R. O. C. Norman
D. J. Waddington

Modern Organic Chemistry

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Modern Organic Chemistry

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Modern Organic Chemistry

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Bell & Hyman
London

Published in 1983 by
BELL & HYMAN LIMITED
Denmark House
37–39 Queen Elizabeth Street
London SE1 2QB

First published in 1972 by
Mills & Boon Limited

Reprinted 1974
Second edition 1975
Reprinted 1977, 1978, 1980
Third edition 1981
Fourth edition 1983
Reprinted 1984

British Library Cataloguing in Publication Data

Norman. R. O. C.
Modern organic chemistry.—4th ed.
1. Chemistry, Organic
I. Title II. Waddington, D. J.
547 QD251.2

ISBN 0 7135 1363 2

Printed by Blantyre Printing & Binding Ltd.,
London and Glasgow

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Preface

This textbook is intended primarily to cover organic chemistry for Advanced Level examinations and University scholarships, but we believe that our readers will also find the book of great use in the beginning of their University work.

As the subject has evolved over the last twenty or so years, so the rather artificial divisions between organic chemistry and other branches of chemistry, and between chemistry and other sciences, have been breaking down; the subjects are now much more interdependent, and gain one from another. We have endeavoured to reflect these developments, so as to place organic chemistry in its proper perspective.

First, whereas the subject was concerned at one time mainly with answering the question 'What product is formed when *A* reacts with *B*?', now it is also concerned with the question '*How* does *A* react with *B* to give *C*?'—a field described as mechanistic organic chemistry. This at once involves the methods and concepts of physical chemistry—for example, reaction kinetics and bond energies.

Secondly, the organic chemist has learned to apply techniques pioneered by the physicist in order to determine the structures of organic compounds, and to do so with much greater rapidity than by the older, 'classical' methods. For example, infrared and nuclear magnetic resonance spectroscopy are now routinely used in organic research laboratories.

Thirdly, organic chemists and biologists have been increasingly working together to elucidate the ways in which organic compounds and their reactions play their crucial roles in living organisms; DNA, which underlies the transmission of inherited characteristics, is after all, an organic compound, and when animals need energy they obtain it by the controlled oxidation of another organic compound, glucose. Now we are on the threshold of another evolutionary wave of science in which organic chemists are combining with biologists and others: biotechnology and genetic engineering are likely to make important strides in improving agricultural methods and medical treatment.

Finally, the importance of organic compounds in our economy has been rising steadily for many years and will continue to do so. New plastics are being invented, new medicines are being tailor-made for specific requirements, there is a new awareness of the problems of pollution which has meant that the organic chemist is concerned with the discovery of new fuels, detergents and pesticides, and we are on the threshold of manufacturing proteins for animal feedstocks which could revolutionise the economies of both developed and developing countries.

We have tried to reflect all these factors in this book. We have set out the preparations and properties of organic compounds in terms of functional groups and against a background of the principles of bonding, energetics and reaction mechanism. Although we believe that these principles can be all the more easily understood in this way, rather than as isolated topics in a physical chemistry course, the book has been written so that students can leave out some sections if these are outside their immediate scope and can go back later to read the book as a whole.

Chapter 2 describes the modern techniques for the preparation and purification of organic compounds and Chapter 3 is concerned with the methods now employed for studying their structures. In Chapter 18, we have related the chemistry of some of the types of compound which occur naturally to their functions in living systems, while Chapter 21 deals with the man-made macromolecules we use as plastics and fibres. We have shown throughout the book how petroleum, including natural gas, is still vital for the chemical industry, and two Chapters, 19 and 20, are specifically devoted to this. It is especially notable here how much the methods employed in the chemical industry have changed since the first edition of this book was written, some ten years ago. New processes have been developed that are more efficient and use less energy, and now new feedstocks are beginning to be employed as alternatives to oil. Finally, we have included a short Chapter—'Looking to the future'—in which we have suggested some of the main directions in which organic chemistry is likely to move over the next decade or so.

The introduction of new syllabuses at every level is encouraging for all of us who teach and study Chemistry, all the more so since, hand-in-hand with these positive changes in our ideas on how theory should be presented, comes the desire to illustrate the work experimentally. We have therefore suggested practicals, with very simple apparatus, at the end of the chapters. Most of these practicals should take less than an hour.

York 1983

R.O.C.N.