" paraffins of high molecular weight, and that the reaction generally fails with tertiary alkyl halides (*q.v.*).

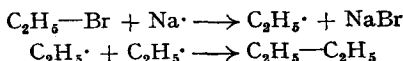
Sodium is used in the Wurtz reaction. Other metals, however, in a finely-divided state, may also be used, *e.g.*, Ag, Cu (see text).

Two mechanisms have been suggested for the Wurtz reaction, and there is evidence in favour of both. It is even possible that both take place simultaneously.

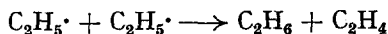
(i) The intermediate formation of an *organo-metallic* compound, *e.g.*, the formation of *n*-butane from ethyl bromide:



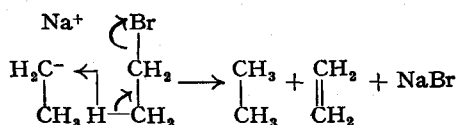
(ii) The intermediate formation of free radicals, *e.g.*,



One of the properties of free radicals is *disproportionation*, *i.e.*, intermolecular hydrogenation, one molecule acquiring hydrogen at the expense of the other, *e.g.*,

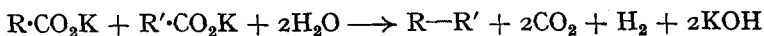


This would account for the presence of ethane and ethylene in the products. According to Morton *et al.* (1942), however, ethane and ethylene may be produced as follows:



This mechanism is particularly interesting in view of the fact that disproportionation is commonly accepted as a criterion for a free-radical mechanism. Furthermore, Bryce-Smith (1956) has obtained evidence that free radicals play only a minor part in the formation of the usual Wurtz coupling and disproportionation products. Also, Le Goff *et al.* (1958) have obtained evidence to show that the Wurtz reaction of sodium with 2-chloro-octane is a bimolecular reaction of an alkylsodium with an alkyl halide.

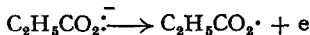
2. **Kolbe's electrolytic method** (1849). A concentrated solution of the sodium or potassium salt of a fatty acid or mixture of fatty acids is electrolysed, *e.g.*,



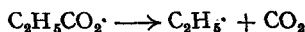
If R and R' are different, then hydrocarbons R—R and R'—R' are also obtained (*cf.* Wurtz reaction). Such mixtures can often be separated readily. Yields of 50–90 per cent. have been obtained with straight-chain acids containing 2–18 carbon atoms. Alkyl groups in the  $\alpha$ -position decrease the yield (usually below 10 per cent.). The by-products are olefins, alcohols (particularly in alkaline solution), and esters. It is also interesting to note that the yields of the alkanes are increased when dimethylformamide is used as solvent (Finkelstein *et al.*, 1960).

The Kolbe electrolytic method now has application in the synthesis of natural compounds, particularly lipids.

The mechanism of the reaction is still obscure; a possibility is via free radicals, *e.g.*, when sodium propionate is electrolysed, *n*-butane, ethane, ethylene and ethyl propionate are obtained. The propionate ion discharges at the anode to form a free radical:



This free propionate radical then breaks up into the free ethyl radical and carbon dioxide:

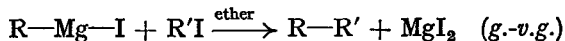


Then:

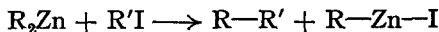
- (i)  $2C_2H_5\cdot \longrightarrow C_4H_{10}$
- (ii)  $C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4$
- (iii)  $C_2H_5\cdot + C_2H_5CO_2\cdot \longrightarrow C_2H_5\cdot CO_2C_2H_5$

Reaction (i) gives *n*-butane; (ii) gives ethane and ethylene by disproportionation (*cf.* Wurtz reaction); and (iii) gives ethyl propionate.

3. By the action of an alkyl halide on a Grignard reagent:



4. **Frankland's method** (1850). Dialkyl-zinc compounds readily react with alkyl halides to form hydrocarbons:



Dialkyl-zinc compounds are difficult to handle and as far as hydrocarbons are concerned, are used only for the preparation of paraffins containing a quaternary carbon atom, *e.g.*,



**General properties of the paraffins.** The name paraffin arose through contracting the two Latin words "*parum affinis*", which means "little affinity". This name was suggested because these hydrocarbons were apparently very unreactive. It is difficult to define the terms "reactive"

and "unreactive", since a compound may be reactive under one set of conditions and unreactive under another. Under "ordinary" conditions, the paraffins are inert towards reagents such as acids, alkalis, oxidising reagents, reducing reagents, etc. In recent years, however, it has been shown that the paraffins are reactive if the "right" conditions are used (see below).

**General physical properties of the paraffins.** The normal paraffins from  $C_1$  to  $C_4$  are colourless gases;  $C_5$  to  $C_{17}$ , colourless liquids; and from  $C_{18}$  onwards, colourless solids. The b.ps. rise fairly regularly as the number of carbon atoms in the compound increases. This holds good only for the normal compounds, and the difference in b.ps. decreases as the higher homologues are reached. Other physical properties, such as m.p., specific gravity, viscosity, also increase in the same way as the b.ps. (of the normal paraffins), *e.g.*, the specific gravity of the normal paraffins increases fairly steadily for the lower members, and eventually tends to a maximum value of about 0.79. Straight-chain paraffins containing at least six carbon atoms form *inclusion compounds* with urea (see p. 387).

At the moment comparatively little is known about the quantitative relationships between physical properties and chemical constitution. It is believed that variation in b.ps. of compounds is due to different *intermolecular* forces such as hydrogen bonding, dipole moments, etc. Hydrogen bonding may produce association, and this will cause the b.p. to be higher than anticipated (see, *e.g.*, alcohols). The greater the dipole moment of the compound, the higher is the b.p., since, owing to the charges, more work is required to separate the molecules, *e.g.*, nitro-compounds,  $R \cdot NO_2$ , which have large dipole moments, have much higher b.ps. than the paraffins in which the dipole moment is absent or very small.

Observation has shown that in a group of isomeric compounds (acyclic), the normal compound *always* has the highest b.p. and m.p., and generally, the greater the branching, the lower the b.p.

The paraffins are almost insoluble in water, but readily soluble in ethanol and ether, the solubility diminishing with increase in molecular weight.

It is believed that solubility depends on the following intermolecular forces: solvent/solute; solute/solute; solvent/solvent. A non-electrolyte dissolves readily in water only if it can form hydrogen bonds with the water. Thus paraffins are insoluble, or almost insoluble, in water. Methane is more soluble than any of its homologues; hydrogen bonding with the water is unlikely, and so other factors—possibly molecular size—must also play a part. A useful rule in organic chemistry with respect to solubility is that "like dissolves like", *e.g.*, if a compound contains a hydroxyl group, then the best solvents usually contain hydroxyl groups. This rule is not rigid (*cf.* paraffins).

X-Ray analysis of *solid* paraffins has shown that the carbon chains are fully extended, *i.e.*, zigzag. In the *liquid* state this extended form is also one of the

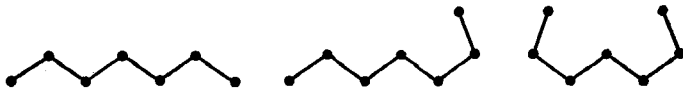


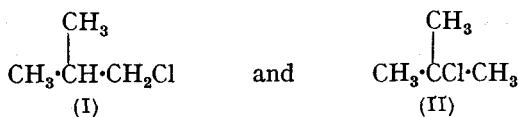
FIG. 3.1.

stable conformations provided that the carbon chain is not very long. When the number of carbon atoms is sixteen or more, the extended form is no longer present in the liquid state. The presence of a number of these different conformations (or *rotational isomers*) has been shown by a study of infra-red and Raman spectra of liquid paraffins. The various conformations arise from the fact that groups can rotate about single bonds (p. 404). Furthermore, it has been found that not all possible conformations are present, *e.g.*, *n*-heptane shows the presence of three conformations (Sheppard *et al.*, 1948, 1949). Fig. 1 shows diagrammatically three possible forms.

Since the dipole moment of methane is zero, the dipole moment of the methyl group is equal to that of the fourth C—H bond (in methane) and is directed along this axis. Thus replacement of hydrogen by a methyl group will not be expected to change the dipole moment, *i.e.*, the dipole moment of all paraffins, whether straight- or branched-chain, will be zero. This has been found to be so in practice. This will always hold good whatever conformation is taken up by the paraffin provided that no deformation of the normal carbon valency angle (of  $109^{\circ} 28'$ ) is produced in the twisting, since all methyl groups will be balanced by a C—H bond. It therefore follows that the electronegativity of *all* alkyl groups is equal to that of hydrogen, namely zero (p. 16). As soon as one hydrogen atom is replaced by another atom or group (other than alkyl), the resultant molecule will now be found to possess a dipole moment (see also p. 106).

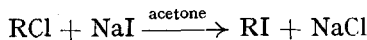
### General Chemical Properties of the Paraffins

1. **Halogenation** (see also the alkyl halides). Chlorination has been studied in very great detail. It may be brought about by light, heat or catalysts, and the extent of chlorination depends largely on the amount of chlorine used. A mixture of all possible isomeric monochlorides is obtained, but the isomers are formed in unequal amounts, due to the difference of the reactivity of primary, secondary and tertiary hydrogen atoms. Markownikoff (1875) found experimentally that the order of ease of substitution is tertiary hydrogen > secondary > primary. This observation is very useful for predicting the possible courses of a reaction, and qualitatively, to what extent each course will proceed, *e.g.*, chlorination of *isobutane* at  $300^{\circ}$  gives a mixture of two isomeric monochlorides:



We should expect to find more of (II) than (I); quantitative experiments show that this is so.

Bromination is similar to chlorination, but not so vigorous. Iodination is reversible, but it may be carried out in the presence of an oxidising agent, such as  $\text{HIO}_3$ ,  $\text{HNO}_3$ ,  $\text{HgO}$ , etc., which destroys the hydrogen iodide as it is formed (see p. 40). Iodides are more conveniently prepared by treating the chloro- or bromo-derivative with sodium iodide in methanol or acetone solution, *e.g.*,

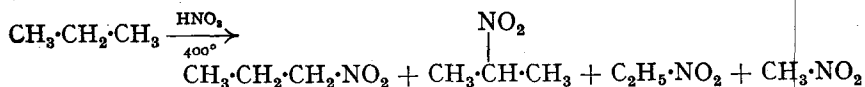


This reaction is possible because sodium iodide is soluble in methanol or acetone, whereas sodium chloride and sodium bromide are not.

Direct fluorination is usually explosive; special conditions are necessary for the preparation of the fluorine derivatives of the paraffins (see p. 120).

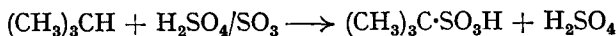
2. **Nitration** (see also p. 302). Under certain conditions, paraffins react with nitric acid, a hydrogen atom being replaced by a *nitro-group*,  $\text{NO}_2$ . This process is known as *nitration*. Nitration of the paraffins may be carried out in the vapour phase between  $150^{\circ}$  and  $475^{\circ}$ , whereupon a complex mixture of mononitroparaffins is obtained. The mixture consists of all the possible mononitro-derivatives and the nitro-compounds formed by every

possibility of *chain fission* of the paraffin; *e.g.*, propane gives a mixture of 1-nitropropane, 2-nitropropane, nitroethane and nitromethane:



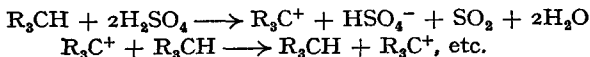
As in the case of halogenation, the various hydrogen atoms in propane are not replaced with equal ease.

3. **Sulphonation** (see also p. 606) is the process of replacing a hydrogen atom by a *sulphonic acid group*,  $\text{SO}_3\text{H}$ . Sulphonation of a normal paraffin from hexane onwards may be carried out by treating the paraffin with oleum (fuming sulphuric acid). The ease of replacement of hydrogen atoms is: tertiary very much greater than secondary, and secondary greater than primary; replacement of a primary hydrogen atom in sulphonation is very slow indeed. *iso*Butane, which contains a tertiary hydrogen atom, is readily sulphonated to give *tert.*-butylsulphonic acid:



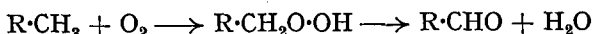
Sulphuryl chloride, in the presence of light and a catalyst, converts hydrocarbons into sulphonyl chlorides (p. 339).

It has been shown that in concentrated sulphuric acid, hydrocarbons containing a tertiary hydrogen atom undergo hydrogen exchange (Ingold *et al.*, 1936). The mechanism is believed to occur via a carbonium ion:



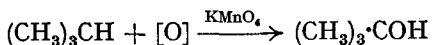
This reaction is of particular interest since optically active hydrocarbons have been racemised in sulphuric acid (see p. 412); *e.g.*, Burwell *et al.* (1948) have shown that optically active 3-methylheptane is racemised in sulphuric acid.

4. **Oxidation.** All paraffins readily burn in excess of air or oxygen to form carbon dioxide and water. Incomplete oxidation, due to insufficient air, produces carbon-black in variable yields. The mechanism of the oxidation of paraffins in the vapour state appears to take place via the formation of a hydrocarbon peroxide; *eg.*,



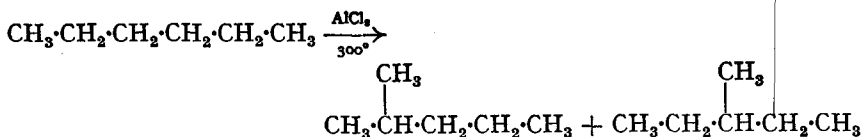
Other products are also obtained by fission of the carbon chain.

Oxidising reagents such as potassium permanganate readily oxidise a *tertiary* hydrogen atom to a hydroxyl group, *e.g.*, *isobutane* is oxidised to *tert.*-butanol:



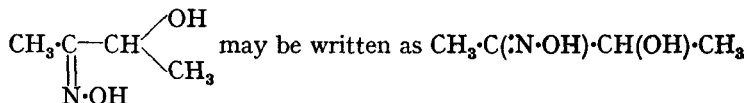
The *catalytic oxidation* of methane produces methanol,  $\text{CH}_3\text{OH}$ , and formaldehyde,  $\text{H} \cdot \text{CHO}$ . The catalytic oxidation of higher homologues ( $\text{C}_{16}$ —) produces long-chain fatty acids and some other products.

5. **Isomerisation** of *n*-paraffins into branched-chain paraffins in which the side-chain is a methyl group, may be brought about by heating the *n*-paraffin with aluminium chloride at  $300^\circ$ , *e.g.*, *n*-hexane isomerises into 2- and 3-methylpentanes:



According to Pines *et al.* (1946), this isomerisation does not occur unless a trace of water is present (to form HCl from the  $\text{AlCl}_3$ ) together with a trace of alkyl halide or an olefin. The isomerisation is believed to be an ionic chain reaction. The olefin "impurity" is converted into a carbonium ion (by the  $\text{AlCl}_3$  and HCl), and this initiates the chain reaction, isomerisation then occurring by 1,2-shift (p. 101).

Instead of writing out the formulæ of the 2- and 3-methylpentanes as shown in the equation, an alternative way is to write the formula in a "straight" line, enclosing in parentheses any side-chain; thus:  $\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$  and  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_3$ . The atoms or groups in parentheses are joined directly to the *preceding* carbon atom in the chain not placed in parentheses, *e.g.*,



In many cases where there is no ambiguity, the parentheses may be omitted, *e.g.*, isopropanol is  $\text{CH}_3 \cdot \text{CH} \cdot \text{CH}_3$ ; this is often written  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CH}_3$ ,



but if the rules are strictly adhered to, it should be written  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$ .

#### 6. The thermal decomposition of the paraffins (see *cracking*).

### PETROLEUM AND NATURAL GAS

Crude **petroleum** (*mineral oil*) is the term usually applied to the gases occurring naturally in the oilfields, the liquid from the wells, and the solids which are dissolved in, or have separated from, the liquid. The composition of crude petroleum varies with the locality of occurrence, but all contain paraffins (from about  $\text{C}_1$  to  $\text{C}_{40}$ ), cycloparaffins or naphthenes, and aromatic hydrocarbons. The low-boiling fractions of almost all petroleums are composed of paraffins; it is the composition of the higher-boiling fractions which differs according to the source of the petroleum. In addition to hydrocarbons, there are also present compounds containing oxygen, nitrogen, sulphur and metallic constituents.

**Natural gas** is the term applied to the large quantities of gas associated with or unassociated with liquid petroleum. The composition of natural gas varies with the source, and consists chiefly of the first six paraffins, the percentage of each decreasing with increasing molecular weight. Other gases such as water vapour, hydrogen, nitrogen, carbon dioxide and hydrogen sulphide may be present in amounts that vary with the locality of occurrence.

The origin of petroleum and natural gas is still uncertain. Many theories have been suggested, but not one explains all the known facts. There is now, however, general agreement that petroleum has organic origin, and this is due to the fact that the higher boiling fractions of petroleum contain optically active compounds (p. 399) and that petroleum has been shown to contain both animal and plant type of porphyrins, *i.e.*, hæmin and chlorophyll (Treibs, 1934-36). The problem is how organic matter is converted into petroleum. A very highly favoured theory is that it takes place by means of bacterial decomposition, but there is a growing belief that bacterial action is only the first stage in the conversion and this is then followed by physical and chemical stages.

Another highly favoured theory is that petroleum is formed from organic matter by the catalytic activity of certain natural inorganic compounds. There is a great deal of experimental work that supports this theory which, in many ways, appears superior to any other. It is probable that both mechanisms are operating.



**Distribution and general composition of crude petroleum.** If the residue of petroleum, after removal of volatile compounds, contains a large amount of paraffins or wax, the petroleum is classified as *paraffinic* or *paraffin base oil*. If naphthenes predominate, the petroleum is classified as *asphaltic* or *asphalt base oil*. The crudes from the wells in Pennsylvania, Iran, Irak and Rumania are paraffinic; those from Baku and Venezuela are asphaltic; and those from Oklahoma, Texas and Mexico are intermediate in composition, and may be classified as paraffinic and asphaltic.

**Distillation of petroleum.** The crude oil is nearly always associated with water and sand; hence the crude petroleum discharged from the top of the well contains water and sand in suspension. The mixture is passed, under pressure, into cylindrical tanks, and the gas, oil and solids are drawn off separately.

Except for the low-boiling hydrocarbons, no attempt is made to separate the individual hydrocarbons. The crude oil is fractionated by continuous distillation into four main fractions: **petrol** (*gasoline*), **kerosene** (*keresine*, *paraffin oil*), **gas oil** (*heavy oil*) and **lubricating oil**. The residue may be fractionated by means of vacuum-distillation to give light, medium and heavy lubricating oils, paraffin wax, and asphaltic bitumen. Each of the four main fractions may be further split up by batch distillation into fractions of narrow boiling range. Recently, it has been possible to isolate individuals by "superfractionation". The final number of fractions taken depends on the purpose in view.

Table II shows one set of fractions that may be obtained.

**Refining of the various fractions.** It appears that refining was originally introduced to remove the bad colour and objectionable odour of petrol. To-day it is realised that it is more important to remove sulphur compounds which lower the response of petrol to added tetraethyl-lead.

An internal-combustion engine, *i.e.*, one which burns fuel within the working cylinder, is more efficient the higher the compression ratio. Petrol engines use "spark ignition", and as the compression ratio increases, a point is reached when "knocking" is observed, *i.e.*, after passage of the firing spark, instead of

TABLE II

Name.	B.P. ° C.	Approximate Composition.	Uses.
Light petrol . . . . .	20-100	$C_5H_{12}$ - $C_7H_{16}$	Solvent
Benzine . . . . .	70-90	$C_6$ - $C_7$	Dry cleaning
Ligroin . . . . .	80-120	$C_6$ - $C_8$	Solvent
Petrol (gasoline) . . . . .	70-200	$C_6$ - $C_{11}$	Motor fuel
Kerosene (paraffin oil) . . . . .	200-300	$C_{12}$ - $C_{18}$	Lighting
Gas oil (heavy oil) . . . . .	above 300	$C_{12}$ - $C_{18}$	Fuel oil
Lubricating oil (mineral oil) . . . . .	"	$C_{16}$ - $C_{20}$	Lubricants
Greases, vaseline, petrolatum . . . . .	"	$C_{18}$ - $C_{22}$	Pharmaceutical preparations
Paraffin wax (hard wax) . . . . .	"	$C_{20}$ - $C_{30}$	Candles, waxed paper, etc.
Residue (asphaltic bitumen) . . . . .	"	$C_{30}$ - $C_{40}$	Asphalt tar; petroleum coke

all the fuel gas burning smoothly, the end portion burns with explosive violence, giving rise to a metallic rattle. The phenomenon of knocking is still not fully understood, but it has been found that, among other factors, the tendency to knock depends on the nature of the petrol. *n*-Paraffins tend to produce knocking far more than branched-chain paraffins. Edgar (1927) introduced 2 : 2 : 4-trimethylpentane (incorrectly known as *iso*-octane), which has higher antiknock properties, and *n*-heptane, which has lower antiknock properties than any commercial petrol, as standards for rating fuels. "*iso*-Octane" is arbitrarily given the value of 100 and *n*-heptane, 0, and the *octane number* of any fuel is the per cent. of "*iso*-octane" in a mixture of this compound and *n*-heptane which will knock under the same conditions as the fuel being tested.

Olefins and aromatic compounds have high octane numbers. Tetraethyl-lead also raises the octane number of a given petrol, but if sulphur compounds are

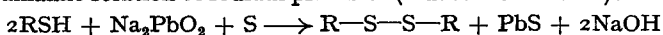
present, the response to this "dope" is lowered. Hence it is very important to remove sulphur compounds from petrol. The method of refining depends on the particular fraction concerned, and it is not practicable to refine before distillation (of the petroleum).

**Gasoline refining.** 1. Petroleum may be treated with concentrated sulphuric acid which reduces the sulphur content and also removes unsaturated compounds which polymerise on standing to form gums (see olefins). For straight-run gasoline, *i.e.*, gasoline obtained directly from crude petroleum, 98 per cent. sulphuric acid is used; for cracked gasoline (see later), 80 per cent. acid is used. This diluted acid removes only unstable unsaturated hydrocarbons, *i.e.*, those which tend to polymerise, leaving the stable unsaturated hydrocarbons, which raise the octane number of the gasoline. The diluted acid, however, causes some polymerisation to take place, but the gasoline is readily separated from these high-boiling polymers by distillation.

2. Instead of sulphuric acid the *adsorption process* can be used to remove thioalcohols (the chief group of sulphur compounds occurring in petroleum) from straight-run gasoline. The gasoline vapour is passed, under pressure, over an adsorbent such as clays, bauxite, etc., heated at about 450° C. Cracked gasoline contains sulphur as thiophens, and these cannot be removed so easily this way. Thiophens, however, are not so objectionable as thioalcohols.

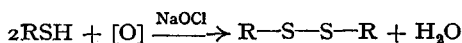
3. Straight-run gasolines may be refined by sodium hydroxide washing, which may remove almost all thioalcohol sulphur. Where this simple sodium hydroxide treatment is insufficient, it is followed by "sweetening". By sweetening, the thioalcohols (which give gasoline an unpleasant odour) are converted into disulphides, thereby improving the odour. Common sweetening agents are:

(i) An alkaline solution of sodium plumbite ("doctor solution"):

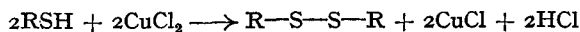


Free sulphur is added as required in carefully controlled amounts. The spent doctor solution is regenerated by blowing with air.

(ii) Sodium hypochlorite:



(iii) Cupric chloride:



Sweetening of "sour" gasoline does not appreciably alter the total sulphur content, and will not improve the octane number or lead susceptibility; in fact sweetened gasoline may have a lower octane number and lead susceptibility than unsweetened; only the odour is improved.

4. The *solutiser process* involves the use of solvents, and the more common ones are a methanolic solution of sodium hydroxide, sodium hydroxide and sodium butyrate, and potassium hydroxide and potassium butyrate. By this means the thioalcohols are removed completely, and thus the octane number and lead susceptibility are raised.

**Kerosene refining.** (i) The kerosene is washed first with sulphuric acid, then with sodium hydroxide solution, and finally with water. (ii) The kerosene is treated with liquid sulphur dioxide, which removes most of the sulphur compounds and aromatic hydrocarbons. Because of the removal of the latter, this method of refining cannot be used for gasoline.

**Gas oil and lubricating oil refining** is carried out by extraction with liquid sulphur dioxide.

## CRACKING

The thermal decomposition of organic compounds is known as *pyrolysis*; pyrolysis, when applied to paraffins, is known as *cracking*.

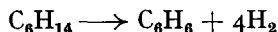
When heated to about 500–600°, paraffins are decomposed into smaller molecules, and the products obtained from a given paraffin depend on: (i) the structure of the paraffin; (ii) the pressure under which cracking is

carried out; and (iii) the presence or absence of catalysts such as silica-alumina, silica-alumina-thoria, silica-alumina-zirconia.

The mechanism of cracking is still obscure. Many theories have been suggested, and one that is highly favoured is a free-radical mechanism, evidence for which has been obtained from the observation that at cracking temperatures many hydrocarbons produce free alkyl radicals.

When petroleum is cracked, of all the compounds produced, the most important are those containing up to four carbon atoms: methane, ethane, ethylene, propane, propylene, butane, butylene and *isobutylene*. All of these have found wide application as the materials for the preparation of a large number of chemicals (see text).

By using suitable catalysts, paraffins containing six or more carbon atoms may be catalytically cyclised, *e.g.*, *n*-hexane, under pressure, passed over chromic oxide carried on an alumina support and heated at 480–550°, gives benzene (see also p. 50):



There are two main types of cracking: (i) liquid phase, and (ii) vapour phase.

(i) **Liquid phase cracking.** Heavy oil (from the petroleum distillation) is cracked by heating at a suitable temperature (475–530°) and under pressure (100–1000 lb/sq. in.), by means of which the cracked material is maintained in the liquid condition. The heavy oil is converted into gasoline to the extent of 60–65 per cent. of the oil (by volume), and has an octane number of 65–70. If attempts are made to increase the yield of gasoline, the octane number decreases.

(ii) **In vapour phase cracking** the cracking temperature is 600° and the pressure is 50–150 lb/sq. in. The cracking stock may be gasoline, kerosene, gas oils, but not the heavy oils, since these cannot be completely vaporised under the above conditions.

**Reforming** is the process whereby straight-run gasoline is cracked in order to raise the octane number. The gasoline is heated to about 600° and under pressure of 400–750 lb/sq. in., and the yield varies from 60 to 90 per cent.; the greater the yield, the lower is the octane number. Catalysts—the oxides of silicon and aluminium, plus small amounts of other oxides such as magnesia, zirconia, etc.—are usually employed in the reforming process, and their use produces a higher octane number (which is partly due to the increased content of benzene and toluene), and also increases the yield of gasoline.

Catalytic cracking is also increasing in use, since it has been found that catalytically cracked gasoline contains few olefins that readily polymerise. Gum formation in cracked gasolines is prevented by the addition of *inhibitors*, which are mainly phenols or aromatic amines, *e.g.*, catechol, *p*-benzylaminophenol, naphthylamine.

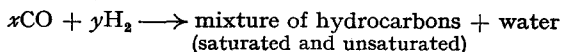
As pointed out above, large quantities of gases up to C<sub>4</sub> (and small amounts of C<sub>5</sub>, *i.e.*, the pentanes and pentenes) are produced in cracking. These gases may be used as the starting materials for various chemicals. Alternatively, by polymerising the olefins under the influence of a catalyst, *e.g.*, phosphoric acid on kieselguhr, or sulphuric acid, a high-octane (80–85) gasoline can be obtained.

**Treatment of natural gas.** When natural gas does not contain hydrocarbons above ethane, it is said to be “lean” or “dry”; when it contains the higher hydrocarbons (up to hexane) it is said to be “rich” or “wet”. The paraffins may be separated by fractional distillation under increased pressure, thereby giving methane, ethane, propane, *n*- and *isobutanes*, *n*-, *iso*- and *neopentanes*, and hexane. These gases are used for various purposes (see text). On the other

hand, natural gas itself may be used in the manufacture of various compounds. Oxidation of natural gas under carefully controlled conditions produces a complex mixture of compounds, among which are formaldehyde, acetaldehyde, acetic acid, acetone, methanol, ethanol, propanols and butanols. These are separated by distillation, solvent extraction, etc.

Wet gas is also used as a source of gasoline. The vapours of the liquid hydrocarbons (pentanes and hexane) in the wet gas are removed by various methods, e.g., compression, and cooling. The liquid product obtained from wet gas is known as "natural" or "casinghead" gas, and is "wild" because of the dissolved gases in it. These gases may be removed by distillation under pressure, and the resulting liquid is known as "stabilised natural gasoline"; this has very high antiknock properties.

**Synthetic Fuels.** (i) **Fischer-Tropsch Gasoline Synthesis or Synthine Process.** Synthesis gas, which is water-gas mixed with half its volume of hydrogen, at about 200–300° and a pressure of 1–200 atm., is passed over a catalyst.



The water-gas is made from coke. One third of the water-gas is passed with steam at 400° over iron, and the hydrogen-enriched water-gas is then mixed with the rest of the water-gas to produce the synthesis gas. This contains about 20 per cent. of inert gases. If the synthine process is carried out at atmospheric pressure, the carbon dioxide (about one third of the volume of the inert gases) is left in; if the synthesis is carried out under pressure, most of the carbon dioxide is washed out.

Synthesis gas contains sulphur compounds, and since these poison the catalyst, their removal is necessary. Hydrogen sulphide is removed by bog-iron ore. Organic sulphur compounds are oxidised under carefully controlled conditions, the sulphur being retained as sodium sulphate. If the synthesis gas contains large amounts of hydrocarbons, the latter are almost completely removed by passing through active carbon adsorbers before removing the sulphur compounds. The purified gas is then passed to the catalyst chambers, with or without compression. Other methods of preparing synthesis gas are also available, e.g., from methane and steam (p. 41).

Various metals and oxides have been used as catalysts. One of the best is: cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguhr (200 parts). When synthesis gas is passed over the catalyst at moderate pressure (9–11 atm.), more of the high-boiling fraction is obtained than when the process is carried out at atmospheric pressure. The liquid products are fractionally distilled, and refined in the same way as are the petroleum fractions; furthermore the higher-boiling fractions are cracked.

Gasoline from the synthine process costs more than that from petroleum. The Fischer-Tropsch oils appear to be more valuable as chemical raw materials than as fuels, and have been used for the production of higher olefins, fatty acids, detergents and in the *oxo*-process (see p. 127).

(ii) **Petrol from coal.** (a) Distillation of coal-tar gives a fuel oil, fractionation of which yields petrol (about one sixth of the volume). On the other hand, hydrogenation of the fuel oil under a pressure of 200 atm. and at about 475° produces petrol in 100 per cent. yield.

(b) In the *Bergius process* coal dust is heated to 400–500° in hydrogen at 250 atm., preferably in the presence of a catalyst, one of the best being an organic compound of tin. The yield of petrol may be as high as 60 per cent. (on the coal used).

(c) In the *I.C.I. process* coal dust is mixed with heavy oil to form a paste (50 per cent. of oil), which is pumped, with hydrogen, under pressure (250 atm.), into chambers containing the catalyst (organic tin compound) heated at 450°. The gases produced are scrubbed and condensed, and the liquid fractions are distilled to give the petrol fraction. The higher-boiling oils may be further hydrogenated to give more petrol.

## QUESTIONS

1. Write out the structures and names (by the three methods described in the text) of the isomeric hexanes. State how many primary, secondary, tertiary and quaternary carbon atoms there are in each isomer.

2. By means of equations, show how you would convert methane into propane.

3. What is the percentage of carbon and hydrogen in the paraffin  $C_{30}H_{62}$ ? Could you distinguish this paraffin from its next homologue by determining the percentage composition of each hydrocarbon?

4. Synthesise all the alkanes you can, by methods dealt with so far, from (a)  $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_3$ ; (b)  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ .

5. Define and give examples of:—(a) isomerism, (b) substitution, (c) homologous series, (d) cracking, (e) nitration, (f) sulphonation, (g) decarboxylation.

6. What reagents could you use to convert:—(a) a monohalogen derivative of a paraffin and (b) carbonyl compounds, into the corresponding and higher paraffins?

7. Write notes on:—(a) the Wurtz reaction, (b) Kolbe's electrolytic method, (c) Frankland's method, (d) Fischer-Tropsch reaction.

The reader should test himself on the general methods of preparation and general properties of any homologous series.

## READING REFERENCES

*Handbook for Chemical Society Authors*. Special Publication No. 14. The Chemical Society (1960).

Rules for I.U.P.A.C. Notation for Organic Compounds, Longmans, Green (1961).

Beezer, Latin and Greek Roots in Chemical Terminology, *J. Chem. Educ.*, 1940, 17, 63.

Hurd, The General Philosophy of Organic Nomenclature, *J. Chem. Educ.*, 1961, 38, 43.

Gilman, *Advanced Organic Chemistry*, Wiley (1942, 2nd ed.), (i) Vol. I, Ch. 1. Reactions of the Paraffins. (ii) Vol. II, Ch. 23. Constitution and Physical Properties of Organic Compounds.

*Advances in Organic Chemistry*, Vol. I (1960). Weedon, The Kolbe Electrolytic Synthesis, p. 1.

Goldstein, *The Petroleum Chemicals Industry*, Spon (1949).

Brooks, *The Chemistry of the Non-benzenoid Hydrocarbons*, Reinhold (1950, 2nd ed.).

Astle, *The Chemistry of Petrochemicals*, Reinhold (1956).

Rossini, Hydrocarbons in Petroleum, *J. Chem. Educ.*, 1960, 37, 554.

CHAPTER IV  
UNSATURATED HYDROCARBONS

**Olefins, Alkylenes or Alkenes**

THE olefins are the unsaturated hydrocarbons that contain one double bond. The simplest member of the series is ethylene,  $\text{CH}_2=\text{CH}_2$ ; hence this homologous series is often referred to as the "ethylene series". The olefins have the general formula  $\text{C}_n\text{H}_{2n}$ , and the double bond is also known as the "olefinic bond" or "ethylenic bond".

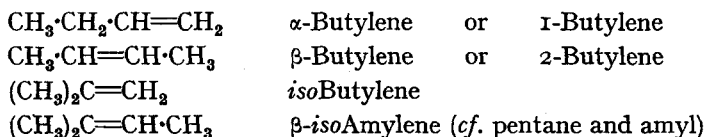
Olefins have recently become very important technically, since they are obtained in huge quantities in the cracking of petroleum, and may be used to prepare a large variety of organic compounds (see text).

**Nomenclature.** The name olefin arose from the fact that ethylene was called "olefiant gas" (oil-forming gas), since it formed oily liquids when treated with chlorine or bromine. The original name given to this homologous series was olefine; but it was later decided to reserve the suffix *-ine* for *basic* substances only. Since the name olefine had gained wide usage, it was decided to compromise and call the series the olefins.

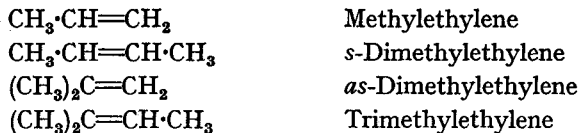
One method of nomenclature is to name the olefin from the corresponding paraffin by changing the suffix *-ane* of the latter into *-ylene*, e.g., (methylene), ethylene, propylene, etc.

The name alkylene is obtained in a similar manner, *alkane* being converted into *alkylene*.

Isomers differing only in the position of the double bond are prefixed by Greek letters or numbers which indicate the position of the double bond. The lowest number is usually given to the double bond (see below), and the number (or Greek letter) indicates the *first* of the two carbon atoms that are joined together by the double bond, e.g.,

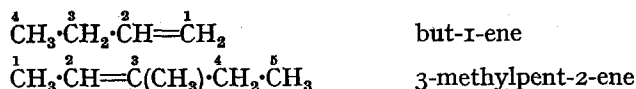


Another method of nomenclature is to consider ethylene as the parent substance and the higher members as derivatives of ethylene. If the compound is a monosubstituted derivative of ethylene, then no difficulty is encountered in naming it; if the compound is a disubstituted derivative of ethylene isomerism is possible, since the alkyl groups can be attached to the same or different carbon atoms. When the groups are attached to the same carbon atom the olefin is named as the *asymmetrical* or *unsymmetrical* compound (abbreviated to *as-* or *unsym-*); when attached to different carbon atoms the olefin is named as the *symmetrical* (*sym-* or *s-*) compound, e.g.,

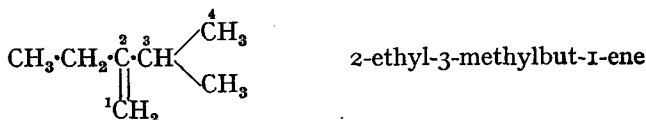


According to the I.U.P.A.C. system of nomenclature, the class suffix of the olefins is *-ene*, and so the series becomes the alkene series. The longest carbon chain containing the double bond is chosen as the parent alkene,

the name of which is obtained by changing the suffix *-ane* of the corresponding paraffin into *-ene*. The positions of the double bond and side-chains are indicated by numbers, the lowest number possible being given to the double bond, and this is placed before the suffix, *e.g.*,

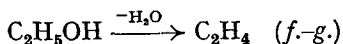


When there are several chains of equal length containing the double bond, then the same principles apply as for the alkanes (p. 47), *e.g.*,



A double or triple bond is regarded as a functional group. When there are several functional groups in the molecule, then the lowest number possible is given, in order of preference: (i) to the *principal* functional group of the compound; (ii) to the double or triple bond; and (iii) to atoms or groups designated by prefixes.

**General Methods of Preparation of the Olefins.** 1. By the action of concentrated sulphuric acid, at 160–170°, on primary alcohols. The acid acts as a dehydrating agent, removing one molecule of water from the alcohol to form the olefin, *e.g.*, ethylene from ethanol:



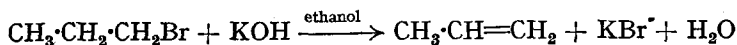
Dehydration of secondary and tertiary alcohols is best carried out using *dilute* sulphuric acid, since the olefins produced from these alcohols (particularly tertiary alcohols) tend to polymerise under the influence of the concentrated acid. The yields of olefin from secondary and tertiary alcohols are very good.

Instead of sulphuric acid, glacial phosphoric acid ( $\text{HPO}_3$ ), phosphorus pentoxide, or alumina may be used. With alumina, at 350°, the yields are *v.g.-ex.* Brandenberg *et al.* (1950) have converted all three classes of alcohols into olefins in excellent yields by means of boric acid as catalyst (borates are formed as intermediates):



Methyl xanthates may also be used to prepare olefins (p. 131).

2. By the action of *ethanolic* potassium hydroxide on monohalogen derivatives of the paraffins, *e.g.*, propylene from propyl bromide:



This is not a very important method for the preparation of the lower alkenes, since these may be prepared directly from the corresponding alcohols, which are readily accessible. The reaction, however, is very important, since by means of it a double bond can be introduced into an organic compound (see text). The yield of olefin depends on the nature of the alkyl halide used; it is fair with primary, and very good for secondary and tertiary alkyl halides. Ethylene cannot be prepared by this method from ethyl halide (see alkyl halides for the mechanism of *dehydrohalogenation*, *i.e.*, removal of halogen acid).



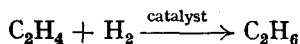


7. A number of olefins are prepared by the cracking of petroleum (p. 58), *e.g.*, ethylene, propylene, butylenes, etc. (see also the individuals). For the production of the lower olefins the most suitable starting material is gas oil, whereas for the higher olefins it is best to use paraffin wax or Fischer-Tropsch wax (p. 60). The lower olefins ( $C_2-C_5$ ) are also prepared by the catalytic dehydrogenation of saturated hydrocarbons, the most satisfactory catalysts being those of the chromium oxide-alumina type.

**General properties of the olefins.** The members containing two to four carbon atoms are gases; five to fifteen, liquids; sixteen onwards, solids at room temperature. All are lighter than water, in which they are insoluble, and they burn in air with a luminous smoky flame.

Owing to the presence of a double bond, the olefins undergo a large number of *addition* reactions, but under special conditions they also undergo substitution reactions. The high reactivity of the olefinic bond is due to the presence of the two  $\pi$ -electrons. These are less firmly held between the two nuclei than the  $\sigma$ -electrons, and are more exposed to external influences, and so are readily polarisable. It is the  $\pi$ -electrons which undergo the electro-meric effect at the requirements of the attacking reagent, and when addition occurs, the trigonal arrangement in the olefin changes to the tetrahedral arrangement in the saturated compound produced (see p. 429).

1. Olefins are readily hydrogenated under pressure in the presence of a catalyst. Finely divided platinum and palladium are effective at room temperature; nickel on a support (Sabatier-Senderens reduction) requires a temperature between  $200^\circ$  and  $300^\circ$ ; Raney nickel is effective at room temperature and atmospheric pressure:



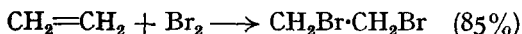
Platinum and palladium-black, *i.e.*, the metals in a very finely divided state, may be prepared by reducing their soluble salts with formaldehyde. Adams' platinum-platinum oxide catalyst is prepared by reducing platinum oxide with hydrogen before the addition of the compound being hydrogenated, or it may be added to the compound, reduction of the oxide taking place during hydrogenation.

One molecule of hydrogen is absorbed for each double bond present in the unsaturated compound.

The olefinic bond is readily reduced *catalytically*, but it is not reduced by metals and acid, or sodium and ethanol, unless the double bond is in the  $\alpha\beta$ -position with respect to certain groups (see text).

The mechanism of catalytic hydrogenation is not yet fully understood. It appears that adsorption occurs to give metal-carbon and metal-hydrogen bonds. In this way the catalyst lowers the energy of activation.

2. Olefins form addition compounds with chlorine or bromine, *e.g.*, ethylene adds bromine to form ethylene bromide:

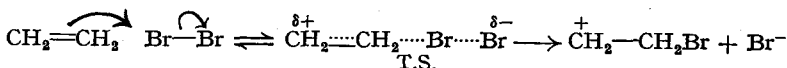


Addition of halogen to olefins can take place by two types of mechanism, polar or free-radical.

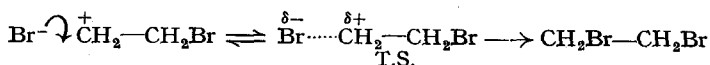
**Polar mechanism.** Evidence for this mechanism is as follows. Stewart *et al.* (1923) showed that the reaction between ethylene and bromine (in the absence of light) occurs only at the surface of the reaction vessel. Norrish (1923) showed that a *polar* surface was necessary. When the walls of the container were coated with paraffin wax (a non-polar substance), the rate of reaction between ethylene and bromine was very much reduced, whereas when the walls were coated with stearic acid (a polar substance), the reaction rate was very much increased. Norrish *et al.* (1926), examining the addition of chlorine to ethylene, showed that a small amount of water vapour catalyses the reaction when the

walls of the container were "bare", but had no effect when the walls had been previously coated with paraffin wax. Water vapour can be adsorbed on bare glass but not on wax-coated glass. All these experiments lead to the conclusion that reaction occurs at the *surface* and takes place by a polar mechanism. That a polar mechanism is operating is supported by the fact that the reaction is also catalysed by inorganic halides such as aluminium chloride, etc. The addition of halogen to olefins may also be carried out in a suitable solvent, e.g., chloroform, carbon tetrachloride.

The next problem to be considered is whether in this addition reaction the halogen behaves as an electrophilic or a nucleophilic reagent. All the evidence has shown that reaction takes place in *two stages*, with the halogen behaving as an electrophilic reagent, e.g., Francis (1925) showed that when ethylene reacts with bromine in aqueous sodium chloride solution, the products are ethylene dibromide and 1-bromo-2-chloroethane; *no ethylene dichloride is obtained*. These results are readily explained by the following mechanism:



The bromine atom that adds on shares a pair of electrons from the ethylene molecule, and in doing so releases its own bonding pair to the other bromine atom (of the bromine molecule), the latter thus being released as a bromide ion. Since the bromine atom that adds on first *gains* a share in the two electrons retained by the ethylene molecule, bromine is thus an electrophilic reagent. The carbonium ion produced can now combine with *any* negative ion, and so, since *both* bromide and chloride ions are available, both of these can add on to give the final products:

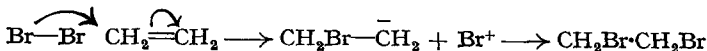


In the same way, the  $\text{Cl}^-$  adds on to give  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$ .

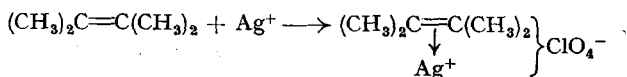
It has been shown, however, that the above mechanism for addition of halogen to olefins satisfies many reactions but not others (Robertson *et al.*, 1937- ).

The addition of halogen to a double bond is *trans*; this stereochemical aspect is discussed on p. 428.

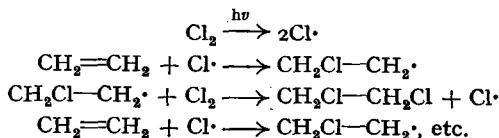
An interesting point about the above mechanism is why, with a symmetrical olefin such as ethylene, the addition is not nucleophilic, *i.e.*,



Several reasons have been proposed to explain electrophilic attack, e.g., negative ions (nucleophilic reagents) are hindered from attacking ethylenic carbon atoms by the screen of  $\pi$ -electrons. In fact,  $\pi$ -electrons are very susceptible to attack by electrophilic reagents. Thus olefins are themselves nucleophilic reagents; e.g., many olefins form addition complexes with the silver ion as, e.g., perchlorate. These addition compounds are known as  $\pi$ -complexes (p. 70).

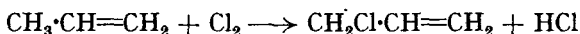


**Free-radical mechanism.** Under suitable conditions, halogens may add to olefins by a free-radical mechanism, e.g., Stewart *et al.* (1935) have shown that the addition of chlorine to ethylene is accelerated by light. This suggests a free-radical mechanism.



It may be asked why the free radical  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot$  does not combine with the other chlorine atom (free radical). There is, of course, always a chance of this occurring, but since the concentration of the chlorine molecules is infinitely greater, the reaction will therefore proceed as shown above. On the other hand, since the concentration of the ethylene is high, it would appear that the free radical  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot$  could react with ethylene molecules. If this were to happen, polymerisation (or at least dimerisation) would take place. There appears to be no evidence for this, and so, if the reaction is via free radicals, we must suppose it to take place as shown. This type of reaction is known as a free-radical chain reaction, and once started, carries on until the reactants are used up, or the chain broken by the destruction of the free radicals (see below, polymerisation).

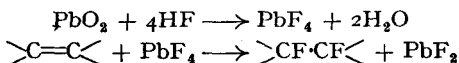
Instead of addition reactions with the halogens, the olefins may undergo substitution provided the right conditions are used. Thus when straight-chain olefins are treated with chlorine at a high temperature, they form mainly monochlorides of the allyl type, *i.e.*, in the chain  $-\text{C}-\overset{\times}{\text{C}}-\text{C}=\text{C}-$ , it is the hydrogen of  $\overset{\times}{\text{C}}$  that is substituted (see allyl compounds); *e.g.*, propylene heated with chlorine between  $400^\circ$  and  $600^\circ$  gives allyl chloride:



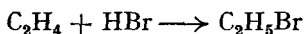
Above a certain temperature range, substitution takes place; below this range, addition takes place. The temperature range varies according to the olefin used, but for most olefins lies between  $300^\circ$  and  $600^\circ$ .

On the other hand, substitution is fairly easy with branched-chain olefins, and again occurs in the allyl position (see, *e.g.*, isobutene).

The action of fluorine on olefins usually results in the formation of carbon tetrafluoride, but addition to the double bond may be effected by treating the olefin with hydrogen fluoride in the presence of lead dioxide (Henne *et al.*, 1945); the fluorinating agent is lead tetrafluoride:

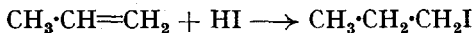


3. Olefins form addition compounds with the halogen acids, *e.g.*, ethylene adds hydrogen bromide to form ethyl bromide:

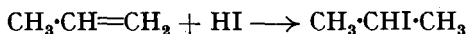


The order of reactivity of the addition of the halogen acids is hydrogen iodide > hydrogen bromide > hydrogen chloride > hydrogen fluoride. The conditions for the addition are similar to those for the halogens; the addition of hydrogen fluoride, however, is effected only under pressure.

In the case of unsymmetrical olefins it is possible for the addition of the halogen acid to take place in two different ways, *e.g.*, propylene might add on hydrogen iodide to form propyl iodide:



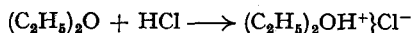
or it might form isopropyl iodide:



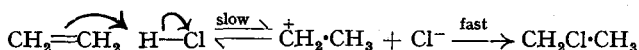
Markownikoff studied many reactions of this kind, and as a result of his work, formulated the following rule: *the negative part of the addendum adds on to the carbon atom that is joined to the least number of hydrogen atoms.*

In the case of the halogen acids the halogen atom is the negative part, and so *isopropyl* halide is obtained.

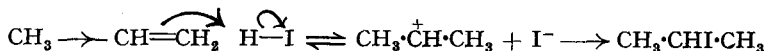
Markownikoff's rule is empirical, but may be explained theoretically on the basis that the addition occurs by a polar mechanism. As with halogens, the addition of halogen acid is an electrophilic reaction, the proton adding first, followed by the halide ion. That the polar mechanism operates is supported by much experimental work. One piece of evidence that may be cited is that Hennion *et al.* (1939, 1941) have shown that the addition of hydrogen chloride or bromide to, *e.g.*, cyclohexene, is faster in hydrocarbon solvents such as heptane than in nucleophilic solvents such as ether. These rate differences may be explained by the fact that ether but not heptane can form oxonium ions with protons and thereby greatly reduce the proton concentration:



This also indicates that the addition of the proton is the rate-determining step. Thus:

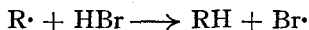


Now consider the case of propylene. Since the methyl group has a +I effect, the electromeric effect will be *away* from the methyl group. Thus the proton adds on to the carbon *farthest* from the methyl group, and the halide ion then adds to the carbonium ion:

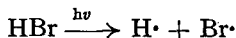


**The Peroxide Effect (Kharasch, 1933).** The presence of oxygen or peroxides that are formed when the olefin stands exposed to the air, or added peroxides such as benzoyl peroxide, causes the addition of hydrogen bromide to take place in the direction opposite to that predicted by Markownikoff's rule. This departure from the rule is known as the "abnormal" reaction, and was shown to be due to the "peroxide effect" (Kharasch *et al.*, 1933). Hydrogen chloride, hydrogen iodide and hydrogen fluoride do not exhibit the abnormal reaction. The abnormal reaction in the presence of peroxides can be prevented by the addition of an "inhibitor" such as diphenylamine, catechol, etc. It has been found that the addition of hydrogen bromide is "abnormally" effected photochemically as well as by peroxide catalysts (Vaughan, *et al.*, 1942).

The mechanism of the peroxide effect is believed to be a free-radical chain reaction, the peroxide generating the free radical R· (*cf.* polymerisation, below):



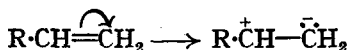
In the photochemical addition, the bromine atom is produced by a quantum of light:



At least two explanations may be offered for the fact that the bromine atom attacks the carbon atom *not* joined to the least number of hydrogen atoms:

(i) Free halogen atoms are *electrophilic* reagents owing to their tendency to complete their octets, and hence will attack the olefin at its point of highest electron density. As we have seen above, the electromeric effect in olefins

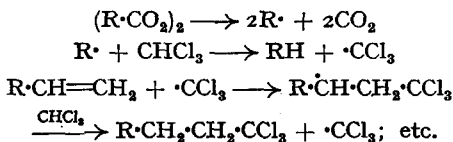
of the type  $R\cdot CH=CH_2$  takes place *away* from the CH group, owing to the electron-repelling effect of the R group, *i.e.*, we have:



(ii) Each of two carbon atoms joined by the double bond retains its  $\pi$ -electron. Thus a bromine atom can attack either carbon atom equally well, but of the two free radicals that can be produced, *viz.*,  $R\cdot \overset{+}{C}H-CH_2Br$  and  $R\cdot CHBr-CH_2\cdot$ , it is the former which has the lower free energy, and hence this one is more likely to be formed.

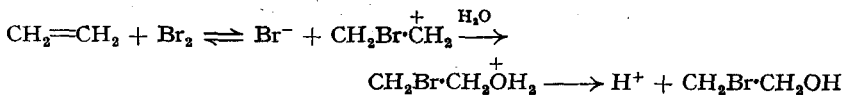
Another problem is why only hydrogen bromide exhibits the peroxide effect. The answer is possibly as follows. In HX, the bond strength order is  $HCl > HBr > HI$ . Thus the H—Cl bond is too strong to be broken (homolytically). On the other hand, since the H—I bond is weaker than that of H—Br, one might have expected HI to also exhibit the peroxide effect. The reason that it does not is believed to be due to the fact that although HI is split into hydrogen and iodine atoms, iodine atoms are not reactive enough to add on to a double bond, but combine with each other to form iodine molecules, thereby continuously breaking the chain reaction.

Tri- and tetra-halogenated methanes also add on to a *terminal* double bond in the presence of peroxides (Kharasch *et al.*, 1945- ). Here again the mechanism is believed to be a free-radical chain reaction, *e.g.*,

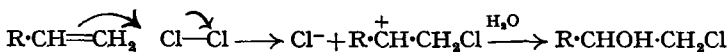


4. Hypohalous acids add on to olefins to form halohydrins. Usually the reaction is carried out by treating the olefin with chlorine- or bromine-water.

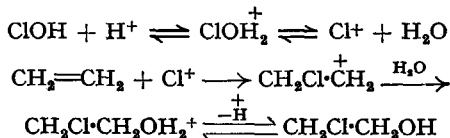
The mechanism is believed to be (*cf.* p. 66):



With unsymmetrical olefins, the hydroxyl group adds on to the carbon atom joined to the least number of hydrogen atoms:



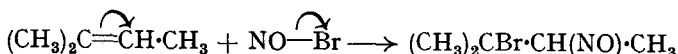
Aqueous solutions of hypohalous acid also add on to olefins in the presence of strong acids to form halohydrins, *e.g.*, the addition of hypochlorous acid to ethylene. The mechanism is probably via the formation of the chlorinium ion:



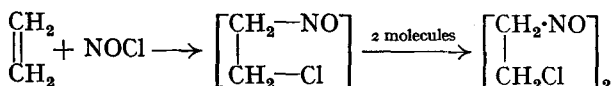
Various sulphenyl halides form adducts with olefins; 2 : 4-dinitrobenzene-sulphenyl chloride in particular has been found extremely useful for identifying olefins (Kharasch *et al.*, 1949- ).



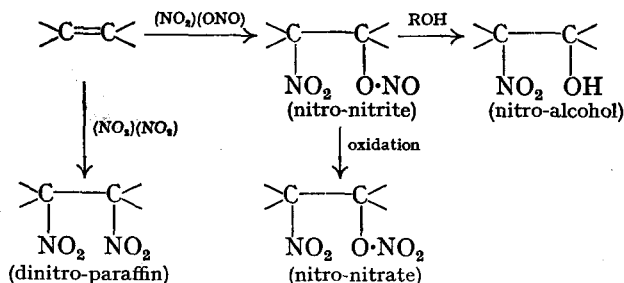
kownikoff's rule), e.g., trimethylethylene adds on nitrosyl bromide to form the following trimethylethylene nitrosobromide:



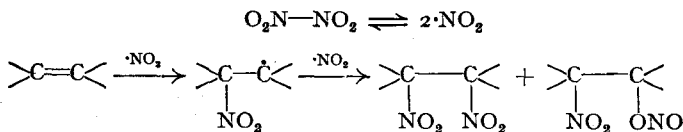
The reaction with nitrosyl chloride is usually carried out by treating a solution of the olefin and ethyl or pentyl (amyl) nitrite in glacial acetic acid with concentrated hydrochloric acid, the temperature being maintained at about  $10^\circ$ . The nitroschlorides (and nitrosobromides) are usually *bimolecular* crystalline solids, e.g.,



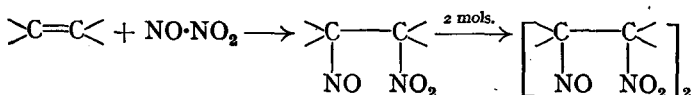
The addition of the oxides of nitrogen to olefins is complicated, and much of the work done is of a doubtful nature. The compound formed depends on the structure of the olefin and the nature of the "nitrous fumes"; usually a mixture of addition products is formed. According to Levy, Scaife *et al.* (1946), when ethylene, propylene, and some other olefins react with dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , then according to the conditions dinitro-paraffin, nitro-alcohols and nitro-alkyl nitrates can be obtained in high yield. The reaction is best carried out in the liquid phase at  $-10^\circ$  to  $+25^\circ$ . Dinitro-compounds or nitro-nitrites are produced, but the latter are usually partly oxidised to nitro-nitrate. The unchanged nitro-nitrite is unstable, tending to explode, but it may be converted into the stable nitro-alcohol when treated in the cold with water or a lower aliphatic alcohol. The nitrogen tetroxide behaves as (i) two  $\text{NO}_2$  groups to give dinitro-compounds, and (ii) one  $\text{NO}_2$  group and one  $\text{ONO}$  group (nitrite radical) to give nitro-nitrites (see also nitro-compounds):



According to Schechter *et al.* (1953), the addition of dinitrogen tetroxide occurs via the formation of the nitronium free-radical:



Dinitrogen trioxide in ether adds on to olefins at  $-70$  to  $5^\circ$  to give mainly dimeric nitro-nitroso compounds:

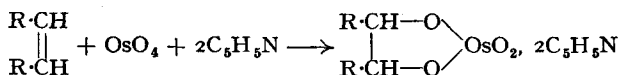






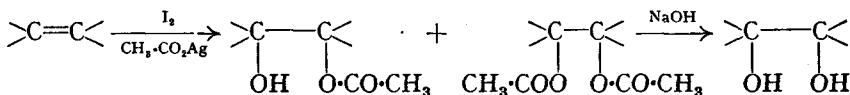
These cyclic compounds (*osmic esters*), on refluxing with aqueous ethanolic sodium hydrogen sulphite, are hydrolysed to 1 : 2-glycols (*cis*-glycols).

If the addition of osmium tetroxide is carried out in the presence of pyridine, coloured crystalline compounds are obtained, usually in theoretical yield:



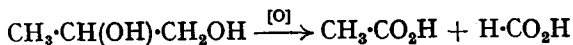
Berkowitz *et al.* (1958) have shown that ruthenium tetroxide is more convenient to use than osmium tetroxide; it is less toxic.

*cis*-Hydroxylation of a double bond may also be effected by treating the olefin with iodine and silver acetate in wet acetic acid, and then hydrolysing the mixed mono- and di-acetates with alkali (Barkley *et al.*, 1954):

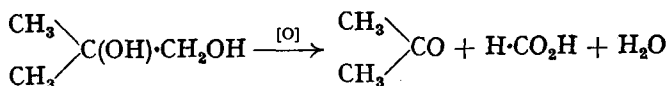


Glycols are readily oxidised to acids or ketones by means of acid permanganate or acid dichromate, the nature of the products being determined by the structure of the glycol, *e.g.*,

(a) propylene glycol gives acetic and formic acid:



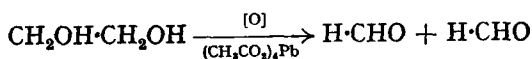
(b) *iso*Butylene glycol gives acetone and formic acid:



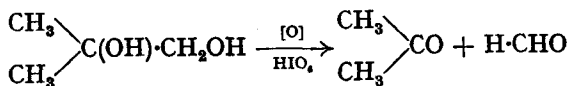
Sodium bismuthate, in acid solution, also effects similar oxidations (Rigby, 1950). An advantage of this reagent is that an aldehyde is one of the products (when possible); it is *not* further oxidised.

Oxidation of a glycol may also be effected by lead tetra-acetate,  $(\text{CH}_3\cdot\text{CO}_2)_4\text{Pb}$ , or by periodic acid,  $\text{HIO}_4$  or  $\text{H}_5\text{IO}_6$ , the products being aldehydes or ketones, according to the structure of the glycol, *e.g.*,

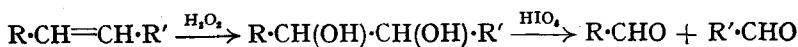
(a) ethylene glycol gives two molecules of formaldehyde:



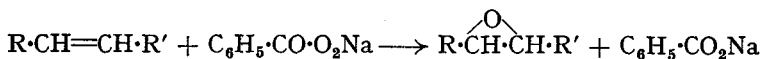
(b) *iso*Butylene glycol gives acetone and formaldehyde:



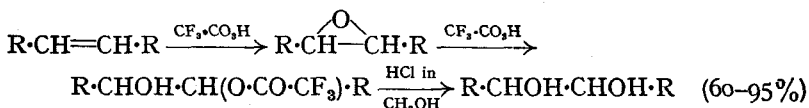
It can be seen that whatever oxidising agent is used the glycol is split into two fragments, the rupture of the carbon chain occurring between the two carbon atoms joined to the hydroxyl groups. Since these two carbon atoms were linked together by the double bond in the original olefin, identification of the two fragments which may be acids, aldehydes or ketones, will indicate the position of the double bond in the olefin, *e.g.*,



9. **Priesschaiev's reaction** (1912). By means of per-acids, the double bond in olefins is converted into the *epoxide* (olefin oxide). Perbenzoic acid,  $C_6H_5 \cdot CO \cdot O_2H$ , and monopero-phthalic acid,  $CO_2H \cdot C_6H_4 \cdot CO \cdot O_2H$ , have been widely used for this reaction, *e.g.*,



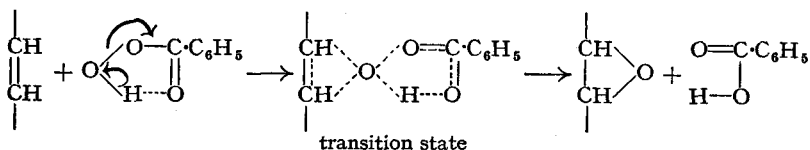
Emmons *et al.* (1954, 1955) have found that peroxytrifluoroacetic acid ( $CF_3 \cdot CO \cdot O_2H$ ) is a very good reagent for epoxidation and hydroxylation.



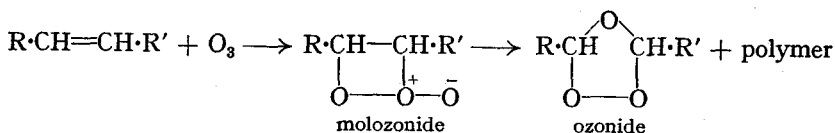
This method is particularly useful for high molecular-weight alkenes with a terminal double bond (these are only slowly hydroxylated by other per-acids). Furthermore, peroxytrifluoroacetic acid may be used to hydroxylate negatively substituted olefins, *e.g.*, ethyl acrylate,  $CH_2=CH \cdot CO_2C_2H_5$ .

Epoxides are readily converted into glycols (p. 248).

Many mechanisms have been proposed for epoxidation, but none is certain. According to Pausacker *et al.* (1955), the mechanism is

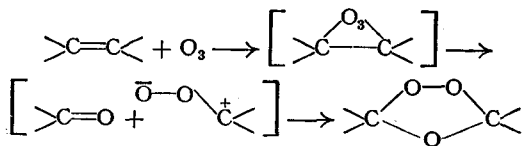


10. Olefins add on ozone to form **ozonides**. These are usually explosive in the free state, and their structure and mechanism of formation have been the subject of a great deal of work. Staudinger (1922) suggested that the *molozone* is formed first, and this then rearranges to the ozonide, some polymerising as well.

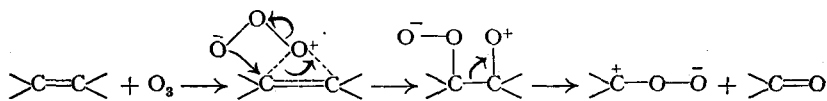


Criegee (1959) has isolated the molozone of *trans*-di-*t*-butylethylene at  $-80^\circ$  ( $R = R' = (CH_3)_3C-$ ); reduction of this compound gives the glycol, thereby showing that one of the C—C bonds is still intact. When the temperature was allowed to rise to  $-60^\circ$ , the molozone rearranged to the ozonide.

According to Criegee *et al.* (1954), the formation of the ozonide takes place as follows:



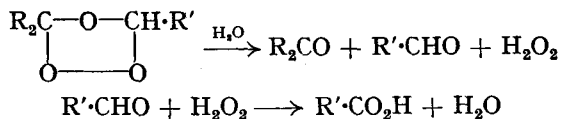
Bailey (1957), however, has proposed a mechanism in which the first step is the formation of a  $\pi$ -complex. This then produces a zwitterion which breaks down to produce the zwitterion and carbonyl compound in the Criegee mechanism:



In this way Bailey explains the ready fission of carbon-carbon multiple bonds.

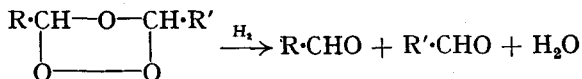
The ozonide is prepared by dissolving the olefinic compound in a solvent that is unaffected by ozone, *e.g.*, chloroform, carbon tetrachloride, glacial acetic acid, light petrol, etc., and a stream of ozonised oxygen is passed through. Subsequent treatment may be by one of the following procedures.

(i) The solvent is evaporated under reduced pressure, and the residual ozonide is treated with water and zinc dust in the presence of traces of silver and hydroquinone (Whitmore, 1932). Aldehydes or ketones are obtained according to the structure of the olefin. The function of the zinc dust is to destroy the hydrogen peroxide which is formed in the reaction, and which tends to oxidise the aldehyde (if this is a primary cleavage product) to the corresponding acid, *e.g.*,



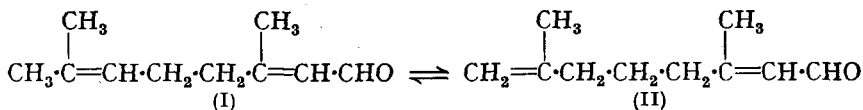
In practice both aldehyde and acid are obtained.

(ii) A better method than the above is the *reductive* decomposition of the ozonide (Fischer, 1928, 1932). A palladium catalyst carried on a calcium carbonate support is added to the solution of the ozonide and then hydrogen is passed in. Usually a good yield (50–90 per cent.) of aldehyde or ketone is obtained:



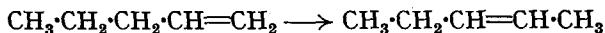
(iii) Wilms (1950) has found that peracetic acid in acetic acid oxidises ozonides to carboxylic acids in high yields.

The resulting aldehydes (or acids) and ketones are identified, and thus the position of the double bond in the olefinic compound is found. The complete process of preparing the ozonide and decomposing it (and identifying the products formed) is known as *ozonolysis*, and this is probably the best method for determining the position of a double bond in any olefinic compound. Recently, however, some doubt has been cast on ozonolysis as a means of determining the positions of double bonds in unsaturated compounds, *e.g.*, according to Barnard *et al.* (1950), during the ozonolysis of citral (an acyclic terpene), partial rearrangement from the *isopropylidene* (I) to the *isopropenyl* structure (II) occurs (this is an example of a three-carbon tautomeric system; see p. 220):

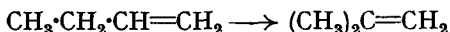


Ozonides may be reduced to alcohols directly by sodium borohydride (*inter alia*, Sousa *et al.*, 1960).

11. Olefins isomerise when heated at high temperature (500–700°), or at a lower temperature (200–300°) in the presence of various catalysts, e.g., aluminium sulphate. Isomerisation may be due (i) to the change in position of the double bond, which always tends to move towards the centre of the chain, e.g., pent-1-ene isomerises to pent-2-ene:

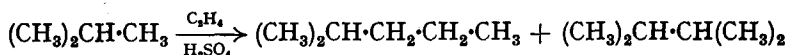


(ii) To the migration of a methyl group, e.g., but-1-ene isomerises to *isobutene*:

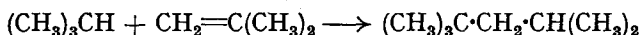


(i) and (ii) may, or may not, occur together.

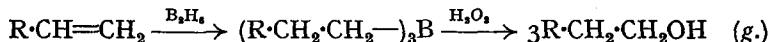
12. Olefins add on to *isoparaffins* in the presence of a catalyst, many of which are known, but the one usually employed is concentrated sulphuric acid, e.g., ethylene adds on to *isobutane* to form a mixture of 2-methylpentane and 2 : 3-dimethylbutane:



This reaction is particularly useful for preparing "*iso-octane*", 2 : 2 : 4-trimethylpentane (see p. 57) by treating *isobutane* with *isobutene* in the presence of concentrated sulphuric acid:

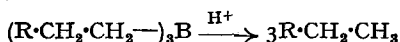


13. Diborane reacts rapidly at room temperature with olefins, giving the trialkylborons. Terminal olefins give the primary alkylborons, which can be oxidised by hydrogen peroxide to primary alcohols (Brown *et al.*, 1957):



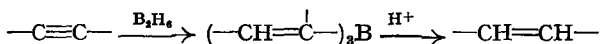
The *s*- and *t*-alkylborons obtained from non-terminal olefins readily undergo isomerisation to primary alkylborons when heated. The addition of diborane is known as *hydroboronation* (*hydroboration*).

If the trialkylboron is treated with a carboxylic acid, the corresponding alkane is obtained by protolysis:

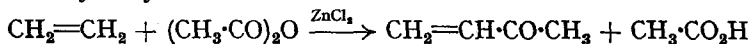


Thus the final product is formed by reduction of an olefin by a *non-catalytic* method.

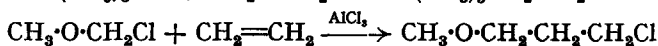
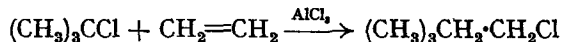
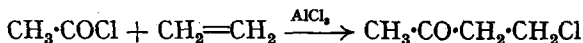
In the same way, acetylenes undergo monohydroboronation and protolysis to give almost pure *cis*-olefin:



14. Olefins condense with acetic anhydride,  $(\text{CH}_3 \cdot \text{CO})_2\text{O}$ , in the presence of a catalyst, e.g., zinc chloride, to form unsaturated ketones, e.g., ethylene forms methyl vinyl ketone:

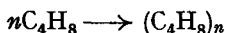


Acid chlorides, alkyl chlorides and  $\alpha$ -halogenated ethers also combine with olefins in the presence of aluminium chloride, e.g.,



All of these condensations are examples of the Friedel-Crafts reaction in aliphatic compounds (see p. 529).

15. Olefins readily polymerise in the presence of suitable catalysts, e.g., *isobutene* gives a polymer in the presence of concentrated sulphuric acid:

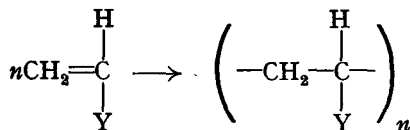


When two compounds have the same empirical formula but differ in molecular weight, the more complicated compound is called a *polymer* of the simpler one. The term *polymerisation* was used originally to indicate the process that took place when a single substance—the *monomer*—gave products having the same empirical formula but different molecular weights, each of these being a multiple of that of the monomer. As the investigation of polymerisation reactions progressed, it was found that many compounds of high molecular weight, although they produced a large number of monomer molecules on suitable treatment, did not always have exactly the same empirical formula as the parent monomer. This led to a modification of the definitions of the terms polymer and polymerisation. According to Carothers (1931) polymerisation is best defined as *intermolecular combinations that are functionally capable of proceeding indefinitely*. This definition implies that there is no limit theoretically to the size of the polymer molecule. In practice, however, the polymer ceases to grow, for various reasons (see below). The terms polymer and polymerisation are now used mainly in connection with high molecular weight compounds, which, in addition to being called polymers, are also known as *macromolecules*.

There are two types of polymerisation, *addition polymerisation* and *condensation polymerisation*.

**Addition Polymerisation.** Addition polymerisation occurs among molecules containing double or triple bonds; but in certain cases it can also occur between bifunctional compounds that result from the opening of ring structures (see, e.g., ethylene oxide). *There is no liberation of small molecules during addition polymerisation.*

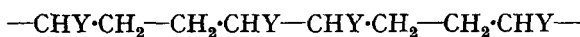
A very important group of olefinic compounds that undergo addition polymerisation is of the type  $\text{CH}_2=\text{CHY}$ , where Y may be H, X,  $\text{CO}_2\text{R}$  CN, etc.:



There are three possible ways in which this polymerisation can occur:

(i) Head to tail:  $-\text{CH}_2\cdot\text{CHY}-\text{CH}_2\cdot\text{CHY}-$

(ii) Head to head and tail to tail:



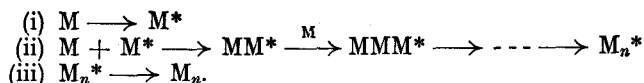
(iii) A random arrangement involving (i) and (ii).

Experimental work seems to indicate that (i) is favoured.

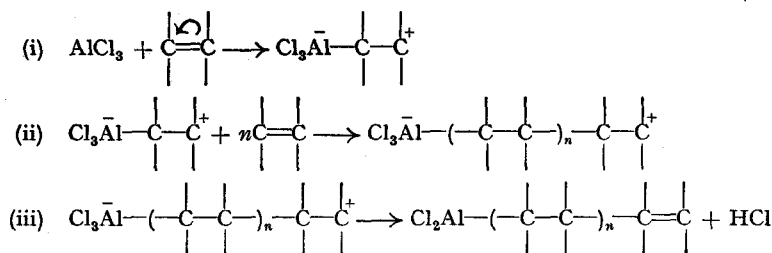
Most polymerisations are carried out in the presence of catalysts, and polymerisation of olefins can be accelerated by ionic-type catalysts or radical-type catalysts. Both types of reaction consist of a number of steps which follow one another consecutively and rapidly, and appear to take place in three principal steps:

- (i) The initiation or activation.
- (ii) The growth or propagation.
- (iii) The termination or cessation.

If M represents the monomer, the series of reactions may be represented as follows:



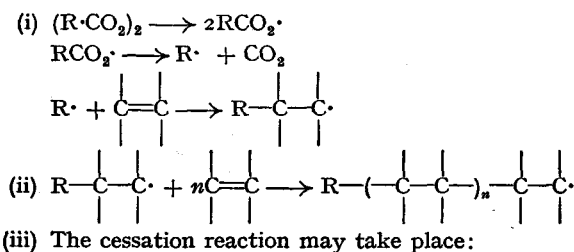
**The Ionic Mechanism of Catalysis.** The ionic mechanism is believed to take place in the presence of certain metallic and non-metallic halides such as  $\text{AlCl}_3$ ,  $\text{SnCl}_4$  or  $\text{BF}_3$ . In certain cases sulphuric acid also catalyses polymerisation. Ionic catalysts are usually electrophilic reagents, and Hunter and Yohe (1933) have suggested that the chain-initiating action of these catalysts depends on their electrophilic nature, and consists in the catalyst acquiring a share in a pair of electrons (the  $\pi$ -electrons) from the double bond of the monomer, *e.g.*,



In (iii) a proton is lost, thus producing a double bond at the end of the chain so that the molecule becomes deactivated, and hence ceases to grow (see also below).

**The Free-Radical Mechanism of Catalysis.** The most important cases of addition polymerisation are those which take place by chain reactions and are brought about by catalysts that are known to generate free radicals. The most widely used catalysts are the organic and inorganic peroxides and the salts of the peracids, *e.g.*, benzoyl peroxide, acetyl peroxide, hydrogen peroxide, potassium perborate, etc.

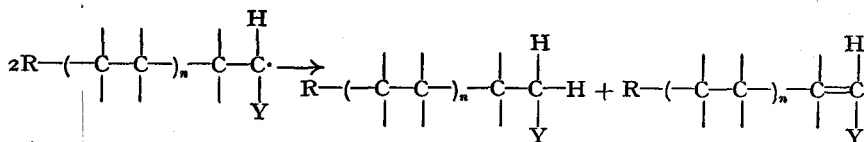
Staudinger (1932) was the first to suggest a free-radical mechanism, and it may be as follows for an organic peroxide:



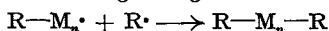
(a) By the collision between two growing chains which unite to form a deactivated molecule:



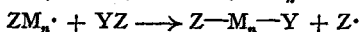
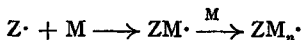
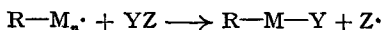
Alternatively, disproportionation (see p. 51) may take place, and thereby deactivate the growing molecules.



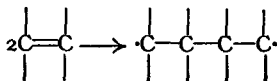
(b) By the collision between the growing chain and a catalyst radical:



(c) By the collision between the growing chain and impurities which have become activated during the polymerisation, *e.g.*,



In "uncatalysed" polymerisation, *i.e.*, in the absence of foreign substances, initiation may begin by *dimerisation* of the monomer:



Not only can addition polymerisation take place among molecules of one kind, but it can also take place among molecules of two kinds, when the phenomenon is known as *copolymerisation* or *interpolymerisation*.

**Condensation Polymerisation or Polycondensation.** In condensation polymerisation, bi- or polyfunctional molecules condense with one another, and in doing so repeatedly eliminate a small molecule such as water, ammonia, hydrogen chloride, etc., as the reaction proceeds. This type of polymerisation takes place by a series of steps, and is discussed in various parts of the text (see, for example, the aldol condensation, the esterification of glycols with dibasic acids, etc.).

Polymers may be classified into three groups:

- (i) *natural*, *e.g.*, rubber, proteins, cellulose; (ii) *semi-synthetic*, *e.g.* nitrocellulose, cellulose acetate; and (iii) *synthetic*, *e.g.*, nylon, bakelite, perspex.

Plastics form a group of high polymers which have a fair range of deformability and mouldability, particularly at high temperatures. In plastics the polymers formed do not all have the same molecular weight, and since the polymers are not amenable to the ordinary methods of separation, the molecular weight of a "polymer" is the *average* molecular weight. Polymerisation is carried out with the object of building up compounds with predicted properties, and since the properties of a plastic depend on the degree of polymerisation it is necessary to stop polymerisation when the desired average molecular weight is reached. This may be done by various means, *e.g.*, variation of the concentration of the catalyst. The average molecular weight of plastics varies from about 20,000 (*e.g.*, nylon) to several hundred thousand (*e.g.*, polyvinyl chloride, 250,000).

Plastics are generally tough, resistant to the action of acids and alkalis, and not very much affected over a fair range of temperature. They can be moulded to any desired shape or form.

Plastics are of two main types, *thermoplastic* and *thermosetting*. Thermoplastics are linear polymers which are soluble in many organic solvents, and which soften on heating and become rigid on cooling. The process of heat-softening, moulding and cooling can be repeated as often as desired, and hardly affects the properties of the plastic. Typical thermoplastics are cellulose acetate, nitrocellulose and vinyl polymers such as polythene, perspex, etc.

Thermosetting plastics are three-dimensional polymers which are insoluble in any kind of solvent, and which can be heat-treated only once before they set, *i.e.*, their formation, after which heating results in chemical decomposition, and hence they cannot be "reworked". Typical thermosetting plastics are phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, silicones, etc.

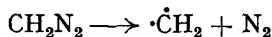
In thermoplastics the chains are, more or less, free chemically, but are held together by van der Waals' forces. It is possible, however, to link together these linear molecules (*cf.* the rungs of a ladder) and the cross-linking agent converts the thermoplastic into a thermosetting plastic, *e.g.*, in the vulcanisation of rubber the

sulphur cross-links the long chains. Furthermore, such thermosetting plastics may be reconverted into thermoplastics by opening the cross-links, *e.g.*, the reclaiming of rubber. Most thermosetting plastics may be regarded as cross-linked polymers.

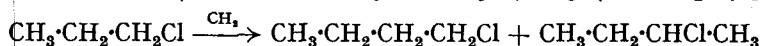
Those plastics which do not soften very much with rise in temperature are made soft and readily workable by the addition of certain compounds known as *plasticisers*; *e.g.*, polyvinyl chloride is extremely stiff and hard, but addition of tricresyl phosphate makes it soft and rubber-like.

### Some Individual Olefins.

The first member of the olefin series is methylene (carbene),  $\text{CH}_2$ , but it exists only as a free *diradical* with a very short life period. It has been prepared by heating diazomethane at very low pressure:

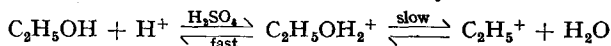


The two electrons must be *unpaired* for methylene to be a diradical. It has been shown that methylene and its derivatives behave as electrophilic reagents. Methylene reacts with alkyl chlorides to attack both the C—Cl and  $\alpha$ -C—H bonds (*inter alia*, Bradley *et al.*, 1961); *e.g.* (see also p. 483):

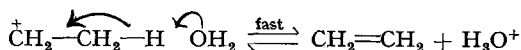


**Ethylene, ethene,  $\text{C}_2\text{H}_4$ .** Ethylene may be prepared by any of the general methods of preparation (except 2), but the most convenient laboratory method is to heat ethanol with excess of concentrated sulphuric acid.

The mechanism of this reaction is the reverse of hydration of olefins (p. 70):

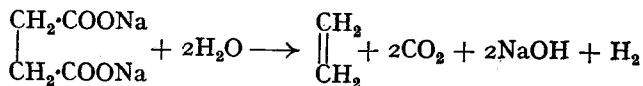


The carbonium ion, which is unstable, stabilises itself by eliminating a proton to form ethylene; the proton is accepted by a water molecule (a Lewis base):

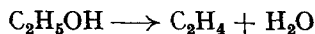


For each molecule of ethanol converted into ethylene, one molecule of water is produced, and hence, after a time the sulphuric acid becomes too dilute to behave as a dehydrating agent.

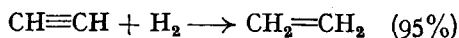
Ethylene may also be prepared by the electrolysis of sodium succinate (Kolbe):



Ethylene is still prepared industrially by passing ethanol vapour over heated alumina at about  $350^\circ$ :



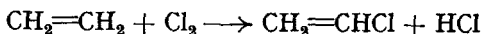
It is, however, now being obtained in huge quantities as a by-product in the cracking of crude oil and of ethane, propane and butane. Ethylene is also manufactured by the partial hydrogenation of acetylene, which is mixed with hydrogen and passed, at  $200^\circ$ , over a palladium catalyst carried on a silica-gel support:



Ethylene is a colourless gas, b.p.  $-105^\circ$ , sparingly soluble in water. It burns with a smoky luminous flame. It has been claimed that carefully

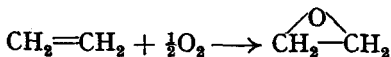


purified ethylene does not react with chlorine in the absence of light. When ethylene is heated with chlorine at 350–450°, vinyl chloride is obtained:

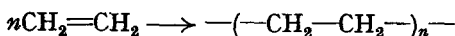


The unsaturated radical  $\text{CH}_2=\text{CH}-$  is known as the *vinyl* or *ethenyl* radical.

Ethylene may be oxidised by atmospheric oxygen in the presence of silver as catalyst, and at a temperature of 200–400°, to ethylene oxide:



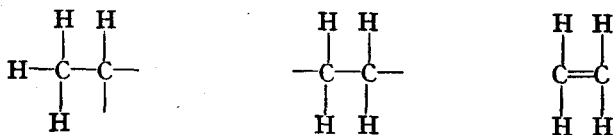
Ethylene polymerises under high pressure and high temperature to form *polyethylene* or *polythene*:



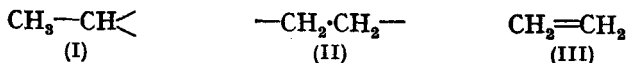
This polymerisation is catalysed by traces of oxygen (which produces the free radicals). Polythene is very resistant to acids, bases, and most of the usual organic solvents.

Ethylene is used for ripening fruit. Unripe fruit may be transported easily without damage, and ripens on exposure to ethylene gas for a few days, the product being apparently indistinguishable from the natural ripened fruit. Ethylene is also used as an anaesthetic, in the manufacture of mustard gas and plastics (polythene, polystyrene), and in the preparation of various solvents such as glycol, dioxan, cellosolves, etc.

**Structure of Ethylene.** The molecular formula of ethylene is  $\text{C}_2\text{H}_4$ . Two carbon atoms have the power to combine with six univalent atoms or groups, as in ethane, *neopentane*, etc. There are only four univalent hydrogen atoms present in ethylene: therefore ethylene is said to be unsaturated, and should be capable of adding on two univalent atoms or groups, and this, as we have seen above, is observed in practice. Thus the structure of ethylene must be such as to be capable of undergoing addition reactions. Assuming carbon to be quadrivalent and hydrogen univalent, three structures are possible for ethylene:



or



Two isomeric compounds of molecular formula  $\text{C}_2\text{H}_4\text{Cl}_2$  are possible:  $\text{CH}_3\text{-CHCl}_2$  and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ . Both isomers are known, one (ethylene chloride) being formed by the direct combination between ethylene and chlorine, and the other (ethylidene chloride) by the action of phosphorus pentachloride on acetaldehyde. The structure of ethylidene chloride is  $\text{CH}_3\text{-CHCl}_2$  (see p. 116); hence the structure of ethylene chloride is  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}$ . If (I) were the structure of ethylene, then the addition of chlorine should give ethylidene chloride, and not ethylene chloride. We may, therefore, reject structure (I). Furthermore, since (I) is unsymmetrical it would have a fairly large dipole moment; actually ethylene has a zero dipole moment.

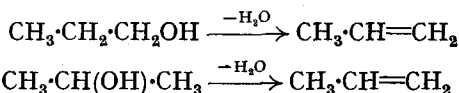
Structure (II) represents ethylene as possessing "free" bonds by means of which addition compounds are formed. If this is the structure, then we might expect that the "free" carbon valencies could be satisfied one at a

time, *i.e.*, a compound such as  $\text{CH}_2\text{Cl}\cdot\text{CH}_2-$  should be possible, since if two "free" valencies can exist independently of each other, it is logical to suppose that one can exist by itself. No such compounds have yet been obtained, and in practice it is found that unsaturated compounds always combine with an *even* number of univalent atoms or groups. Hence structure (III) is accepted for ethylene, and the presence of the double bond (consisting of one  $\sigma$ -bond and one  $\pi$ -bond) is supported by other evidence (length of the carbon-carbon bond; geometrical isomerism).

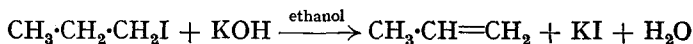
In structures (I) and (II) the *unconnected* bonds indicate *one* electron. If the two electrons in (II) are *paired*, they form a covalent bond, and so (II) and (III) are the same. On the other hand, if the two electrons in (II) are *unpaired*, then (II) is a diradical. Since ethylene does not exhibit the usual properties of a free diradical, we must reject (II).

The presence of a double (or triple bond) in an organic compound may be found readily by means of bromine water, bromine in chloroform solution, or dilute alkaline permanganate. If the compound under investigation is unsaturated, then the above reagents are decolorised. Perbenzoic acid or monopero-phthalic acid can be used to detect the presence of a double bond, and also to estimate the number of double bonds (see also iodine value, p. 261).

**Propylene, propene**,  $\text{C}_3\text{H}_6$ , may be prepared by heating propanol or *iso*-propanol with sulphuric acid (mechanism as for ethylene from ethanol):



It may also be prepared by heating propyl iodide with ethanolic potassium hydroxide:



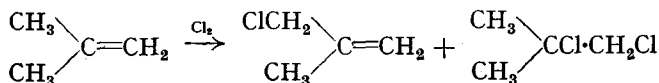
Propylene is obtained commercially in huge quantities as a by-product in the cracking of petroleum. It is a colourless gas, b.p.  $-48^\circ$ , insoluble in water but fairly soluble in ethanol. It is used industrially for the preparation of *isopropanol*, glycerol, etc.

The unsaturated radical  $\text{CH}_2=\dot{\text{C}}\text{H}\cdot\text{CH}_2-$  is known as the allyl radical.

**Butylenes, butenes**,  $\text{C}_4\text{H}_8$ . There are three isomeric butylenes, and all are gases:

$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$ ,  $\alpha$ -butylene, but-1-ene (b.p.  $-6.1^\circ$ );  $\text{CH}_3\cdot\text{CH}=\dot{\text{C}}\text{H}\cdot\text{CH}_3$ ,  $\beta$ -butylene, but-2-ene (b.p.  $1^\circ$ );  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ , *isobutylene*, *isobutene* (b.p.  $-6.6^\circ$ ).

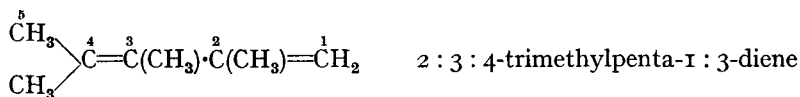
All the butylenes are obtained from cracked petroleum. The 1- and 2-butenes are used for the preparation of *sec.*-butanol (*q.v.*), and *isobutene* for *tert.*-butanol (*q.v.*). But-2-ene differs from its isomers in that it exhibits geometrical isomerism (see p. 425). *iso*Butene differs from its isomers in that it reacts with chlorine *at room temperature* to give mainly *substitution* products, substitution occurring in the allyl position (see p. 67). Thus 3-chloro-2-methylprop-1-ene is the main product, and is accompanied by a small amount of the addition product 1 : 2-dichloro-2-methylpropane:



UNSATURATED COMPOUNDS WITH TWO OR MORE  
DOUBLE BONDS

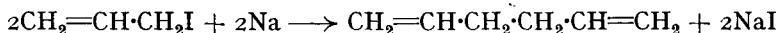
When the compound contains two double bonds, it is known as a diolefin or alkadiene, and has the general formula  $C_nH_{2n-2}$ ; when there are three double bonds present, the compound is known as a triolefin or alkatriene, and has the general formula  $C_nH_{2n-4}$ ; etc.

**Nomenclature.** The longest carbon chain containing the maximum number of double bonds is chosen as the parent hydrocarbon, and the chain is so numbered as to give the lowest possible numbers to the double bonds, *e.g.*,



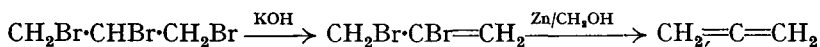
There are three different types of compounds with two double bonds.

1. **Hydrocarbons with isolated double bonds** contain the arrangement  $>C=CH \cdot (CH_2)_n \cdot CH=C<$ , where  $n > 0$ . One of the simplest compounds of this type is **diallyl** or **hexa-1 : 5-diene**, which may be prepared by the action of sodium on allyl iodide (Wurtz reaction):



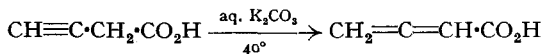
Diallyl is a liquid, b.p.  $59.6^\circ$ . It resembles the olefins chemically, but since there are two double bonds present, it may add on two or four univalent atoms or groups according to the relative concentration of the addendum; *e.g.*, with excess bromine, diallyl forms 1 : 2 : 5 : 6-tetrabromohexane.

2. **Hydrocarbons with cumulated double bonds** contain the arrangement  $>C=C=C<$ . The simplest compound of this type is **allene** or **propadiene**, which may be prepared by heating 1 : 2 : 3-tribromopropane with solid potassium hydroxide, and then treating the resulting 2 : 3-dibromopropylene with zinc dust in methanol solution:

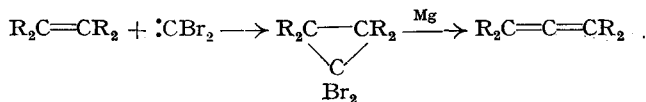


Allene is a gas, b.p.  $-32^\circ$ . With bromine it forms 1 : 2 : 2 : 3-tetrabromopropane; with sulphuric acid it forms acetone; and when treated with sodium in ether, the sodium derivative of propyne ( $\text{CH}_3 \cdot \text{C} \equiv \text{CNa}$ ) is produced. Allene compounds are very important from the view of stereochemistry (see p. 432).

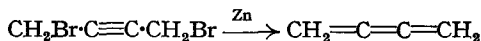
In recent years, allenes have been prepared from acetylenes by rearrangement, *e.g.*,



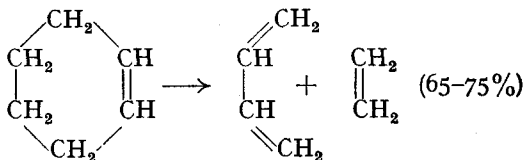
A novel way of preparing allenes is by treating the cyclopropane derivative formed from an olefin and bromoform and alkali with magnesium in ether (Doering *et al.*, 1958). Dibromomethylene is an intermediate (p. 117).



An extended allene type of linkage gives the *cumulene* system, the simplest member of which is butatriene, and this has been prepared by debrominating 1:4-dibromobut-2-yne with zinc (Schubert *et al.*, 1952, 1954):



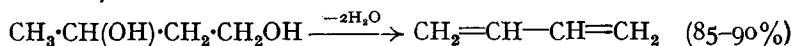
3. **Hydrocarbons with conjugated double bonds** contain single and double bonds arranged *alternately*, *i.e.*, they contain the arrangement  $-\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ . The simplest member of this group of compounds is **buta-1:3-diene**, which may be prepared by passing *cyclohexene* over a heated nichrome wire (an alloy of nickel, chromium and iron):



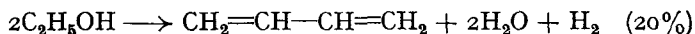
Butadiene is prepared technically:

(i) By dehydrogenating *n*-butane (from natural gas or from petroleum gas) or but-1-ene (from cracked petroleum) by passing the gas over a heated catalyst, *e.g.*, chromic oxide on an alumina support.

(ii) By passing a mixture of butane-1:3-diol and steam, in proportions 4:1, over trisodium phosphate containing 20 per cent. free phosphoric acid, heated at 270°:



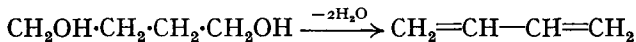
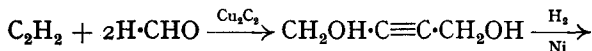
(iii) By passing ethanol vapour over a catalyst of alumina-zinc oxide heated at 420-470°:



The yield is low owing to the production of many by-products such as acetic acid, ethyl acetate, ether, etc. The yield of butadiene has been improved by passing a mixture of ethanol and acetaldehyde over a heated catalyst of silica-gel plus 2 per cent. tantalum oxide:

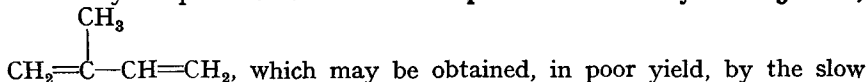


(iv) By passing a mixture of acetylene and formaldehyde over copper acetylide as catalyst, whereupon butynediol  $\text{CH}_2\text{OH}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\text{OH}$  is formed. This is hydrogenated catalytically to butane-1:4-diol, which, on catalytic dehydration, gives butadiene:



Butadiene is a gas, b.p.  $-2.6^\circ$ . Under the influence of sodium as catalyst, butadiene readily polymerises to a product which has been used as a rubber substitute known as *buna* (*butadiene* + *Na*). The mechanism of this polymerisation is uncertain, but a possibility is discussed in connection with isoprene (see below).

A very important diolefin is **isoprene** or **2-methylbut-1:3-diene**,





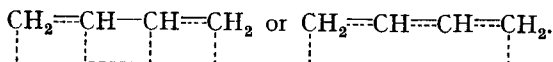
(one molecule), two dibromo-derivatives are obtained, the "expected" 3:4-dibromobut-1-ene (1:2-addition), and the "unexpected" 1:4-dibromobut-2-ene (1:4-addition):



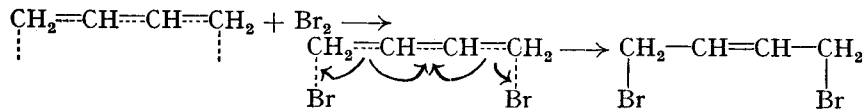
It has been found that 1:2- and 1:4-additions usually take place together, and the relative amount of each generally depends on the nature of the addendum and the conditions of the experiment, e.g., type of solvent, temperature.

Thiele (1899) suggested his theory of *partial valencies* to account for 1:4-addition. According to Thiele, a single bond is sufficient to hold two carbon atoms together, and the two valencies of the double bond are not used completely to link the two carbon atoms, but only one valency and *part* of the other, leaving a surplus on each carbon atom. Thiele called this surplus valency the *residual* or *partial* valency, and if we represent it by a broken line, the formula of butadiene (and similarly for any other conjugated compound) may be written  $\text{CH}_2\text{---CH}-\text{CH}=\text{CH}_2$ . Thiele

thought that the two middle partial valencies mutually satisfied each other rather than remain free. Thus the actual state of butadiene is

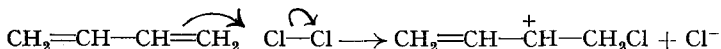


The ends of this molecule are therefore the most active parts, and so addition of, e.g., bromine will occur at these ends, first by attachment through the partial valencies, and then by each bromine atom acquiring a full valency, causing the two middle carbon atoms to utilise completely the two valencies left:

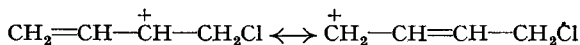


Thiele's theory explains 1:4-addition so well that it does not account at all for 1:2-addition!

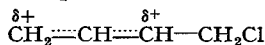
The mechanism of addition to conjugated systems is now believed to be as follows. The first problem to solve is which carbon atom in butadiene is attacked initially. Assuming that the addition mechanism is the same as for monoolefins (i.e., a two-stage electrophilic reaction), then attack on butadiene will be at a *terminal* carbon atom since this becomes electron rich through the +E effect of the vinyl group:



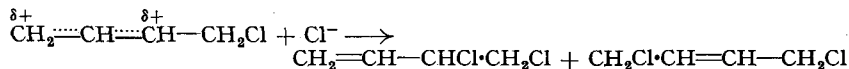
The carbonium ion produced is a resonance hybrid:



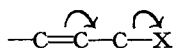
This resonance hybrid may be represented as



Thus there are *two* positive centres which may be attacked by the chloride ion in the second step.



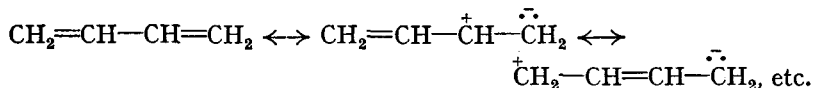
Since both the 1:2- and 1:4-dichlorides are formed in practice, the interesting question is whether one can predict which isomer will predominate. The answer to this depends on whether the isomers are interconvertible or not under the conditions of the experiment. If the conditions permit interconversion, then the thermodynamically controlled product (*i.e.*, the more stable one) will predominate. If the conditions do not permit interconversion, then the kinetically controlled product (*i.e.*, the one formed faster) will predominate (p. 32). Consider the following:



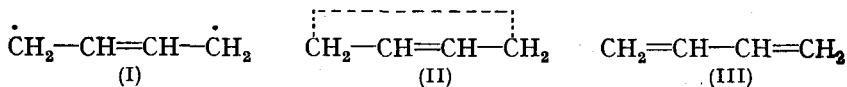
In this type of structure, halogen hyperconjugation is possible (p. 270), and this makes the molecule more stable than one in which such hyperconjugation is not possible. Inspection of the two butadiene dichlorides shows that the 1:2-product has one chlorine-hyperconjugated system whereas the 1:4-product has two. Thus, the latter is more stable and so should be the thermodynamically controlled product if the two forms are interconvertible, and consequently will be the predominant product under these conditions. These predictions have been observed experimentally, *e.g.*, Muskat *et al.* (1930) treated butadiene with chlorine under conditions where the two isomers were not interconvertible, and obtained about 60 per cent. of the 1:2- and 40 per cent. of the 1:4-product. This implies that the 1:2-compound is the kinetically controlled product. Pudovic (1949) heated each isomer at 200° and obtained the same equilibrium mixture containing about 30 per cent. 1:2- and 70 per cent. 1:4-. Thus, the 1:4-isomer is the thermodynamically controlled product, and predominates under conditions of interconvertibility.

The addition of halogen acid to butadiene also produces two products, the 1:2- and the 1:4-. Furthermore, since the proton adds on first, this adds always to the *terminal* carbon, the halogen then adding at position 2 or 4.

In the foregoing account of the reactions of butadiene, we have assumed that the molecule has the structure  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ . There are, however, alternative electronic structures which are *charged*. Hence butadiene is a resonance hybrid of a number of resonating structures:

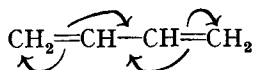


There is still, however, another contributing structure of butadiene, *viz.*, (I). The two electrons have antiparallel spins, since the number of unpaired electrons in each resonating structure must be the same (p. 17). Thus these paired electrons would, in the ordinary way, form a covalent bond. The distance between them, however, is too great for them to form an *effective* bond. Consequently this bond is referred to as a *formal bond*, and may be



represented by a dotted line (II). Structure (II) carries no charges and so (II) and (III) (also uncharged) are probably the main contributing resonance structures (p. 20). If only these two contribute significantly to the resonance hybrid, the resonance energy can be expected to be small. Actually, calculation has shown it to be about 3.5 k.cal./mole. Thus in butadiene there are no "pure" single or double bonds. The lengths of the bonds will therefore be somewhere between the extremes (of single and double bonds), the actual values depending on the relative contributions of the resonating structures to the resonance hybrid. Furthermore, if we assume that the charged structures make a very small contribution, it might at first sight

appear that the butadiene molecule possesses a dipole moment. This, however, is not so in practice, the reason being that the terminal carbon atoms can be either positive or negative, since the electronic displacements can occur equally well in either direction. For this reason butadiene is said to exhibit *balanced conjugation*, and this may be represented as:



So far we have considered the structure of conjugated compounds from V.B. theory. When we consider their structure from M.O. theory, we get a different picture. Each carbon atom in butadiene has the trigonal arrangement, and Fig. 1(a) shows the  $p_z$  electrons associated with each carbon atom. If the molecule is planar, the  $p_z$  electron of  $C_2$  overlaps that of  $C_1$  as much as it does that of  $C_3$ , etc. Therefore all four  $p_z$  orbitals can be treated as forming an *M.O. covering all four carbon atoms* (b). In this condition, a pair of electrons are no longer mainly confined to the region between two nuclei, *i.e.*, the bond formed is no

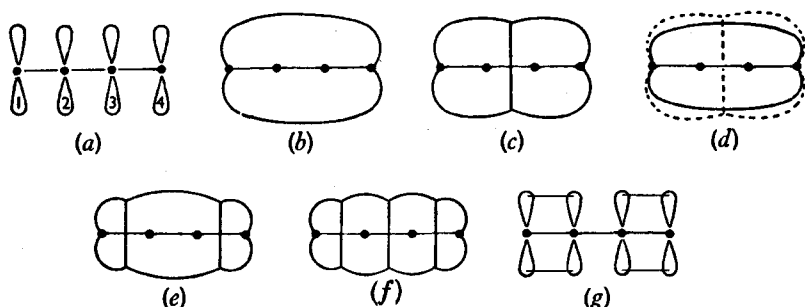


FIG. 4.1.

longer a *localised* bond. The bonds produced are therefore called *delocalised* bonds. In all, there are four delocalised M.O.s possible from the combination of the four  $\pi$ -electrons, two bonding and two anti-bonding M.O.s (p. 30). The two bonding M.O.s are shown in Fig. 1(b) and (c), the former having one nodal plane, and the latter, two. The two anti-bonding M.O.s are shown in (e), with three nodal planes, and in (f), with four nodal planes. As pointed out on p. 31, as the number of nodes in an orbital increases, so does the energy associated with that orbital. Furthermore, according to the Pauli exclusion principle, no more than *two* electrons can occupy the same M.O. Therefore in the ground state of butadiene, two of the  $\pi$ -electrons will occupy the M.O. in (b), and the other two the M.O. with the next higher energy level, *i.e.*, (c). Fig. (d) represents these two in one diagram, *i.e.*, (d) represents the ground state of butadiene. In any excited state of butadiene, electrons will occupy orbitals (e) or (f) (see p. 777).

In general, in a conjugated system containing  $2n$   $\pi$ -electrons, there are  $n$  bonding and  $n$  anti-bonding orbitals, and in the ground state these electrons will occupy, *in pairs*, the  $n$  M.O.s of lowest energy.

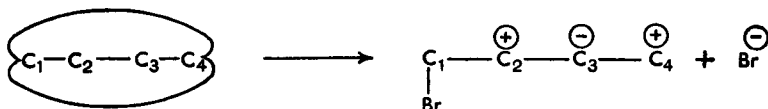
In delocalised bonds, the electrons have greater freedom of movement than in localised bonds. Thus the total energy of the system is lowered, *i.e.*, delocalisation of bonds makes the molecule more stable. Hence the butadiene molecule in state (d) is more stable than in state (g), in which the  $\pi$ -electrons are paired as "*isolated*" pairs, each pair covering *two* carbon atoms. This energy of stabilisation could be called the *delocalisation energy* (Coulson), but it is more usual to call it the resonance energy. It should here be noted that *delocalisation of bonds* is in M.O. theory what *resonance* is in V.B. theory.

It can be seen from the foregoing discussion that the M.O. treatment of conjugated systems does away with the idea of "*bonds*" between atoms (this applies to the  $\pi$ -bonds, and not to the  $\sigma$ -bonds). Also the term *conjugation* is



used in M.O. theory to indicate the existence in any part of a molecule of *molecular orbitals which embrace three or more nuclei*. It is important to note that a conjugated system (defined as above) *always* contains double bonds, but that the reverse is not necessarily the case, *e.g.*, ethylene.

Since the electron cloud covers the *whole* of the butadiene molecule, an electrical influence in one part of the system is easily propagated to another (*cf.* p. 517). Calculation (Coulson and Longuet-Higgins, 1947) has shown that when, for example, bromine attacks butadiene, the bromine molecule approaches the *end* of butadiene molecule most easily, and produces an *alternate* polarity:



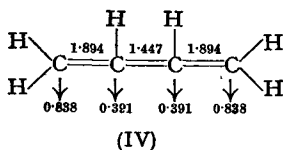
$\delta^+$   
Br  
 $\delta^-$   
Br

The negative bromide ion can then attack  $C_2$  or  $C_4$ .

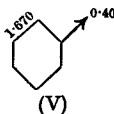
The relationship between the observed bond-length and the value expected on the assumption that it is a "pure" single or double bond has been put on a quantitative basis. In the V.B. method the *double-bond character* of a bond may be calculated from a knowledge of the observed bond length, the values of the single bond in ethane, and the double bond in ethylene being taken as standard lengths for "pure" single and double bonds, respectively. Calculations by Pauling *et al.* (1933) have shown that the "single" bond in butadiene has about 20 per cent. double-bond character (see also below).

In the M.O. method, the character of a bond is defined by its *fractional bond order*, where the bond orders of 1, 2 and 3 are given to the bonds in ethane, ethylene and acetylene, respectively. Since also the method of calculation is different from that of the V.B. method, the numerical values obtained by the two methods are different. Even so, these values always correspond.

Coulson (1941, 1947) has shown that the butadiene molecule may be represented as shown in (IV).



(IV)



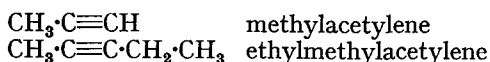
(V)

Calculation gives a bond order of 1.894 to the two outer "double" bonds, and a bond order of 1.447 to the central "single" bond. Thus the total *bond number* of either of the end carbon atoms is  $2 \times 1.0 + 1.894 = 3.894$ , and the total bond number of either middle carbon is  $1.0 + 1.447 + 1.894 = 4.341$ . Furthermore, since calculation has shown that the maximum bond number for a carbon atom is 4.732, it follows that each carbon atom in butadiene has the "free valency" shown in (IV) (Coulson has suggested that free valency be represented by an arrow). On the other hand, if a structure containing fractional double bonds is written with single bonds labelled with the bond order, and charges are placed on the atoms, then the resulting diagram is known as a *molecular diagram*, *e.g.*, the molecular diagram for benzene is (V) (see also p. 528). Among other things, a molecular diagram enables one to estimate the most likely points of attack (see, *e.g.*, pyrrole, p. 750).

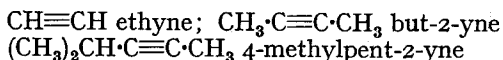
#### ACETYLENES OR ALKYNES

The acetylenes are unsaturated hydrocarbons that contain one triple bond. The simplest member of the series is acetylene  $\text{CH}\equiv\text{CH}$ , and hence this homologous series is often referred to as the "acetylene series". The acetylenes have the general formula  $\text{C}_n\text{H}_{2n-2}$  and the triple bond is also known as the "acetylenic bond".

**Nomenclature.** One method is to name higher homologues as derivatives of acetylene, the first member of the series, *e.g.*,

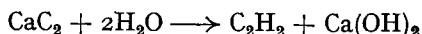


In the I.U.P.A.C. system of nomenclature the class suffix is *-yne*, and the rules for numbering are as for the olefins (p. 63), *e.g.*,

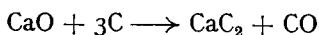


**Acetylene** or **ethyne**,  $\text{C}_2\text{H}_2$ , is the most important member of this series, and it may be prepared by any of the following methods:

1. By the action of water on calcium carbide:



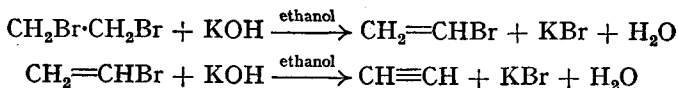
This method of preparation is used industrially, since calcium carbide is readily manufactured by heating calcium oxide with coke in an electric furnace:



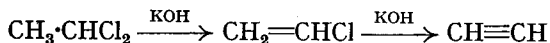
Acetylene prepared from calcium carbide is not pure, but contains small amounts of phosphine, hydrogen sulphide, arsine, ammonia, etc.; the impurities present depend on the purity of the calcium carbide used. Scrubbing with water is usually sufficient to reduce the amount of all the impurities, except phosphine, below the limit necessary for the safe application of acetylene for technical purposes. Phosphine is removed by means of oxidising agents, *e.g.*, acid dichromate or bleaching-powder, whereby the phosphine is retained as phosphoric acid.

A more recent industrial preparation of acetylene is by the electric arc cracking of methane-ethane mixtures which are derived from coal hydrogenation (p. 60).

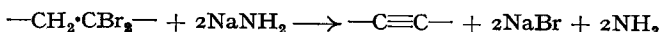
2. By the action of ethanolic potassium hydroxide on ethylene bromide. The reaction proceeds in two steps, and under suitable conditions the intermediate product vinyl bromide may be isolated:



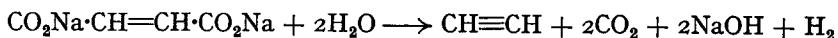
Ethylidene chloride may be used instead of ethylene bromide (or chloride), and this reaction also proceeds in two steps:



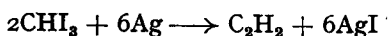
Sodamide can be used instead of ethanolic potassium hydroxide, and the yields are usually better since there is less tendency to form by-products, *e.g.*,



3. By the electrolysis of a concentrated solution of sodium (or potassium) salt of maleic or fumaric acid (*q.v.*):



4. By heating a trihalogen derivative of methane with silver powder; *e.g.*, iodoform gives acetylene when heated with silver powder:

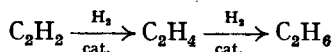


Acetylene may be synthesised from its elements by striking an electric arc between carbon rods in an atmosphere of hydrogen. It is also formed by the incomplete combustion of hydrocarbons, *e.g.*, when a bunsen burner "strikes back".

Acetylene is a colourless gas, b.p.  $-84^{\circ}$ , and has an ethereal smell when pure. It is sparingly soluble in water but readily soluble in acetone. When compressed or liquefied acetylene is explosive, but its solution under pressure (10 atm.) in acetone adsorbed on some suitable porous material can be handled with safety. Acetylene burns with a luminous smoky flame (due to the high carbon content), and hence is used for lighting purposes. It is also used in the oxy-acetylene blow-pipe, a temperature above  $3000^{\circ}$  being reached. Acetylene is used for the preparation of a large number of compounds, *e.g.*, acetaldehyde, ethanol, acetic acid, etc. (see text).

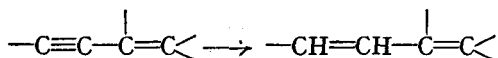
Owing to the presence of a triple bond, acetylene is more unsaturated than ethylene, and forms addition products with two or four univalent atoms or groups, never one or three (*cf.* ethylene). A triple bond consists of one  $\sigma$ -bond and two  $\pi$ -bonds. When two univalent atoms add on to a triple bond the digonal arrangement changes into the trigonal, and the further addition of two univalent atoms changes the trigonal into the tetrahedral arrangement. Under suitable conditions it is possible to isolate the intermediate olefin.

1. Acetylene adds on hydrogen in the presence of a catalyst, the reaction proceeding in two stages:



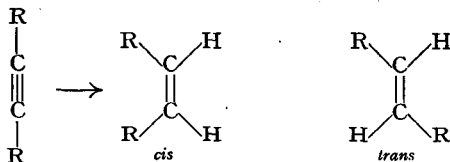
The intermediate product, ethylene, can be obtained in very good yield if the hydrogenation is carried out with a *measured* amount of hydrogen in the presence of Adams' platinum-platinum oxide catalyst (p. 65), or palladium carried on a barium sulphate support.

The partial catalytic reduction of a triple bond in a wide variety of acetylenic compounds has been carried out, but great difficulty has been encountered in partially reducing a triple bond conjugated with a double bond, *i.e.*, the following reduction has proved difficult:



Lindlar (1952), however, has now developed a catalyst for the partial hydrogenation of a triple bond in a wide variety of compounds; it consists of a Pd-CaCO<sub>3</sub> catalyst partially inactivated by treatment with lead acetate, or better, by the addition of quinoline.

Dialkylacetylenes may be catalytically reduced to a mixture of *cis*- and *trans*-olefins, the former predominating. On the other hand, reduction with sodium in liquid ammonia produces the *trans*-olefin. Acetylenes are also reduced to *trans*-olefins by lithium in aliphatic amines of low molecular weight (Benkeser *et al.*, 1955) *cis*-Reduction may be carried out with diborane (p. 76).



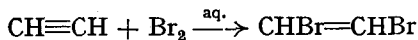
Lithium aluminium hydride may also be used to partially reduce a triple bond provided the molecule contains the grouping  $-\text{C}\equiv\text{C}-\text{C}(\text{OH})<$ .

2. Acetylene adds on gaseous chlorine or bromine in the dark to form acetylene di- and tetrahalides; the addition is catalysed by light and metallic halides (*cf.* olefins):

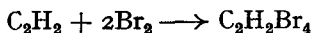


Direct combination of acetylene with chlorine may be accompanied by explosions, but this is prevented by the presence of a catalyst.

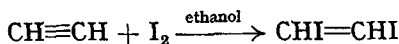
Acetylene reacts with dilute bromine water to produce acetylene dibromide:



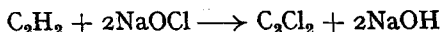
With liquid bromine and in the absence of a solvent, acetylene forms acetylene tetrabromide:



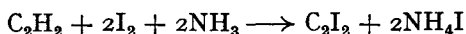
Acetylene adds on iodine with difficulty, but if the reaction is carried out in ethanolic solution, acetylene di-iodide is obtained:



Acetylene also undergoes substitution with halogen provided the right conditions are used, *e.g.*, dichloroacetylene is formed when acetylene is passed into sodium hypochlorite solution at 0° in the absence of air and light:

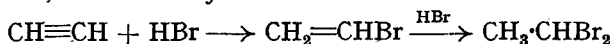


Similarly, if acetylene is passed into a solution of iodine in liquid ammonia, di-iodoacetylene is formed (Vaughan and Nieuland, 1932):



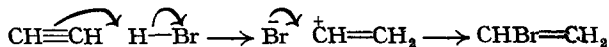
These substitution reactions of acetylene are characteristic of hydrogen only in the  $\equiv\text{CH}$  group. Thus, for example, but-1-yne, but not but-2-yne, can undergo these substitutions. Furthermore, it should be noted that the halogen of the  $\equiv\text{CX}$  group is very unreactive (*cf.* vinyl halides, p. 266).

3. Acetylene can add on the halogen acids, their order of reactivity being  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ ; HF adds on only under pressure (*cf.* ethylene). The addition of the halogen acids can take place in the dark, but is catalysed by light or metallic halides. The addition is in accordance with Markownikoff's rule, *e.g.*, acetylene combines with hydrogen bromide to form first vinyl bromide, and then ethylidene bromide:

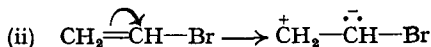
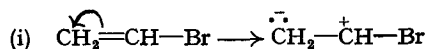


Peroxides have the same effect on the addition of hydrogen bromide to acetylene as they have on olefins (p. 68).

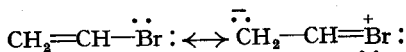
The mechanism of the addition of halogens and halogen acids is probably the same as that for the olefins, *e.g.*, the addition of hydrogen bromide may be as follows:



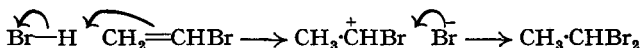
Vinyl bromide may undergo the electromeric effect in two ways:



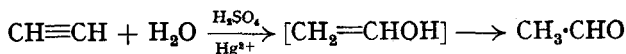
At the same time vinyl bromide is also capable of existing as a resonance hybrid (*cf.*, *e.g.*, chlorobenzene, p. 546):



Considering the high electron-affinity of bromine, (ii) would seem to be more likely than (i), and the bromine atom would therefore cause the electron drift to take place *towards* itself. Considering the resonance effect, the tendency would be to drive the electrons in the *opposite* direction to that of (ii), and since the resonance effect is much stronger than the inductive effect (p. 519) direction (i) will be the result; hence the addition of a molecule of hydrogen bromide to vinyl bromide is:

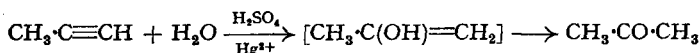


4. When passed into dilute sulphuric acid at 60° in the presence of mercuric sulphate as catalyst, acetylene adds on one molecule of water to form acetaldehyde. The mechanism of this hydration probably takes place via the formation of vinyl alcohol as an intermediate (*cf.* p. 70). Vinyl alcohol has not yet been isolated; all attempts to prepare it result in the formation of acetaldehyde (p. 265). Since we are suggesting it is an intermediate product, but that it has never been isolated in this reaction, we indicate this by enclosing vinyl alcohol in square brackets:\*

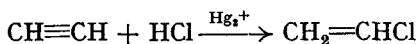


The conversion of acetylene into acetaldehyde is very important technically, since acetaldehyde can be used for the preparation of many important compounds (see text).

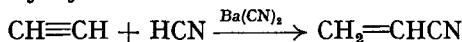
The homologues of acetylene form ketones when hydrated, *e.g.*, methylacetylene gives acetone:



5. When acetylene is passed into dilute hydrochloric acid at 65° in the presence of mercuric ions as catalyst, vinyl chloride is formed:

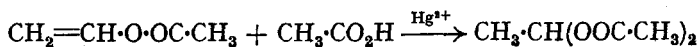
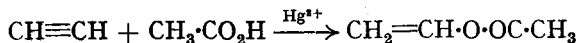


Acetylene adds on hydrogen cyanide in the presence of barium cyanide as catalyst to form vinyl cyanide:



Vinyl cyanide is used in the manufacture of *Buna N* synthetic rubber, which is a copolymer of vinyl cyanide and butadiene.

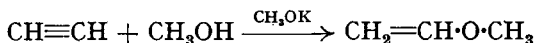
When acetylene is passed into warm acetic acid in the presence of mercuric ions as catalyst, vinyl acetate and ethylidene acetate are formed:



Vinyl acetate (liquid) is used in the plastic industry. Ethylidene acetate (liquid), when heated rapidly to 300–400°, gives acetic anhydride and acetaldehyde.

\* In this book any compound that is suggested as an intermediate will be enclosed in square brackets *provided that it has not been isolated in the reaction shown.*

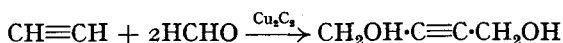
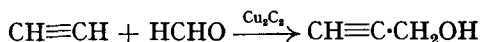
Acetylene reacts with nitric acid in the presence of mercuric ions to form nitroform,  $\text{CH}(\text{NO}_2)_3$ . Acetylene combines with arsenic trichloride to form Lewisite (p. 345). When acetylene is passed into methanol at 160–200° in the presence of a small amount (1–2 per cent.) of potassium methoxide and under pressure just high enough to prevent boiling, methyl vinyl ether is formed:



This is used for making the polyvinyl ether plastics.

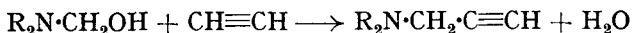
This process whereby acetylene adds on to compounds containing an active hydrogen atom (p. 350) to form vinyl compounds is known as **vinylation**.

Acetylene and formaldehyde interact in the presence of copper acetylide as catalyst to form butynediol, together with smaller amounts of propargyl alcohol,  $\text{CH}\equiv\text{C}\cdot\text{CH}_2\text{OH}$ :

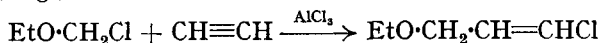


Propargyl alcohol is used to prepare allyl alcohol, glycerol, etc. Butynediol is used to prepare butadiene, etc.

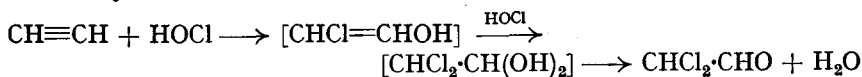
This reaction in which acetylene (or any compound containing the  $\equiv\text{CH}$  group, *i.e.*, a methyne hydrogen atom) adds on to certain unsaturated links (such as in the carbonyl group), or eliminates a molecule of water by reaction with certain hydroxy-compounds, is known as **ethinylation**. Thus the above reactions with formaldehyde are examples of ethinylation; another example is the following:



Alkyl bromo- and chloro-methyl ethers (p. 354) add to acetylenes in the presence of the corresponding aluminium halide to form olefins (Bindácz *et al.*, 1960); *e.g.*,

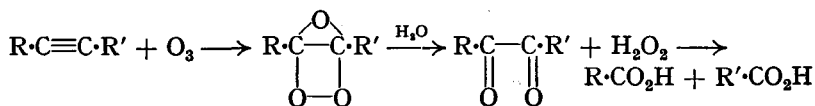


6. When acetylene is passed into hypochlorous acid solution, dichloroacetaldehyde is formed:

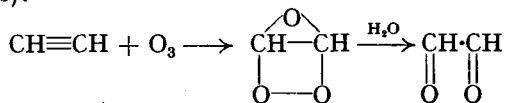


Dichloroacetic acid,  $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ , is also formed by the oxidation of dichloroacetaldehyde by the hypochlorous acid.

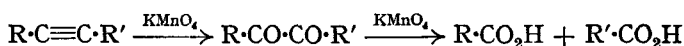
7. Acetylene and its homologues form ozonides with ozone, and these compounds are decomposed by water to form diketones, which are then oxidised to acids by the hydrogen peroxide formed in the reaction:



Acetylene is exceptional in that it gives glyoxal as well as formic acid (Hurd and Christ, 1936):

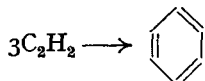


The triple bond in acetylenes is usually oxidised by potassium permanganate to give acid fission products:

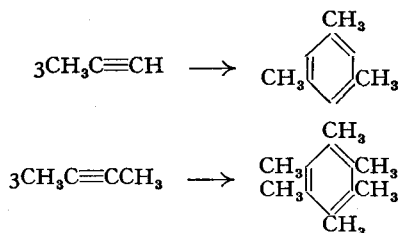


The intermediate  $\alpha$ -diketone can be isolated if the oxidation is carried out in the presence of magnesium sulphate.

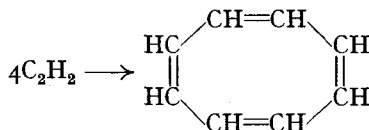
8. When passed through a heated tube acetylene polymerises, to a small extent, to benzene.



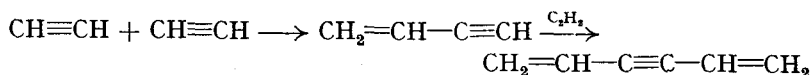
Homologues of acetylene behave in a similar manner, *e.g.*, methylacetylene polymerises to *s*-trimethylbenzene, and dimethylacetylene to hexamethylbenzene:



Under suitable conditions acetylene polymerises to *cyclooctatetraene* (*q.v.*):

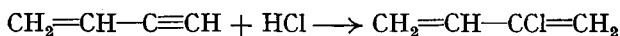


In addition to the above type of *cyclic* polymerisation, acetylene undergoes *linear* polymerisation when passed into a solution of cuprous chloride in ammonium chloride to give vinylacetylene and divinylacetylene:



Compounds containing both a double and triple bond are named systematically as *alkenynes*. The double bond is always expressed first in the name, and numbers as low as possible are given to the double and triple bonds, even though this may give "yne" the lower number. Thus vinylacetylene is but-1-en-3-yne, and divinylacetylene is hexa-1:5-dien-3-yne. The following compound,  $CH_3 \cdot CH = CH \cdot C \equiv CH$ , however, is pent-3-en-1-yne.

Vinylacetylene adds on one molecule of hydrogen chloride to the triple bond to form *chloroprene* or 2-chlorobuta-1:3-diene, the addition taking place in accordance with Markownikoff's rule:

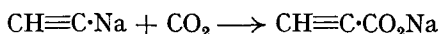


Chloroprene readily polymerises to a rubber-like substance known as *neoprene*.

9. Acetylene forms metallic derivatives by replacement of one or both hydrogen atoms, *e.g.*, if acetylene is passed over heated sodium, both the monosodium and disodium acetylides are formed:



By using a large excess of acetylene the main product is monosodium acetylide, which is also obtained by passing acetylene into a solution of sodium in liquid ammonia until the blue colour disappears. By treatment of a fine dispersion of sodium in xylene at 100–105° with acetylene, sodium acetylide can be obtained in 98 per cent. yield (Rutledge, 1957). The monosodium derivative possesses the interesting property of being able to absorb dry carbon dioxide to form the sodium salt of propiolic acid (*q.v.*):



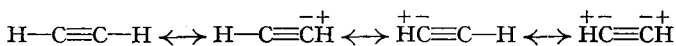
The alkali metal acetylides react with carbonyl compounds to form acetylenic alcohols:



Acetylene also forms Grignard reagents by reaction with alkylmagnesium halides (p. 351).

When acetylene is passed into an ammoniacal solution of cuprous chloride or silver nitrate, cuprous acetylide  $\text{Cu}_2\text{C}_2$  (red) or silver acetylide  $\text{Ag}_2\text{C}_2$  (white) is precipitated. Both these compounds, when dry, explode when struck or heated. When they are treated with potassium cyanide solution pure acetylene is obtained, but on treatment with inorganic acid, the acetylene liberated is impure.

The acidic nature of hydrogen in acetylene is characteristic of hydrogen in the group  $\equiv\text{CH}$ , and it has been suggested that this is because the C—H bond has considerable ionic character due to resonance.



There is, however, evidence to show that the electronegativity of a carbon atom depends on the number of bonds by which it is joined to its neighbouring carbon atom (Walsh, 1947). Since  $\pi$ -electrons are more weakly bound than  $\sigma$ -electrons, the electron density round a carbon atom with  $\pi$ -bonds is less than that when only  $\sigma$ -bonds are present. Thus, a carbon atom having one  $\pi$ -bond has a slight positive charge compared with a carbon atom which has only  $\sigma$ -bonds. Thus, the electronegativity of an  $sp^2$  hybridised carbon atom is greater than that of an  $sp^3$  hybridised carbon atom. Similarly, a carbon atom which has two  $\pi$ -bonds carries a small positive charge which is greater than that carried by a carbon atom with only one  $\pi$ -bond. Thus the electronegativity of an  $sp$  hybridised carbon atom is greater than that of an  $sp^2$  hybridised carbon atom. It therefore follows that the more  $s$  character a bond has, the more electronegative is that carbon atom. Thus the attraction for electrons by hybridised carbon will be  $sp > sp^2 > sp^3$ . Therefore the ionic character of a C—H bond depends on the state of hybridisation of the carbon atom and is greatest for  $sp$  hybridisation and least for  $sp^3$  hybridisation. Hence, in acetylene, the hydrogen atoms have a large amount of ionic character (relative to ethylene and methane) and consequently are more readily released as protons (than hydrogen in ethylene and methane).

This interpretation of change in electronegativity with change in hybridisation has a very important bearing on the problem of hyperconjugation (p. 271).

The structure of metallic carbides, *i.e.*, compounds formed between carbon and metals, is still a matter of dispute. It appears certain, so far, that the carbides of the strongly electropositive metals: Na, K, Ca, Sr, Ba, are ionic—X-ray crystal analysis has shown the lattice of these carbides to be ionic, containing the

ion  $\overset{-}{\text{C}}\equiv\overset{-}{\text{C}}$ . These carbides react with water to produce acetylene. Copper and silver carbides are not affected by water, and are explosive when dry. On account of these differences it seems likely that the carbides of these two metals are covalent, *e.g.*,  $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ . Thus these compounds may be regarded as *acetylides*.



In addition to the above carbides, there are a number of carbides which react with water or dilute acids to produce methane, *e.g.*, aluminium carbide; or a mixture of hydrocarbons, *e.g.*, uranium carbide which gives acetylene and other unsaturated hydrocarbons; iron carbide which gives methane and hydrogen. Many authors believe these carbides to be ionic, and include carbides of copper and silver in this group.

There is also one other group of carbides which are highly refractory, and which are extremely stable chemically; *e.g.*, vanadium carbide is not attacked by water or hydrochloric acid even at 600°. These carbides are believed to be *interstitial* compounds, *i.e.*, their lattice is not composed of ions, but resembles a metallic or atomic lattice.

**Structure of acetylene.** By reasoning similar to that used for ethylene, the structure of acetylene is shown to be  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , and may be repre-



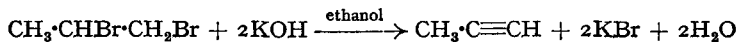
FIG. 4.2.

sented as Fig. 2(a). This representation, however, appears to be inadequate. According to Coulson (1952), the two  $\pi$ -bonds form a charge cloud which has cylindrical symmetry about the carbon-carbon axis (Fig. 2b).

#### HOMOLOGUES OF ACETYLENE

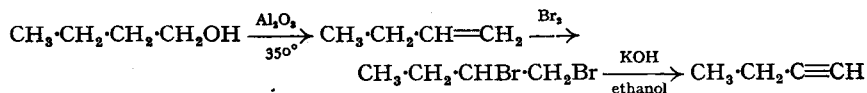
Homologues of acetylene may be prepared by any of the following methods:

1. By the action of ethanolic potassium hydroxide on *vic*- or *gem*-dihalogen derivatives of the paraffins (*cf.* preparation of acetylene, method 2), *e.g.*, methylacetylene from propylene bromide:

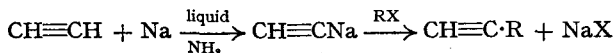


Since *gem*-dihalides are not usually readily accessible, and the *vic*-dihalides are, the latter are used.

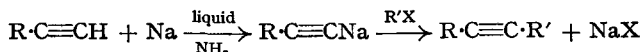
This method affords a simple means of introducing a triple bond into an organic compound, *e.g.*, *n*-butanol is catalytically dehydrated to but-1-ene, which on treatment with bromine gives 1:2-dibromobutane, and this, when heated with ethanolic potassium hydroxide, yields but-1-yne:



2. Monosodium acetylide (see reaction 9 of acetylene) is treated with an alkyl halide, preferably a bromide, whereupon an acetylene homologue is produced:

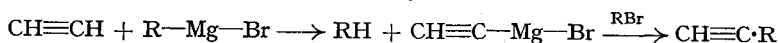


This reaction may be carried further as follows:

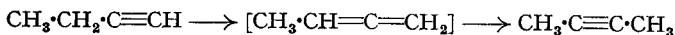


In practice this method is limited to the use of primary alkyl halides, since higher *sec.* and *tert.* halides give mainly olefins when they react with the monosodium derivatives of acetylene or its homologues.

3. By the action of acetylene on a Grignard reagent (*q.v.*) and then treating the resulting magnesium complex with an alkyl halide:

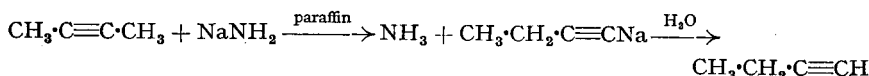


The properties of the homologues of acetylene are very similar to those of acetylene, particularly when they are of the type  $\text{R}\cdot\text{C}\equiv\text{CH}$ , *i.e.*, contain the  $\equiv\text{CH}$  group. A very interesting reaction of the acetylene homologues is their ability to isomerise when heated with ethanolic potassium hydroxide, the triple bond moving towards the centre of the chain, *e.g.*, but-1-yne isomerises to but-2-yne:



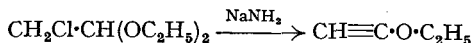
There is a great deal of evidence to show that an allene is formed as an intermediate.

On the other hand, when alkynes are heated with sodamide in an inert solvent, *e.g.*, paraffin, the triple bond moves towards the end of the chain; *e.g.*, but-2-yne gives the sodium derivative of but-1-yne, which is converted into but-1-yne by the action of water:



This reaction affords a means of stepping up the alkyne series by method 2 above.

A very useful acetylene derivative for synthetic work is ethoxyacetylene. This may conveniently be prepared by the action of sodamide on chloroacetaldehyde diethyl acetal (Jones *et al.*, 1954):



Lithium derivatives of monosubstituted acetylenes can be prepared by inter-action of the acetylene and lithium amide in dioxan (Schlubach *et al.*, 1958).

## QUESTIONS

- Write out the structures of the isomeric pentenes and name them (use three methods of nomenclature).
- Give an account of the evidence for the structure of propylene.
- Give as many methods as you can for separating a mixture of *isobutane* and but-1-ene into its constituents.
- Show how you would distinguish experimentally between the three isomeric butylenes.
- Name the compounds and indicate the conditions under which they are formed when but-1-ene is treated with:—(a) bromine, (b) hydrogen bromide, (c) hydrogen chloride, (d) hypochlorous acid, (e) ozone, (f) conc. sulphuric acid, (g) hydrogen, (h) chlorine, (i) nitrosyl chloride, (j) peracetic acid, (k) heat.
- Define and give examples of:—(a) unsaturation, (b) dehydration, (c) dehydrohalogenation, (d) conjugation, (e) 1 : 4-addition, (f) polymerisation, (g) hydroxylation of a double bond, (h) peroxide effect, (i) ozonolysis, (j) Prileschaiev's reaction, (k) polycondensation, (l) plastics, (m) thermoplastic, (n) thermo-setting plastic, (o) plasticiser, (p) ethinylation, (q) vinylation, (r) Wittig reaction, (s) hydroboronation.
- Write out the structures and names (by two methods) of the isomeric pentynes.
- Give an analytical table to show how you would distinguish between ethane, ethylene and acetylene.
- Name the compounds and indicate the conditions under which they are formed when acetylene reacts with the reagents named in question 5.
- Prepare methylpropylacetylene using only acetylene and methyl iodide and any inorganic compounds you wish.
- Give an account of the evidence for the structure of acetylene.
- Discuss the structures of butadiene and acetylene from the M.O. point of view.

## READING REFERENCES

Gilman, *Advanced Organic Chemistry*, Wiley (1942, 2nd ed.).

- Vol I. (a) Ch. 1. The Reactions of the Aliphatic Hydrocarbons.  
(b) Ch. 7. Unsaturation and Conjugation.  
(c) Ch. 8. Synthetic Polymers.

- Mayo and Walling, The Peroxide Effect, *Chem. Reviews*, 1940, **27**, 357.  
Riebsomer, Reactions of Nitrogen Tetroxide with Organic Compounds, *ibid.*, 1945, **36**, 197-211.  
Levy, Scaife *et al.*, Addition of Dinitrogen Tetroxide to Olefins, *J.C.S.*, **1946**, 1093, 1096, 1100; **1948**, 52.  
Gorin, Kuhn, and Miles, Mechanisms of the Catalysed Alkylation of *iso*Butane with Olefins, *Ind. Eng. Chem.*, 1946, **38**, 745.  
Groll and Hearne, Substitution in Straight-Chain Olefins, *ibid.*, 1939, **31**, 1530.  
Bailey, The Reactions of Ozone with Organic Compounds, *Chem. Reviews*, 1958, **58**, 925.  
*Organic Reactions*, Wiley. Vol. II (1944), Ch. 8. Periodic Acid Oxidation.  
*ibid.*, 1945, **42**, 143-145. Oxidation with Lead Tetra-acetate.  
De la Mare, Kinetics of Thermal Addition of Halogens to Olefinic Compounds, *Quart. Reviews (Chem. Soc.)*, 1949, **3**, 126.  
*Organic Reactions*, Wiley. Vol. V (1949), Ch. I. The Synthesis of Acetylenes.  
Raphael, *Acetylenic Compounds in Organic Synthesis*, Butterworth (1955).  
*Organic Reactions*, Wiley. Vol. VII (1953), Ch. 7. Epoxidation and Hydroxylation of Ethylenic Compounds with Organic Per-acids.  
Lynch and Pausacker, The Oxidation of Olefins with Perbenzoic Acids. A Kinetic Study, *J.C.S.*, **1955**, 1525.  
Trapnell, Specificity in Catalysis by Metals, *Quart. Reviews (Chem. Soc.)*, 1954, **8**, 404.  
Bond, The Mechanism of Catalytic Hydrogenation and Related Reactions, *ibid.*, 1954, **8**, 279.  
Cadogan and Hey, Free-Radical Addition Reactions to Olefinic Systems, *ibid.*, 1954, **8**, 308.  
Bu'Lock, Acetylenic Compounds as Natural Products, *ibid.*, 1956, **10**, 371.  
Kharasch, The Unique Properties of 2 : 4-Dinitrobenzenesulphenyl Chloride, *J. Chem. Educ.*, 1956, **33**, 585.  
Langford and Lawson, Characterisation of Organic Compounds with 2 : 4-Dinitrobenzenesulphenyl Chloride, *ibid.*, 1957, **34**, 510.  
Crawford, Infrared Spectra of Adsorbed Gases, *Quart. Reviews (Chem. Soc.)*, 1960, **14**, 378.  
*Advances in Organic Chemistry*, Interscience, Vol. I (1960). Trippett, The Wittig Reaction, p. 83. Gunstone, Hydroxylation Methods, p. 103.  
Bradley and Ledwith, The Reaction of Carbene with Alkyl Halides, *J.C.S.*, **1961**, 1495.

## HALOGEN DERIVATIVES OF THE PARAFFINS

HALOGEN derivatives of the paraffins are divided into mono-, di-, tri-, etc., substitution products according to the number of halogen atoms in the molecule.

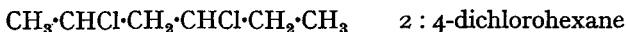
**Nomenclature.** Monohalogen derivatives are usually named as the halide of the corresponding alkyl group, e.g.,  $C_2H_5Cl$  ethyl chloride;  $CH_3\cdot CHBr\cdot CH_3$  isopropyl bromide;  $(CH_3)_3CCl$  *tert.*-butyl chloride.

**Dihalogen derivatives.** (i) When both halogen atoms are attached to the *same* carbon atom, they are said to be in the *geminal* (*gem-*) position. Since the loss of two hydrogen atoms from the same carbon atom gives the *alkylidene* radical, *gem*-dihalides are named as the alkylidene halides, e.g.,  $CH_3\cdot CHBr_2$  ethylidene bromide;  $CH_3\cdot CCl_2\cdot CH_3$  isopropylidene chloride.

(ii) When the two halogen atoms are on *adjacent* carbon atoms they are said to be in the *vicinal* (*vic-*) position, and these dihalides are named as the halide of the olefin from which they may be prepared by the addition of halogen, e.g.,  $CH_2Cl\cdot CH_2Cl$  ethylene chloride;  $(CH_3)_2CBr\cdot CH_2Br$  isobutylene bromide.

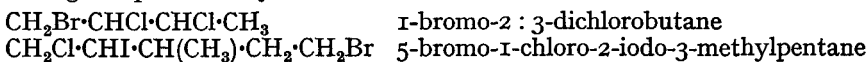
(iii) When there is a halogen atom on each of the *terminal* carbon atoms of the chain, *i.e.*, in the  $\alpha\omega$ -position, the compound is named as the polymethylene halide, e.g.,  $CH_2Cl\cdot CH_2\cdot CH_2\cdot CH_2Cl$  tetramethylene chloride.

(iv) When the two halogen atoms occupy positions other than those mentioned above, the compounds are named as dihalogen derivatives of the parent hydrocarbon, the positions of the halogen atoms being indicated by numbers (use principle of lowest numbers), e.g.,



The alkyl halides, *gem-*, *vic-* and  $\alpha\omega$ -dihalides may also be named by this (I.U.P.A.C.) system, e.g.,  $CH_3\cdot CH_2\cdot CHBr\cdot CH_3$  2-bromobutane;  $CH_2Cl\cdot CH_2\cdot CH_2Cl$  1:3-dichloropropane.

**Polyhalogen derivatives** are best named by the I.U.P.A.C. system (method iv), and the names of the halogens (and any other substituents present) are arranged alphabetically:

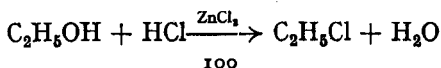


## ALKYL HALIDES

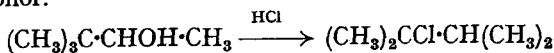
The alkyl halides have the general formula  $C_nH_{2n+1}X$  or  $RX$ , where  $X$  denotes chlorine, bromine or iodine. Fluorine is not included, since fluorides were, until fairly recently, chemical curiosities, and also do not behave like the other halides. Fluorine compounds are discussed separately at the end of this chapter.

**General methods of preparation.** 1. The method most widely used is to replace the hydroxyl group of an alcohol by an  $X$  atom. This may be done by means of various halogen reagents, and the accessibility of the reagent is usually the factor deciding which one is used for the preparation of a particular alkyl halide.

(i) **Alkyl chlorides** may be prepared by passing hydrogen chloride into the alcohol in the presence of anhydrous zinc chloride (Groves' process), e.g., ethyl chloride from ethanol:



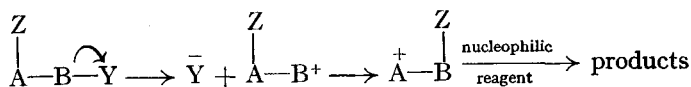
The yield of alkyl chloride depends on the nature of the alcohol. Primary alcohols of the type  $R\cdot CH_2\cdot CH_2OH$  and  $R_2CH\cdot CH_2OH$  usually give good yields of alkyl chloride, but when the alcohol is of the type  $R_3C\cdot CH_2OH$ , the main product is a tertiary alkyl chloride formed by rearrangement of the molecule (see *neopentyl* alcohol, below). Secondary alcohols, except for *isopropanol* and *sec.-butanol*, react with hydrogen chloride to give mixtures of chlorides, *e.g.*, pentan-2-ol gives a mixture of 2- and 3-chlorides. Secondary alcohols containing highly branched radicals attached to the carbinol group tend to give tertiary chlorides by molecular rearrangement, *e.g.*, pinacolyl alcohol:



Tertiary alcohols give very good yields of tertiary chloride with concentrated hydrochloric acid in the absence of zinc chloride.

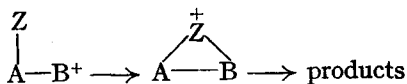
The reaction between an alcohol and hydrogen chloride is reversible, and it is believed that the zinc chloride functions as a dehydrating agent, thus inhibiting the backward reaction.

The formation of the various halides by rearrangement is one example of class of rearrangements often referred to as **1,2-shifts**. In this type of rearrangement a group migrates from a *carbon* atom (the *migration origin*) to an *adjacent* atom (the *migration terminus*), which is usually carbon or nitrogen. The rearrangement may be expressed in the following general form:

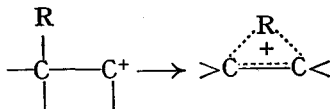


When Y ionises, B is left with only six valency electrons (open sextet), and consequently carries a positive charge. Z migrates *with its bonding pair of electrons*, and A now has an open sextet. Attack now takes place at A by  $Y^-$  or some other nucleophilic reagent to form the products. This mechanism was first suggested by Whitmore (1932) and is often referred to as the *Whitmore mechanism*.

The nature of Z is quite varied; the "key" atom (*i.e.*, the atom joined to the bonding pair which migrates) may be carbon, halogen, oxygen, etc. If Z has a lone pair of electrons, *e.g.*, halogen, then this pair may be used in the migration to give a cyclic intermediate, *i.e.*, a **bridged ion**.



If Z is an aryl group, then this group can supply an electron pair to form a bridged ion (see, *e.g.*, p. 172). If Z is an alkyl group, then there are no lone pairs or multiple bonds, but again it is believed that a bridged ion is possible, *i.e.*,



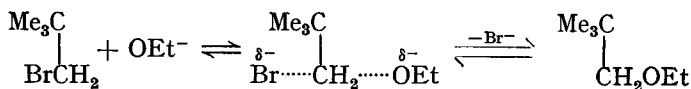
This type of bridged ion contains three *partial* bonds formed from *one pair of electrons*. This idea of bridged carbonium ions was first suggested by Nevell *et al.* (1939), but it must be admitted that the existence of such an ion has not yet been definitely established when the migrating group is an

alkyl group. The formation of these bridged ions in the 1,2-shifts is an example of *neighbouring group participation*, and when the rate of the rearrangement is increased because of this effect, the rearrangement is said to be *anchimerically assisted* (Winstein *et al.*, 1953; see also p. 415).

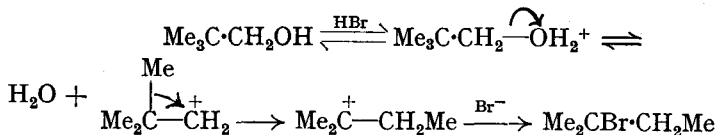
A very important point about 1,2-shifts is that they are *intramolecular*, *i.e.*, Z is never actually free. If the mechanism were such that Z was free during its migration, then the rearrangement would be called *intermolecular*. The intramolecular nature of the 1,2-shifts has been established by using a group Z which contains an asymmetric carbon atom attached to A, *i.e.*, have type  $abcC-A$ . If Z actually separated during the migration, then it means that the free migrating unit is a carbanion, *i.e.*,  $abcC^-$ . Examination of such carbanions has shown that none ever retains its configuration; it racemises, *i.e.*, half the molecules have their configuration inverted, and so the product is no longer optically active (the student should read pp. 413-416 before proceeding further). Thus if Z moves with its bonding pair and the configuration is *retained* in the product, then Z can never have been free, *i.e.*, the rearrangement is intramolecular.

We can now illustrate the foregoing discussion with *neopentyl* alcohol as our example. Whitmore *et al.* (1932) showed that the reactions undergone by *neopentyl* alcohol and *neopentyl* halides are of two types: (i) replacement reactions, which occur very slowly (if at all) and produce *neopentyl* compounds; (ii) replacement (and elimination) reactions, which occur very fast and produce *t*-amyl compounds.

Hughes and Ingold (1946) have shown that the slow reactions take place by the  $S_N2$  mechanism (p. 106) and consequently without rearrangement, *e.g.*, *neopentyl* bromide reacts with ethanolic sodium ethoxide to give ethyl *neopentyl* ether:

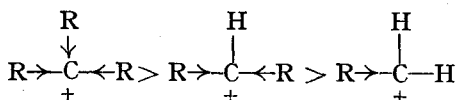


On the other hand, when *neopentyl* alcohol reacts with hydrobromic acid, the reaction is fast, proceeds by the  $S_N1$  mechanism (p. 106), and produces *t*-amyl bromide by rearrangement (a 1,2-shift):



There is no definite evidence that the intermediate is a bridged ion rather than the classical carbonium ion.

A point of interest here is that the "driving force" of the rearrangement is probably due to the stabilities of carbonium ions being tertiary > secondary > primary due to the delocalisation of the charge by the inductive effect of the alkyl groups increasing with the number of alkyl groups attached to the positively charged carbon atom (in the classical carbonium ion; *cf.* p. 33):

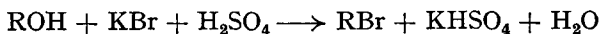


**Alkyl bromides may be prepared:**

(a) By refluxing the alcohol with excess constant-boiling hydrobromic acid (48 per cent.) in the presence of a little sulphuric acid, which must behave catalytically, since in its absence the reaction is slow.

The yield of alkyl bromide is usually excellent; when a secondary or tertiary alcohol is used, it is better to omit the sulphuric acid, since this would dehydrate these alcohols to olefins and thereby reduce the yield.

(b) By heating the alcohol with potassium bromide and concentrated sulphuric acid in excess:



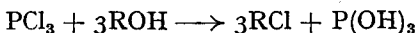
The yield is very good for primary alcohols only; secondary and tertiary are readily dehydrated to olefins under these conditions.

**Alkyl iodides** may be prepared in good yield by refluxing the alcohol with excess of constant-boiling hydriodic acid (57 per cent.). Stone *et al.* (1950) have shown that alkyl iodides may be prepared in good yields by heating alcohols, ethers or olefins with sodium or potassium iodide in 95 per cent. phosphoric acid.

(ii) Any alkyl halide may be prepared by the action of a phosphorus halide on the alcohol. Phosphorus pentachloride gives variable yields depending on the alcohol:

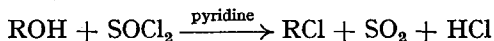


Phosphorus trichloride gives poor yields of alkyl chloride except with alcohols which tend to react by an  $\text{S}_{\text{N}}1$  mechanism, *e.g.*, *tert.*-alcohols behave in accordance with the equation:



The yields of alkyl halide with phosphorus tribromide or tri-iodide are *v.g.-ex.* for primary alcohols; less for secondary alcohols, and still less for tertiary. These phosphorus trihalides are usually prepared *in situ*; bromine or iodine is added to a mixture of red phosphorus and alcohol, and warmed.

(iii) Thionyl chloride (one molecule) refluxed with alcohols (one molecule) forms alkyl chlorides in the presence of pyridine (one molecule) [**Darzens procedure**] (see also p. 415):

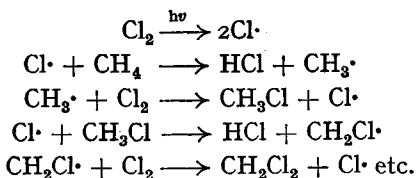


In a number of cases only a small amount of pyridine need be used to give the same yield of alkyl chloride as in the Darzens procedure.

2. By the addition of halogen acids to an olefin.

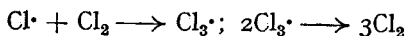
3. By direct halogenation, *i.e.*, substitution reactions of the paraffins with halogen, and this may be brought about by (a) light, (b) catalysts or (c) heat.

(a) **Photohalogenation** is carried out by treating the paraffin with chlorine or bromine at ordinary temperature in the presence of light. The reaction is believed to take place by a free-radical chain mechanism, the initiation being brought about by the formation of chlorine atoms by the U.V. part of the spectrum of the light:



The termination of the chain reaction may take place by adsorption of the chlorine atoms on the walls of the containing vessel, or by two chlorine atoms combining with each other to form a chlorine molecule. There

appears to be no evidence to show that  $\text{CH}_3\cdot$ ,  $\cdot\text{CH}_2\text{Cl}$ , etc., radicals combine to terminate the chain reaction (*cf.* addition of chlorine to ethylene, p. 66). Ritchie and Winning (1950) suggest that the chain-ending involves the formation of  $\text{Cl}_3$  molecules:



(b) **Catalytic halogenation** is carried out by treating the paraffin with halogen in the presence of various metallic halides, *e.g.*, cupric chloride catalyses chlorination; ferric bromide, bromination.

(c) **Thermal halogenation.** Thermal chlorination has been studied in great detail by Hass, McBee and their co-workers (1935 onwards), and as a result of their work they suggested a number of rules for chlorination:

(i) If high temperature is avoided, no carbon skeleton rearrangements occur in either thermal or photochemical chlorination.

(ii) Every possible monochloride is formed, and over-chlorination, *i.e.*, chlorination beyond monosubstitution, may be suppressed by controlling the ratio of chlorine to paraffin (this rule also holds good for photochemical chlorination).

(iii) The order of ease of substitution is tertiary hydrogen > secondary > primary. At  $300^\circ$ , with reaction in the vapour phase, the relative rates of substitution of primary, secondary and tertiary hydrogen atoms are 1.00 : 3.25 : 4.43.

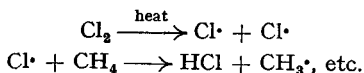
(iv) As the temperature rises above  $300^\circ$  the relative rates of substitution tend to become equal, *i.e.*, 1 : 1 : 1. Increased pressure causes an increase in the relative rate of primary substitution.

(v) In vapour-phase chlorination the presence of a chlorine atom on a carbon atom tends to prevent further reaction on that carbon atom during the second substitution. According to Tedder *et al.* (1960), this generalisation is a poor approximation to the truth. These authors have shown the effect of the halogen atom already present in the molecule is to retard substitution at a  $\beta$ -carbon atom, and also affects substitution at an  $\alpha$ -carbon atom.

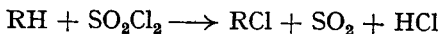
In the past it was believed that paraffins always tended to *complete* substitution. Rule (ii) shows this is not the case. Methane, however, has been found to be an exception; chlorination of methane always results in a mixture of all four substitution products, their relative amounts depending on the ratio of chlorine to methane (*see, e.g.*, methyl chloride).

Bromination takes place with greater difficulty than chlorination, and there is less tendency for polysubstitution.

The mechanism of thermal halogenation is believed to take place by a free-radical chain reaction (*cf.* photohalogenation). The initiation of the chain reaction is brought about by the thermal dissociation of chlorine molecules into separate atoms:



4. Direct chlorination of paraffins may be effected by means of sulphuryl chloride. Sulphuryl chloride in the absence of light and catalysts does not react with paraffins even at their boiling points, but in the presence of light and a trace of an organic peroxide the reaction is fast:



The mechanism of this reaction is still obscure, but in view of the fact that it is catalysed by organic peroxides (which are known to generate free radicals), it is quite likely that chlorination with sulphuryl chloride proceeds by a free-radical chain reaction.



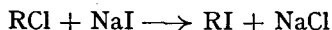
In general, the products obtained by chlorination with sulphuryl chloride are the same as those obtained by photochemical or thermal chlorination, and it has been found that when sulphuryl chloride is used:

(i) The order of ease of replacement of a hydrogen atom is tertiary > secondary > primary.

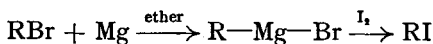
(ii) The second chlorine atom tends to substitute on that carbon atom which is as far away as possible from the carbon atom already joined to the chlorine atom.

(iii) It is difficult to get two, and impossible to get three, chlorine atoms on the same carbon atom.

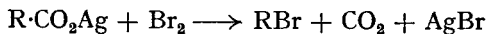
Alkyl chlorides and bromides are generally obtained fairly easily, iodides not so easily. Fluorides have to be prepared by special means (see later in this chapter). In many cases the iodide may be obtained from the corresponding chloride or bromide by treating the latter in acetone or methanol solution with sodium iodide (see p. 54):



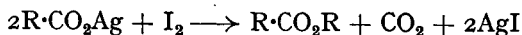
Iodides may also be prepared from the corresponding bromide via the Grignard reagent:



5. Hunsdiecker *et al.* (1935) found that various salts of the fatty acids are decomposed by chlorine or bromine to form the alkyl halide, *e.g.*,



The silver salt appears to give the best yield, but the yield also depends on the solvent used; Stoll *et al.* (1951) found that trichloroethylene is a better solvent than either carbon tetrachloride or carbon disulphide. The yield of halide is primary > secondary > tertiary, and bromine is generally used, chlorine giving a poorer yield of alkyl chloride, and iodine tending to form esters.



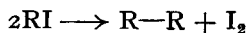
Apart from preparing alkyl halides, this reaction also offers a means of stepping down the fatty acids and alcohols.

The reaction considered above is often referred to as the *Hunsdiecker reaction* or the *Borodine-Hunsdiecker reaction*.

6. Rydon *et al.* (1954) have shown that alkyl halides may be prepared, in good yield, by the addition of halogen to a mixture of an alcohol and triphenyl phosphite:



**General properties of the alkyl halides.** The lower members methyl chloride, methyl bromide and ethyl chloride are gases; methyl iodide and the majority of the higher members are sweet-smelling liquids. The order of the values of the boiling points (and densities) of the alkyl halides is iodide > bromide > chloride > fluoride. In a group of isomeric alkyl halides, the order of the boiling points is primary > secondary > tertiary. Many of the alkyl halides burn with a green-edged flame. The chemical reactions of the alkyl halides are similar, but they are not equally reactive, the order of reactivity being iodide > bromide > chloride; the reactivity of alkyl fluorides depends on the nature of the fluoride (p. 122). Alkyl iodides are sufficiently reactive to be decomposed by light, the iodide darkening due to the liberation of iodine:



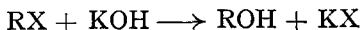
Alkyl halides (and the polyhalides) are covalent compounds, insoluble in water, with which they cannot form a hydrogen bond, but soluble in organic solvents.

The alkyl halides are classified as primary, secondary and tertiary, according as the halogen atom is present in the respective groups  $-\text{CH}_2\text{X}$ ,  $=\text{CHX}$  and  $\equiv\text{CX}$ , *i.e.*, according as the halogen atom is joined to a primary, secondary or tertiary carbon atom.

It has already been pointed out that alkyl groups have a +I effect. Before considering the reactions of the alkyl halides, it is important to explain why an alkyl group is electron-repelling. Several explanations have been offered; the following is a highly favoured one. As we have seen, methane and ethane are non-polar (p. 54). Thus the methyl group has a zero inductive effect; and this is true for all alkyl groups since all paraffins, whether straight- or branched-chain, have a zero dipole moment. When, however, one hydrogen atom in a paraffin is replaced by some polar atom (or group), the alkyl group now exerts a polar effect which is produced by the presence of the polar atom. Thus, in an alkyl halide, the alkyl group possesses an inductive effect, but it is one which is produced mainly by the mechanism of *interaction polarisation* (*cf.* p. 20). It therefore follows that the alkyl group is more polarisable than a hydrogen atom, and since most of the groups attached to the alkyl group are electron-attracting groups, the alkyl group thus usually becomes an electron-repelling group, *i.e.*, alkyl groups normally have a +I effect.

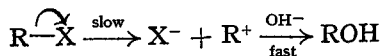
**General reactions of the alkyl halides.** The alkyl halides are extremely important reagents because they undergo a large variety of reactions that make them valuable in organic syntheses.

1. Alkyl halides are hydrolysed to alcohols very slowly by water, but rapidly by silver oxide suspended in boiling water, or by boiling aqueous alkalis (see also 5):

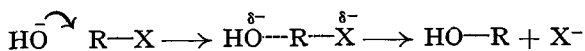


This type of reaction is an example of nucleophilic substitution ( $\text{S}_{\text{N}}$ ) since the attacking reagent is a nucleophilic reagent (p. 33). It has been assumed that this type of heterolytic reaction in solution can take place by two different mechanisms, unimolecular or bimolecular.

**Unimolecular mechanism.** This is a *two-stage process*, the first stage consisting of *slow* heterolysis of the compound to form a carbonium ion, followed by *rapid* combination between the carbonium ion and the substituting nucleophilic reagent. Since the rate-determining step is the first one, and since in this step only *one* molecule is undergoing a covalency change, this type of mechanism is called *unimolecular*, and is labelled  $\text{S}_{\text{N}}1$  (Ingold *et al.*, 1928, 1933). Thus, if the hydrolysis of an alkyl halide is an  $\text{S}_{\text{N}}1$  reaction, it may be written:



**Bimolecular mechanism.** This is a *one-stage process*, two molecules simultaneously undergoing covalency change in the rate-determining step. This type of mechanism is called *bimolecular*, and is labelled  $\text{S}_{\text{N}}2$ . Since the rate-determining step in this reaction is the formation of the transition state, the hydrolysis of an alkyl halide by an  $\text{S}_{\text{N}}2$  reaction may be written:



Any factor that affects the energy of activation of a given type of reaction will affect the rate and/or the mechanism. Attempts have been made to

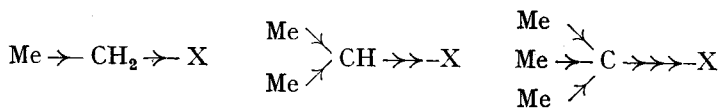
calculate E in terms of bond strengths, steric factor, heats of solution of ions, etc., but apparently the results are conflicting. The following discussion is therefore largely qualitative, and because of this, one cannot be sure which are the predominant factors in deciding the value of the energy of activation.

The main difference between the two mechanisms is the kinetic order of the reaction.  $S_N2$  reactions would be expected to be second order, whereas  $S_N1$  reactions would be expected to be first order. These orders are only true under certain circumstances, *e.g.*, in a bimolecular reaction, the order is second-order if both reactants are present in small and controllable concentrations. If, however, one of the reactants is the solvent, this will be in constant excess, and so such a bimolecular mechanism will lead to first-order kinetics.

Another important difference is that in the  $S_N2$  mechanism, the molecule is *always* inverted. In the  $S_N1$  mechanism, the configuration of the resulting molecule depends on various factors (see p. 415).

Let us first consider the nature of R. There are two effects to be considered, the polar factor and the steric factor.

*Polar factor.* Consider the series of ethyl, *isopropyl*, and *t*-butyl halides. Since the methyl group has a +I effect, the larger the number of methyl groups on the carbon atom of the C—X, the greater will be the electron density on this carbon. If we use one arrow-head to represent (qualitatively) the electron-repelling effect of a methyl group, then we have the following state of affairs:



This increasing electron density on the central carbon atom increasingly opposes attack at this carbon atom by a negatively charged nucleophilic reagent. Thus the formation of the transition state for the  $S_N2$  mechanism becomes increasingly difficult. It can therefore be anticipated that the  $S_N2$  mechanism is made more difficult in passing from EtX to *t*-BuX. On the other hand, since the  $S_N1$  mechanism involves ionisation as the first step, then it can be expected that as the electron density increases on the central carbon atom, the bonding pair in C—X becomes more and more displaced towards the X atom, and consequently ionisation of X as a negative ion will become easier. It therefore follows that the tendency for the  $S_N1$  mechanism should increase from EtX to *t*-BuX. These anticipated results have been realised in practice. Hughes, Ingold *et al.* (1935-1940) examined the hydrolysis of alkyl bromides in alkaline aqueous ethanol and showed that MeBr and EtBr undergo hydrolysis by the  $S_N2$  mechanism, *iso*PrBr by both  $S_N2$  and  $S_N1$  mechanisms, and *t*-BuBr by the  $S_N1$  mechanism only. It has also been shown, however, that the actual position where the mechanism changes over from  $S_N2$  to  $S_N1$  in a given graded polar series (such as the one above) is not fixed but also depends on other factors such as the concentration of the nucleophilic reagent and the nature of the solvent (see below).

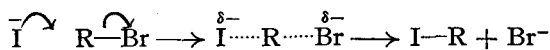
*Steric effects.* The steric effect was originally thought to be a spatial effect brought into play by mechanical interference between groups, and was described as *steric hindrance* (see p. 686). The term steric hindrance considered the geometry of the reactant molecule. When, however, a molecule undergoes chemical reaction, it does so via a transition state. Consequently the geometry of both the initial and transition state must be taken into consideration. Thus steric factors may affect the speed and/or the

mechanism of a reaction. It is, however, often very difficult to distinguish between steric and polar factors. Nevertheless, the effects of the steric factor can often be assessed in some sort of qualitative manner. When steric effects slow down a reaction, that reaction is said to be subject to **steric hindrance** (or **retardation**), and when they speed up a reaction, that reaction is said to be subject to **steric acceleration**.

When there is repulsion between *non-bonded* atoms in a molecule due to their close proximity, forces of **steric repulsion** are said to be acting. When the stability of a molecule is decreased by internal forces produced by interaction between the constituent parts, that molecule is said to be under **steric strain**. There are three sources of steric strain: (i) repulsion between non-bonded atoms (steric repulsion); (ii) distortion of bond angles (*angle strain*); (iii) dipole interactions.

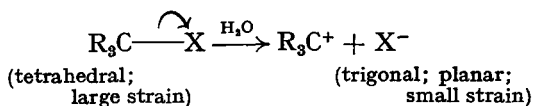
In an  $S_N2$  reaction there will be five groups "attached" to the carbon atom at which reaction occurs (p. 414). Thus there will be "crowding" in the transition state, and the bulkier the groups, the greater will be the *compression energy*, and consequently the reaction will be hindered sterically.

Let us consider the following example. Hughes *et al.* (1946) examined the rate of exchange of iodide ions in acetone solution with MeBr, EtBr, *iso*PrBr, and *t*-BuBr under conditions where only the  $S_N2$  mechanism operated. The relative reactivities were found to be 10,000; 65; 0.50; 0.039.



Thus increasing the number of methyl groups on the central carbon atom increases the steric retardation.

The problem is somewhat different for the  $S_N1$  mechanism. Here the transition state does not contain more than four groups attached to the central carbon atom, and hence one would expect steric hindrance to be less important in the  $S_N1$  mechanism. If, however, the molecule contains bulky groups, then by ionising, the molecule can relieve the steric strain, since the carbonium ion produced is flat (trigonal hybridisation) and so there is more room to accommodate the three alkyl groups. Thus, in such  $S_N1$  reactions, there will be steric acceleration. Brown *et al.* (1949) showed that the solvolysis of tertiary halides is subject to steric acceleration (*solvolysis* is a nucleophilic substitution reaction in which the *solvent* is the nucleophilic reagent).



These authors showed that as R increases in size, the rate of solvolysis increases. However, the larger the R groups are, the more slowly will the carbonium ion be expected to react with solvent molecules, since steric strain will be re-introduced into the molecule. In cases like this, the carbonium ion tends to undergo an elimination reaction to form an olefin (*cf.* ethylene), and Brown *et al.* (1950) have shown that this elimination process increases as the alkyl groups become larger (see p. 112).

It should be noted that a fundamental part of the  $S_N1$  mechanism is the postulate of the transient existence of carbonium ions. Symons *et al.* (1959) have shown that monoaryl-carbonium ions are stable in dilute solutions of sulphuric acid. These authors have also concluded, from a spectroscopic examination of *t*-butanol in sulphuric acid, that there is the trimethylcarbonium ion,  $\text{CMe}_3^+$ , in solution and that this ion is probably planar (*cf.* p. 366). It is interesting to note that of the ions  $\text{Me}^+$ ,  $\text{MeCH}_2^+$ ,  $\text{Me}_2\text{CH}^+$ ,  $\text{Me}_3\text{C}^+$ , the order of stability would be expected to increase from left to right, since the charge is

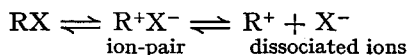
being increasingly neutralised by the +I effect of the methyl groups. On the other hand, the triphenylmethyl carbonium ion,  $(C_6H_5)_3C^+$ , has been isolated as its perchlorate and borofluoride (Dauben *et al.*, 1960).

Now let us consider the effect of the nature of the halogen atom. Experimental work has shown that the nature of X has very little effect, if any, on *mechanism*, but it does affect the *rate* of reaction for a given mechanism, *e.g.*, it has been found that in  $S_N1$  reactions, the rate follows the order  $RI > RBr > RCl$ . This may be explained by consideration of the C—X bond energy, the values of which are C—Cl, 77 k.cal.; C—Br, 65 k.cal.; C—I, 57 k.cal. Thus the C—I bond is most easily broken and the C—Cl bond least easily. These energy differences also explain the same order of increasing rate in  $S_N2$  reactions. As we have seen, the stronger the C—X bond, the greater will be the energy of activation.

The more pronounced the nucleophilic activity of the attacking reagent, *i.e.*, the greater the availability of its unshared pair, then the more the  $S_N2$  mechanism will be favoured, since in the  $S_N1$  mechanism the reagent does not enter into the rate-determining step of ionisation. However, it can also be expected that as the nucleophilic activity of the reagent decreases, a point will be reached where the nucleophilic activity is so low that the mechanism will change from  $S_N2$  to  $S_N1$ . Hughes, Ingold, *et al.* (1935) examined the mechanism and rate of decomposition of various trimethylsulphonium salts  $(Me_3S^+X^-)$ ; see also p. 335) and showed that for  $X = OH$ , the mechanism is  $S_N2$ , and for  $X = I, Cl, \text{ or } Br$ , the mechanism is  $S_N1$  and the rate decreases in this order.

Mechanism and rate of reaction are very much affected by the nature of the solvent. It has been found that the ionising power of a solvent depends on its dielectric constant and its power of solvation, and it appears that the latter is more important than the former. Solvation is due to the "attachment" between solvent and solute molecules, and one important contributing factor is attraction of a charge for a dipole. Since electrostatic work is done in the process of solvation, energy is lost by the system, and consequently the system is more stable.

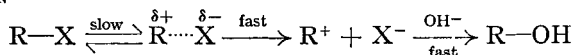
Although the solute molecules have ionised, the oppositely charged pair of ions may become enclosed in a "cage" of the surrounding solvent molecules, and may therefore recombine before they can escape from the cage. Such a complex is known as an *ion-pair*, and their recombination is known as *internal return*. It has now been shown that many organic reactions proceed via ion-pairs rather than dissociated ions (see p. 273) Thus we have the possibility of the following steps:



Many attempts have been made to correlate reaction rates and nature of the solvent. Hughes and Ingold (1935, 1948) proposed the following qualitative theory of solvent effects:

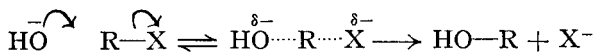
- (i) Ions and polar molecules, when dissolved in polar solvents, tend to become solvated.
- (ii) For a given solvent, solvation tends to increase with increasing magnitude of charge on the solute molecules or ions.
- (iii) For a given solute, solvation tends to increase with the increasing dipole moment of the solvent.
- (iv) For a given magnitude of charge, solvation decreases as the charge is spread over a larger volume.
- (v) The decrease of solvation due to the dispersal of charge will be less than that due to its destruction.

Since the rate-determining step in an  $S_N1$  reaction is ionisation, any factor that assists this ionisation will therefore facilitate  $S_N1$  reactions. Solvents with high dipole moments (*i.e.*, high polarity) are usually good ionising media and, in general, it has been found that the more polar the solvent, the greater is the rate of the  $S_N1$  reaction. Let us consider the following  $S_N1$  reaction:



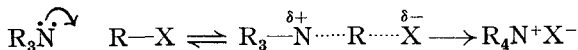
Since the transition state has a larger charge than the reactant molecule, the former will be more solvated than the latter (rule ii). Thus the transition state is more stabilised than the reactant molecule, *i.e.*, the energy of activation is lowered, and so the reaction proceeds faster than had there been no (or less) solvation.

The rates of  $S_N2$  reactions are also affected by the polarity of the solvent:



A solvent with a high dipole moment will solvate both the reactant ion (nucleophilic reagent) and the transition state, but more so the former than the latter, since in the latter the charge, although unchanged in magnitude ( $\delta^- = 1/2$ ), is more dispersed than in the former. Therefore solvation tends to stabilise the reactants more than the transition state (rule iv). Thus the activation energy is increased, and so the reaction is retarded.

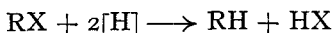
The rate of the following  $S_N2$  reaction is increased as the polarity of the solvent increases.



Here the charge on the transition state is greater than that on the reactants. Hence the transition state is more solvated than the reactants and consequently stabilised, and so the activation energy is lowered.

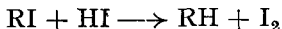
The polarity of the solvent may *change* the mechanism of a reaction, *e.g.*, Olivier (1934) showed that the alkaline hydrolysis of benzyl chloride in 50 per cent. aqueous acetone proceeds by both  $S_N2$  and  $S_N1$  mechanisms. When water was used as solvent, the mechanism was now mainly  $S_N1$ . The dipole moment of water is greater than that of aqueous acetone, and so ionisation of the benzyl chloride is facilitated.

2. Alkyl halides are reduced by nascent hydrogen (Zn/Cu or Na and ethanol, Sn and HCl, etc.) to form the corresponding paraffins:



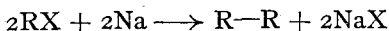
Lithium aluminium hydride also effects this reduction.

Alkyl *iodides* may be reduced by heating them with concentrated hydriodic acid and a small amount of red phosphorus at 150°.

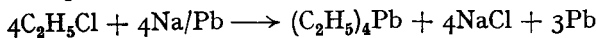


Since alcohols are readily converted into the corresponding halide, this offers a method of converting alcohols into paraffins with the *same* number of carbon atoms.

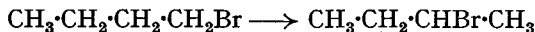
3. Alkyl halides undergo the Wurtz reaction to form paraffins (p. 51):



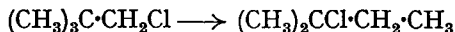
On the other hand alkyl halides, when heated with certain metallic alloys, form *organo-metallic* compounds, *e.g.*, ethyl chloride heated with a sodium lead alloy under pressure gives tetraethyl-lead:



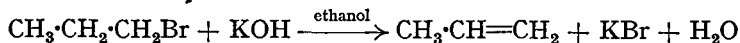
4. When an alkyl halide is heated at about 300°, and at a lower temperature in the presence of aluminium chloride as catalyst, the alkyl halide undergoes rearrangement, *e.g.*, 1-bromobutane rearranges to 2-bromobutane:



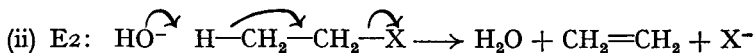
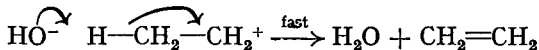
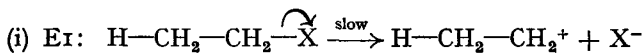
If there is no hydrogen atom on the carbon adjacent to the C—X group, an alkyl group migrates; *e.g.*, neopentyl chloride rearranges to 2-chloro-2-methylbutane (see also p. 102):



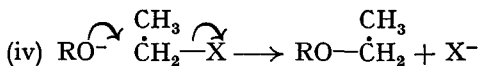
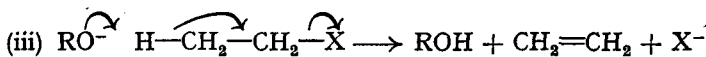
5. When alkyl halides are boiled with ethanolic potassium hydroxide, olefins are obtained, *e.g.*, propyl bromide gives propylene:



According to Hughes and Ingold (1941), the elimination reaction between an alkyl halide and aqueous potassium hydroxide may take place by either a unimolecular (E1) or a bimolecular (E2) mechanism.

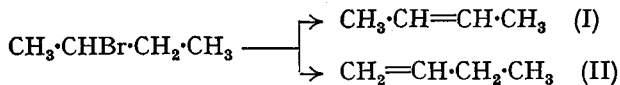


On the other hand, in ethanolic potassium hydroxide, which contains potassium alkoxide  $\text{RO}^- \text{K}^+$ , the reaction tends to take place by an E2 (iii) or an  $\text{S}_{\text{N}}2$  (iv) mechanism.



The course of the reaction depends on the nature of the alkyl halide and on the conditions used. Under the most favourable conditions for ethylene formation, ethyl halides give only 1 per cent. ethylene, the main products being replacement products. *iso*Propyl halide gives up to 80 per cent. propylene, and tertiary butyl halide 100 per cent. *isobutene* if the reaction is carried out in *ethanolic* potassium hydroxide, which favours the bimolecular mechanisms (iii) and (iv).

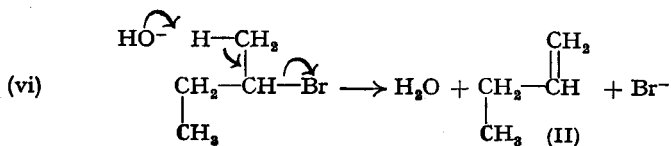
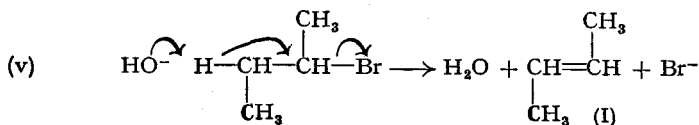
When two olefins may be formed by dehydrohalogenation of an alkyl halide, the one that predominates is that which is the most substituted olefin, *i.e.*, the one carrying the largest number of alkyl substituents (*Saytzeff's rule*, 1875), *e.g.*,



(I) predominates (this is a *disubstituted* ethylene, whereas (II) is a *monosubstituted* ethylene).

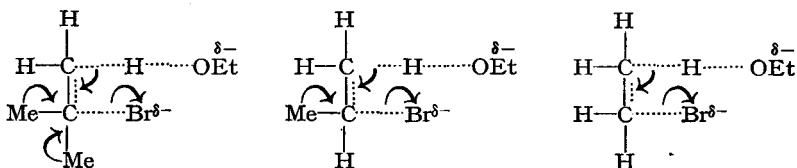
Another way of stating *Saytzeff's rule* is that hydrogen is eliminated from that carbon atom joined to the least number of hydrogen atoms. Ingold *et al.* (1941)

have offered the following explanation for this rule. If (I) and (II) are produced by an E2 mechanism, their formation may be written as follows:



In the transition state of (v), the CH<sub>3</sub> group can enter into hyperconjugation with the partly formed double bond (p. 269), thereby lowering the energy of the transition state. In (vi), however, the CH<sub>3</sub> group cannot enter into hyperconjugation with the partly formed double bond, and so the energy of this transition state is higher than that of (v), and consequently the latter path is favoured.

On the basis that the hyperconjugative effect determines the stability of the olefin produced, it can be deduced that the ease of formation of olefin from an alkyl halide by the E2 mechanism should be *t*-R > *s*-R > *p*-R, e.g., *t*-Bu (2 Me groups) > *iso*Pr (1 Me group) > Et (no Me groups):



Saytzeff's rule also applies when the mechanism is E<sub>1</sub>. In this mechanism the formation of the carbonium ion is the rate-determining step (as for the S<sub>N</sub>1 mechanism), and then the carbonium ion stabilises itself by elimination of a proton to form an olefin, the stability of which will be largely determined by the hyperconjugative effect.

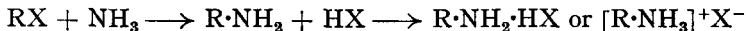
Steric factors also appear to play a part in the direction of olefin formation. Thus Brown *et al.* (1953) have shown that potassium *t*-butoxide gives 53.4 per cent. of (II), and potassium ethoxide 19 per cent. of (II). Brown *et al.* (1956) have also shown that in the molecule R·CH<sub>2</sub>·CBr(CH<sub>3</sub>)<sub>2</sub>, as R increases in branching (methyl < ethyl < *isopropyl* < *t*-butyl), a regular increase is obtained in the ratio of 1-/2-olefin in the product. These authors also showed that when the potassium salts of ethanol, *t*-butanol, *t*-pentanol and triethylmethanol are used with secondary and tertiary alkyl bromides, the yield of 1-olefin is increased from the left to the right alkoxide.

A point of interest here is that substitution and elimination often occur together. Experimental results have shown that for a given compound, the olefin yield is higher for the E2 mechanism than for the E<sub>1</sub>. Since a high concentration of the base with high nucleophilic power favours the E2 mechanism, olefin preparation is best carried out in concentrated solutions of strong bases. Furthermore, since ionising solvents favour the E<sub>1</sub> mechanism, the preparation of olefins is best carried out in solvents with low ionising power. Thus ethanolic sodium hydroxide solution (solvent of low ionising power and a very strong base, OEt<sup>-</sup>) gives better olefin yield than does aqueous sodium hydroxide (solvent of high ionising power and a base, OH<sup>-</sup>, which is weaker than OEt<sup>-</sup>). Also, a base of weak nucleophilic power will have little affinity for hydrogen, and consequently olefin forma-



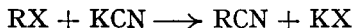
tion will be decreased and substitution encouraged. The acetate ion is a very weak base, and hence its use will give an ester as the main product rather than olefin. Thus the conversion of an alkyl halide into the alcohol is often best carried out via the ester, which is then hydrolysed.

6. When alkyl halides are heated with ethanolic ammonia under pressure, a mixture of *amines*, *i.e.*, substituted ammonias, is obtained, *e.g.*,



Only primary alkyl halides give good yields of amines; secondary—except *isopropyl* halide—and tertiary halides form mainly olefins.

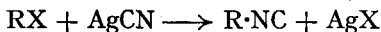
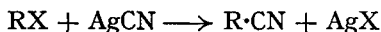
7. When alkyl halides are heated with aqueous ethanolic potassium cyanide, alkyl *cyanides* are obtained:



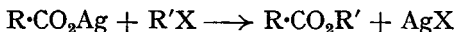
Tertiary alkyl cyanides cannot usually be prepared this way, since tertiary alkyl halides tend to eliminate hydrogen halide very readily when treated with potassium cyanide.

Alkyl cyanides are very important compounds, since they may be used to prepare many other compounds, *e.g.*, acids, amines, etc.

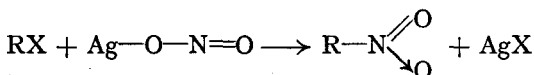
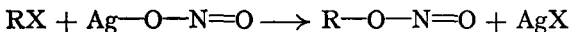
When alkyl halides are heated with aqueous ethanolic silver cyanide, cyanides and the *isocyanides* are formed:



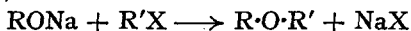
8. When alkyl halides are heated with an ethanolic solution of a silver salt, *esters* are obtained:



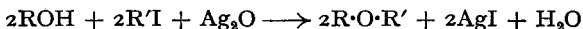
The acid may be organic or inorganic. If the salt is silver nitrite two isomeric compounds are obtained, the *nitrite* (ester) and the *nitro*-compound:



9. When alkyl halides are heated with sodium alkoxides, *i.e.*, sodium derivatives of the alcohols, *ethers* are obtained. This is the *Williamson synthesis* (see p. 141):

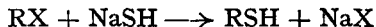


A modification of this reaction is to heat together an alkyl halide and an alcohol in the presence of *dry* silver oxide:

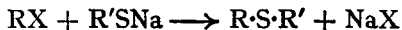


This reaction is known as the *Purdie method of alkylation*, and is very important in sugar chemistry.

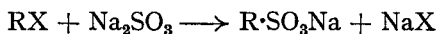
10. Alkyl halides heated with aqueous ethanolic sodium hydrogen sulphide form *thioalcohols*:



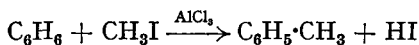
11. Alkyl halides heated with an ethanolic solution of a mercaptide, *i.e.*, a metallic derivative of a thioalcohol, form *thioethers*:



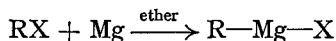
12. When alkyl halides are heated with sodium, potassium or ammonium sulphite, a *sulphonate* is formed. This is known as the *Strecker reaction*:



13. Alkyl halides may be used in the *Friedel-Crafts* reaction, e.g., benzene reacts with methyl iodide in the presence of anhydrous aluminium chloride to form toluene:

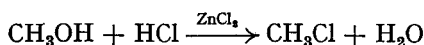


14. Alkyl halides are used to prepare Grignard reagents:

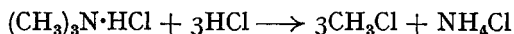


**Methyl chloride**,  $CH_3Cl$ , is prepared industrially:

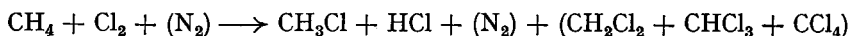
(i) By the action of hydrogen chloride on methanol in the presence of anhydrous zinc chloride:



(ii) By heating trimethylamine hydrochloride with hydrochloric acid under pressure:



(iii) By chlorinating methane with chlorine diluted with nitrogen, the ratio by volume of  $CH_4 : Cl_2 : N_2$  being 8 : 1 : 80. The reaction is carried out in the presence of partly reduced cupric chloride as catalyst. All four chloromethanes are obtained, the methyl chloride comprising 90 per cent. of the chlorine used:

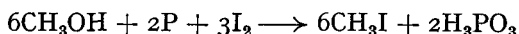


By adjusting the ratio of chlorine to methane, each chloromethane can be obtained as the main product.

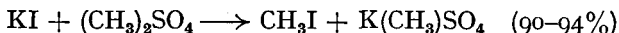
Methyl chloride is a colourless gas, b.p.  $-24^\circ$ . It is fairly soluble in water, and readily in ethanol. It is used in the manufacture of aniline dyes, as a refrigerating agent, local anæsthetic and as a fire extinguisher.

**Methyl iodide**,  $CH_3I$ , is prepared industrially:

(i) By warming a mixture of methanol and red phosphorus with iodine:



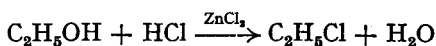
(ii) By the action of methyl sulphate on potassium iodide solution in the presence of calcium carbonate:



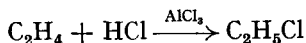
Methyl iodide is a sweet-smelling liquid, b.p.  $42.5^\circ$ . Since it is a liquid, it is easier to handle than methyl chloride, and so is used a great deal as a methylating agent in laboratory organic syntheses, but the chloride is used industrially, since it is cheaper.

**Ethyl chloride**,  $C_2H_5Cl$ , is prepared industrially:

(i) By the action of hydrogen chloride on ethanol in the presence of anhydrous zinc chloride:



(ii) By the addition of hydrogen chloride to ethylene (from cracked petroleum) in the presence of aluminium chloride as catalyst:

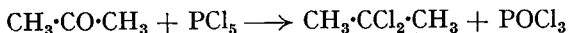


Ethyl chloride is a gas, b.p.  $12.5^\circ$ . It is used in the preparation of tetra-ethyl-lead, sulphonal, etc., and as a refrigerating agent.

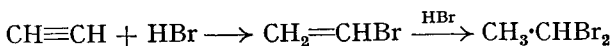
#### DIHALOGEN DERIVATIVES

**General methods of preparation.** *gem*-Dihalides may be prepared:

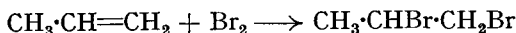
(i) By the action of phosphorus pentahalides on aldehydes or ketones; *e.g.*, acetone gives isopropylidene chloride when treated with phosphorus pentachloride:



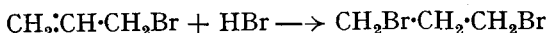
(ii) By the addition of halogen acids to the acetylenes, *e.g.*, ethylidene bromide from acetylene and hydrogen bromide:



*vic*-Dihalides may be prepared by the addition of halogen to olefins, *e.g.*, propylene bromide from propylene and bromine:



The method of preparing an  $\alpha\omega$ -dihalide is special to the particular halide, *e.g.*, trimethylene bromide may be prepared by the addition of hydrogen bromide to allyl bromide at low temperatures:



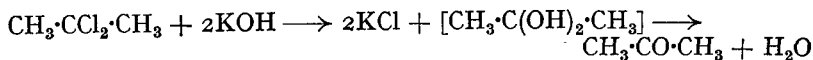
Oldham (1950), however, has found that  $\alpha\omega$ -dibromides may be prepared by the action of bromine in carbon tetrachloride on the silver salt of a dibasic acid (*cf.* p. 105):



The yields are very good provided  $n$  is 5 or more.

**General properties and reactions of the dihalides.** The dihalides are sweet-smelling, colourless liquids. *gem*-Dihalides are not as reactive as the alkyl halides. It has been found that the polarity of the C—Cl bond *decreases* progressively from methyl chloride, methylene chloride, chloroform and carbon tetrachloride. Therefore the reactivity of chlorine decreases progressively in these compounds in the same order (*i.e.*, from methyl chloride to carbon tetrachloride; *cf.* p. 105).

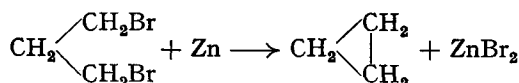
*gem*-Dihalides are hydrolysed by aqueous alkalis to the corresponding carbonyl compound (aldehyde or ketone), *e.g.*, isopropylidene chloride gives acetone:



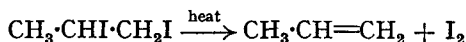
It has generally been found that a compound containing two (or more) hydroxyl groups attached to the *same* carbon atom is unstable, and readily eliminates a molecule of water (see p. 168).

*gem*-Dihalides give olefins when treated with zinc dust and methanol (p. 64), and acetylenes when treated with ethanolic potassium hydroxide (p. 90).

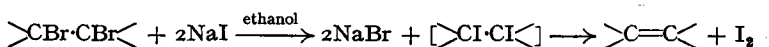
*vic*- and  $\alpha\omega$ -Dihalides are just as reactive as the alkyl halides. When heated with zinc and methanol, *vic*-dihalides give olefins (p. 64), but  $\alpha\omega$ -dihalides in which the two halogen atoms are in the 1 : 3 to the 1 : 6 positions give cyclic compounds, e.g., trimethylene bromide gives cyclopropane:



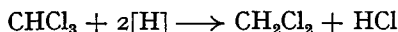
*vic*-Di-iodides tend to eliminate iodine, particularly at raised temperatures, to form olefins, e.g., propylene iodide gives propylene:



This property has been used to regenerate the double bond from *vic*-dichlorides or dibromides. These are heated with sodium iodide in ethanol, and the *vic*-diiodide formed decomposes into the olefin:

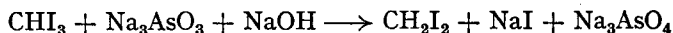


**Methylene chloride**,  $\text{CH}_2\text{Cl}_2$  (liquid, b.p.  $40^\circ$ ), was formerly prepared industrially by partially reducing chloroform with zinc and hydrogen chloride in ethanolic solution:



It is now also prepared industrially by the direct chlorination of methane (see methyl chloride). It is used as an industrial solvent.

**Methylene bromide**,  $\text{CH}_2\text{Br}_2$  (b.p.  $97^\circ$ ), and **methylene iodide**,  $\text{CH}_2\text{I}_2$  (b.p.  $181^\circ$ ), are prepared by the partial reduction of bromoform and iodoform, respectively, with sodium arsenite in alkaline solution (the yield of  $\text{CH}_2\text{Br}_2$  is 88–90 per cent.;  $\text{CH}_2\text{I}_2$ , 90–97 per cent.), e.g.,



All the methylene halides are used in organic syntheses.

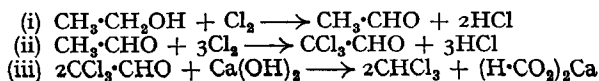
**Ethylene chloride**,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$  (b.p.  $84^\circ$ ), and **ethylidene chloride**,  $\text{CH}_3 \cdot \text{CHCl}_2$  (b.p.  $57^\circ$ ), are isomers; the former is prepared from ethylene and chlorine, and the latter by the action of phosphorus pentachloride on acetaldehyde (*q.v.*).

### TRIHALOGEN DERIVATIVES

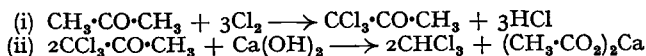
The most important trihalogen derivatives are those of methane, and they are usually known by their trivial names: chloroform,  $\text{CHCl}_3$ , bromoform,  $\text{CHBr}_3$  and iodoform,  $\text{CHI}_3$ .

**Chloroform** may be prepared in the laboratory or industrially by heating ethanol or acetone with bleaching powder, or with chlorine and alkali (yield about 40 per cent.). The reaction is extremely complicated, and the mechanism is obscure (see chloral, p. 168).

The equations usually given for the action of bleaching powder on ethanol are: (i) oxidation of ethanol to acetaldehyde; (ii) chlorination of acetaldehyde to trichloroacetaldehyde; (iii) decomposition of trichloroacetaldehyde (chloral) by free calcium hydroxide (present in the bleaching powder) into chloroform and formic acid:

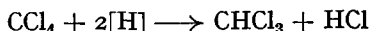


When acetone is used, the first product given is trichloroacetone, which is then decomposed by the calcium hydroxide into chloroform and acetic acid:



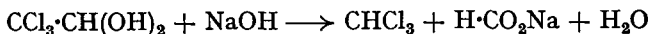
Chloroform is also prepared industrially:

- (i) By the chlorination of methane (see methyl chloride).
- (ii) By the partial reduction of carbon tetrachloride with iron filings and water:



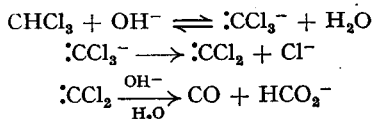
When prepared this way chloroform is used for solvent purposes, and not for anaesthesia (see later).

Pure chloroform may be prepared by distilling chloral hydrate with aqueous sodium hydroxide:

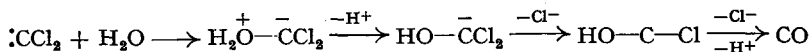


Chloroform is a sickly, sweet-smelling, colourless liquid, b.p.  $61^\circ$ . It is sparingly soluble in water but readily soluble in ethanol and ether. It does not burn in air under usual conditions, but its vapour may be ignited, when it burns with a green-edged flame. According to Hine (1950, 1954), chloroform (and other haloforms) undergoes alkaline hydrolysis to produce the formate ion and carbon monoxide by what Hine calls the *alpha-elimination mechanism*; this involves the removal of hydrogen and chloride ions from the *same* carbon atom.

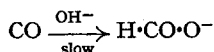
The mechanism proposed is as follows, involving the intermediate formation of dichloromethylene:



Robinson (1961) has proposed, on kinetic evidence, that the intermediate dichloromethylene most likely decomposes to carbon monoxide as follows:

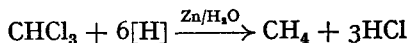


Formate is then formed as follows:

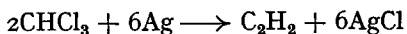


An interesting point about dichloromethylene is its reluctance to react with hydroxide ion.

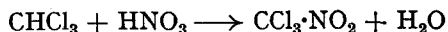
When chloroform is treated with zinc and hydrogen chloride in ethanolic solution, methylene chloride (*q.v.*) is obtained; when treated with zinc and water, methane is obtained:



When chloroform is warmed with silver powder, acetylene is obtained:

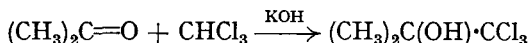


When treated with concentrated nitric acid, chloroform forms *chloropicrin*:

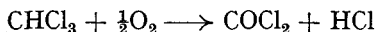


Chloropicrin or nitrochloroform (liquid, b.p.  $112^\circ$ ) is used as an insecticide, and has been used as a war-gas. Chloroform adds on to the carbonyl

group of ketones in the presence of potassium hydroxide, *e.g.*, with acetone it forms *chloretone* (colourless needles, m.p. 97°), which is used as a drug:

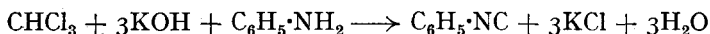


Chloroform is employed in surgery as an anæsthetic, and for this purpose it should be pure. In the presence of air and light, chloroform slowly forms carbonyl chloride, which is extremely poisonous:



Chlorine, water and carbon dioxide are also produced. Anæsthetic chloroform is therefore kept in well-stoppered dark-brown or blue bottles. Ethanol is also added (1 per cent.), but its function is not quite clear. According to some authors, it *retards* the decomposition of the chloroform. This is supported by the fact that infra-red measurements of such mixtures show the absence of the carbonyl frequency.

A delicate test for chloroform is the "*isocyanide test*". This is carried out by heating chloroform with ethanolic potassium hydroxide and aniline, whereby phenyl *isocyanide* is formed, and is readily detected by its nauseating odour:



Chloroform is widely used in industry as a solvent for fats, waxes, resins, rubber, etc.

**Bromoform** may be prepared by methods similar to those used for chloroform, but it is prepared industrially by the electrolysis of an aqueous solution of acetone or ethanol containing sodium carbonate and potassium bromide (acetone gives a better yield than ethanol). The solution is maintained at about 20°, and hydrobromic acid is run in to neutralise the sodium hydroxide produced during the electrolysis. Bromine is set free at the anode, and probably reacts in the same way as does chlorine in the preparation of chloroform.

Bromoform is a liquid, b.p. 149.5°, and smells like chloroform, which it closely resembles chemically.

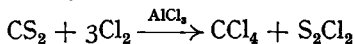
**Iodoform** is prepared industrially by the electrolysis of an aqueous solution of ethanol or acetone containing sodium carbonate and potassium iodide (ethanol gives a better yield than acetone). The solution is maintained at 60–70°, and a current of carbon dioxide is passed through the solution to neutralise the sodium hydroxide formed.

Iodoform crystallises in yellow hexagonal plates, m.p. 119°. It is insoluble in water, but is readily soluble in ethanol and ether. It is used as an antiseptic, but its antiseptic properties are due to the liberation of free iodine, and not to iodoform itself. Iodoform chemically resembles chloroform and bromoform.

#### POLYHALOGEN DERIVATIVES

**Carbon tetrachloride**,  $\text{CCl}_4$ , is prepared industrially in several ways:

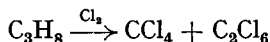
(i) By the action of chlorine on carbon disulphide in the presence of aluminium chloride as catalyst:



The sulphur monochloride is removed by fractional distillation, and the carbon tetrachloride is then shaken with sodium hydroxide, and finally distilled.

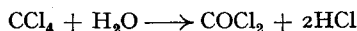
(ii) By the chlorination of methane (see methyl chloride).

(iii) By *chlorinolysis*. This term was suggested by McBee, Hass and co-workers (1941) to describe the process of chlorinating an organic compound under conditions which rupture the carbon-carbon bond to yield chloro-compounds with fewer carbon atoms than the original compound. Chlorinolysis may be effected with or without a catalyst, *e.g.*, the hydrocarbon and chlorine are heated at high temperature (300–400°) and under high pressure (about 1000 lb./sq. in.). The product is usually a mixture, *e.g.*, propane gives both carbon tetrachloride and hexachloroethane:



Carbon tetrachloride is a colourless liquid, b.p. 77°, which has a sickly smell. It is insoluble in water but readily soluble in ethanol and ether. Since its vapour is non-inflammable, carbon tetrachloride is widely used as an industrial solvent (for fats, oils, resins, lacquers, etc.). It is also used as a fire-extinguisher under the name of *Pyrene*.

Carbon tetrachloride is stable at red heat (about 500°), but when its vapour comes into contact with water vapour at this temperature, some carbonyl chloride is formed:



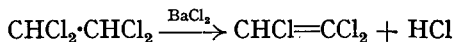
Hence after using pyrene to extinguish a fire, the room should be well ventilated.

Carbon tetrachloride is reduced by moist iron filings to chloroform (*q.v.*). The alkaline hydrolysis of carbon tetrachloride gives the same products (formate and carbon monoxide) as chloroform, but the rate of reaction is slower (Hine, 1954).

**Tetrachloroethane** or **acetylene tetrachloride**,  $\text{CHCl}_2 \cdot \text{CHCl}_2$ , is prepared by passing acetylene and chlorine into chambers filled with a mixture of kieselguhr and iron filings. This method is used since the combination of acetylene and chlorine is usually explosive unless a catalyst (and preferably a diluent) is present.

Acetylene tetrachloride is a very toxic, colourless liquid, b.p. 146°. It smells like chloroform; it is non-inflammable, and hence is widely used, under the name of *Westron*, as a solvent for oils, fats, paints, varnishes, rubber, etc.

When passed over heated barium chloride as catalyst, acetylene tetrachloride eliminates a molecule of hydrogen chloride to form trichloroethylene:

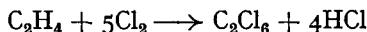


Trichloroethylene is a colourless liquid, b.p. 88–90°. It smells like chloroform, and is non-inflammable. It is more stable and less toxic than acetylene tetrachloride, and hence is more widely used as an industrial solvent, under the name of *Westrosol*, than *Westron*.

**Hexachloroethane** (*perchloroethane*),  $\text{C}_2\text{Cl}_6$ , may be prepared:

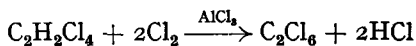
(i) By the chlorinolysis of propane (see carbon tetrachloride).

(ii) By passing ethylene mixed with 10 per cent. excess of chlorine through a pyrex tube packed with activated charcoal at 300–350°:

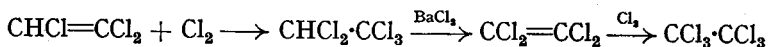


The excess chlorine prevents the formation of lower chlorinated products.

(iii) By passing a mixture of acetylene tetrachloride and chlorine over aluminium chloride as catalyst:

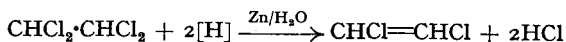


(iv) By treating trichloroethylene with chlorine and passing the *penta-chloroethane* so produced over heated barium chloride, thus forming *tetra-chloroethylene*, which, in turn, gives hexachloroethane when treated with chlorine:



Hexachloroethane is a solid, m.p. 187°. It smells like camphor and is used as a substitute for it.

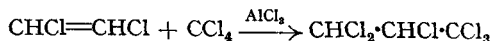
*s*-Dichloroethylene,  $\text{CHCl}=\text{CHCl}$ , may be prepared by the action of finely divided zinc on acetylene tetrachloride in the presence of water:



It is a liquid and exists in two forms, the *cis*, b.p. 60°, and *trans*, b.p. 48° (see p. 427 for the meanings of *cis* and *trans*).

Dichloroethylene is used as a rubber solvent.

The halogen atom in the group  $=\text{CHX}$  is very unreactive (see p. 266). An important property of the chlorinated unsaturated hydrocarbons is their ability to add on chloroform or carbon tetrachloride in the presence of aluminium chloride, as catalyst, *e.g.*, dichloroethylene forms 1:1:1:2:3:3-hexachloropropane with carbon tetrachloride:



Paraffin wax has been chlorinated, and the products are used for dielectric materials, protective coatings for fabrics, etc. Polychloro-derivatives of ethane, propane and butadiene are used as dielectric materials, solvents (non-inflammable), insecticides, plasticisers, etc.

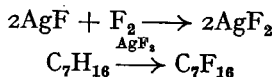
#### FLUORINE DERIVATIVES OF THE PARAFFINS

Most organic compounds burn or explode when treated with fluorine gas. Carbon heated in fluorine is attacked, sometimes explosively, with the formation of mainly  $\text{CF}_4$ , and small amounts of  $\text{C}_2\text{F}_6$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_3\text{F}_8$  and some other products.

Aliphatic fluorine compounds may be obtained in several ways:

(i) Direct fluorination of hydrocarbons may be carried out successfully by diluting the fluorine with nitrogen, and carrying out the reaction in a metal tube packed with copper gauze at a temperature of 150–350°. It is very difficult to control the fluorination, and the product is usually a complex mixture, *e.g.*, methane gives  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$ ; ethane gives  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CH}_3\cdot\text{CHF}_2$ ,  $\text{CH}_2\text{F}\cdot\text{CHF}_2$ ; no mono- or *s*-difluoroethane is obtained.

When catalysts other than copper (actually  $\text{CuF}_2$ ) are used, *e.g.*,  $\text{AgF}$ ,  $\text{CoF}_2$ ,  $\text{CeF}_3$ ,  $\text{MnF}_2$ , perfluoro-compounds are obtained, *e.g.*, *n*-heptane gives perfluoroheptane:

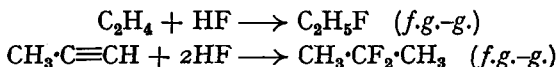


It appears that when a catalyst is used, the perfluoro-compound obtained usually has the same number of carbon atoms as the original compound; if no catalyst is used, fluoro-compounds with fewer carbon atoms are usually obtained.

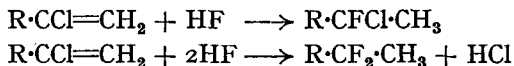
The mechanism of direct fluorination is still obscure, but it appears that the first step is the conversion of the catalyst into a higher fluoride, *e.g.*,  $\text{AgF}$  into  $\text{AgF}_2$ ;  $\text{CoF}_2$  into  $\text{CoF}_3$ , etc. Some of these higher fluorides have been isolated, *e.g.*,  $\text{AgF}_2$ .



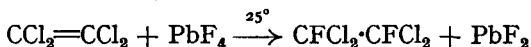
(ii) Olefins and acetylenes add on hydrogen fluoride under pressure to form fluoro-derivatives of the paraffins, *e.g.*,



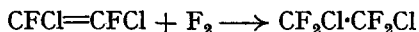
If the unsaturated compound contains a halogen atom (other than fluorine), this atom may be replaced by fluorine, *e.g.*,



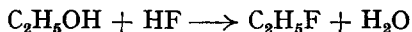
Lead tetrafluoride (from lead dioxide and hydrogen fluoride) is particularly useful for introducing two fluorine atoms into an olefin containing chlorine, *e.g.*,



It is also possible to add fluorine directly without a catalyst to highly halogenated olefins, *e.g.*,

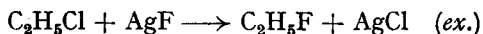


(iii) By treating an alcohol with hydrogen fluoride, *e.g.*,



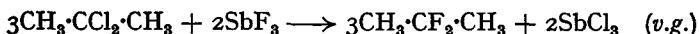
This reaction is very little used in practice. On the other hand, alkyl fluorides may be prepared by heating alkyl toluene-*p*-sulphonates with potassium fluoride (Bergmann *et al.*, 1958).

(iv) Fluorine compounds may be prepared indirectly by heating organic halides with inorganic fluorides such as  $\text{AsF}_3$ ,  $\text{SbF}_3$ ,  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ , etc., *e.g.*,

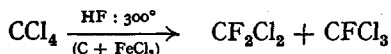


This method was first used by Swarts (1898), and so is known as the *Swarts reaction*.

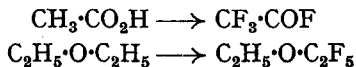
When the organic halide contains two or three halogen atoms attached to the same carbon atom, the best yield of fluoride is obtained when  $\text{CoF}_3$  is used, but  $\text{SbF}_3$  gives yields almost as good (and is more accessible), *e.g.*,



Alternatively, hydrogen fluoride may be used under pressure in the presence of a catalyst, *e.g.*,

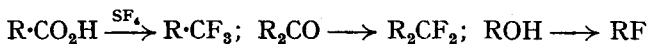


(v) A newer method of fluorination is the direct electrolytic method. Nickel electrodes are used, and electrochemical fluorination takes place at the anode, the reaction being carried out by the electrolysis of a solution of the organic compound in anhydrous hydrogen fluoride, *e.g.*,

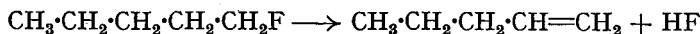


The particular merit of this method is that it usually leaves untouched many types of functional groups.

Sulphur tetrafluoride is a very useful fluorinating agent, since it replaces oxygen atoms by fluorine; thus:



The lower *n*-alkyl fluorides are gases. The first four members are stable, and the higher members tend to decompose spontaneously into olefin and hydrogen fluoride, *e.g.*,

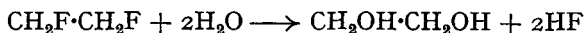


Secondary and tertiary alkyl fluorides are so unstable that it is impossible to prepare them free from olefin.

*vic*-Difluorides are also usually unstable, *e.g.*, ethylene fluoride decomposes spontaneously at 0° into hydrogen fluoride and butadiene:



Alkyl fluorides are readily hydrolysed by strong acids to the corresponding alcohols; alkalis have no effect. On the other hand, ethylene fluoride is immediately hydrolysed by water to glycol:

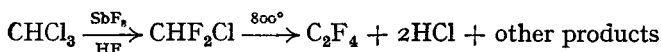


Fluorides with two or three fluorine atoms on the same carbon atom are stable to water and strong acids, *e.g.*,  $\text{CHF}_3$ ,  $\text{CHF}_2\cdot\text{CHF}_2$ , etc.

Alkyl fluorides do not react with sodium, *i.e.*, do not undergo the Wurtz reaction, and do not form Grignard reagents. An interesting compound is trifluoromethyl iodide,  $\text{CF}_3\text{I}$ . It is converted into fluoroform,  $\text{CHF}_3$ , by potassium hydroxide, and it combines directly with many non-metals such as P, As, Sb, S, Se, to give, *e.g.*, with phosphorus,  $(\text{CF}_3)_3\text{P}$ ,  $(\text{CF}_3)_2\text{PI}$  and  $\text{CF}_3\cdot\text{PI}_2$ .

Chlorofluoro-derivatives of methane and ethane are used as refrigerants and for air-conditioning under the name of *Freons*, which are prepared by the action of hydrogen fluoride on carbon tetrachloride, chloroform and hexachloroethane.

Tetrafluoroethylene,  $\text{C}_2\text{F}_4$  (gas), is prepared by the action of antimony trifluoride and hydrogen fluoride on chloroform, and then heating the chlorodifluoromethane so produced at 800°:



When tetrafluoroethylene is polymerised, the plastic *Teflon* is produced. Teflon is difficult to work, but is inert to chemical reagents, even to boiling aqua regia.

Polychlorofluoroethylenes are valuable as oils and greases. Perfluoroheptane is useful in a process for the separation of uranium isotopes by gaseous diffusion.

### QUESTIONS

- Write out the structures and names of all the dichloro-derivatives of butane and isobutane.
- By means of equations show how you would convert ethanol into: (a) trichloroethylene, (b) hexachloroethane, (c) *s*-dichloroethylene, (d) tetrachloroethylene, (e) pentachloroethane.
- Name the products and state the conditions under which they are obtained when ethyl iodide reacts with: (a) HI, (b) KCN, (c) KOH, (d)  $\text{H}_2$ , (e) Mg, (f) Na, (g)  $\text{NH}_3$ , (h) AgCN, (i)  $\text{NaNO}_2$ , (j)  $\text{AgNO}_2$ , (k)  $\text{NaHSO}_3$ , (l)  $\text{C}_6\text{H}_6$ .
- Name the products and state the conditions under which they are obtained when chloroform reacts with (a) nascent hydrogen, (b) KOH, (c)  $\text{C}_6\text{H}_5\text{NH}_2$ , (d)  $\text{O}_2$ , (e) Ag, (f)  $\text{HNO}_3$ , (g)  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ , (h)  $\text{CHCl}=\text{CHCl}$ .
- Define and give examples of:—(a) halogenation, (b) chain reaction, (c) Strecker reaction, (d) Darzens procedure, (e) molecular rearrangement, (f) elimination reaction, (g) alkylation, (h) Williamson synthesis, (i) Friedel-Crafts reaction, (j) Grignard reagent, (k) hyperconjugation, (l) chlorinolysis, (m) Swarts reaction.
- Discuss (i) the inductive effect of the alkyl group, (ii)  $\text{S}_\text{N}$  and E mechanisms, (iii) steric hindrance and steric acceleration, (iv) Saytzeff's rule.

## READING REFERENCES

- Hass, McBee *et al.*, Chlorination of Paraffins, *Ind. Eng. Chem.*, 1935, **27**, 1190; 1936, **28**, 333; 1941, **33**, 137, 176, 181, 185; 1943, **35**, 317.
- Vaughan and Rust, Chlorination of Paraffins, *J. Org. Chem.*, 1940, **5**, 449.
- Fredricks and Tedder, Free-radical Substitution in Aliphatic Compounds, *J.C.S.*, 1960, **144**.
- Bethell and Gold, The Structure of Carbonium Ions, *Quart. Reviews (Chem. Soc.)*, 1958, **12**, 173.
- Brown, Sulphuryl Chloride in Organic Chemistry, *Ind. Eng. Chem.*, 1944, **36**, 787.
- Organic Reactions*, Wiley, Vol. II (1944), Ch. 2. The Preparation of Aliphatic Fluorine Compounds.
- Bigelow, Action of Fluorine upon Organic Compounds, *Chem. Reviews*, 1947, **40**, 51.
- Ann. Reports (Chem. Soc.)*, 1954, **51**, 279. Perfluoroalkyl Compounds.
- Cook (Ed.), *Progress in Organic Chemistry*, Butterworths. Vol. 2 (1953). Ch. 2. Organic Fluorine Compounds.
- Musgrave, The Reactions of Organic Fluorine Compounds, *Quart. Reviews (Chem. Soc.)*, 1954, **8**, 331.
- Stacey *et al.* (Eds.), *Advances in Fluorine Chemistry*, Butterworths. Vol. I (1960).
- Hughes, Reactions of Halides in Solution, *Quart. Reviews (Chem. Soc.)*, 1951, **5**, 245.
- Clark and Streight, Systematic Study of the Preparation of Alkyl Chlorides from the Corresponding Alcohols, *Trans. Roy. Soc., Can.*, 1929, [3], **23**, 77.
- Huntress, *Organic Chlorine Compounds*, Wiley (1949).
- Johnson, The Degradation of Carboxylic Acids by means of Halogen: The Hunsdiecker Reaction, *Chem. Reviews*, 1956, **56**, 219.
- Organic Reactions*, Wiley. Vol. IX (1957), Ch. 5. The Reaction of Halogens with Silver Salts of Carboxylic Acids.
- Streitwieser, Solvolytic Displacement Reactions at Saturated Carbon Atoms, *Chem. Reviews*, 1956, **56**, 571.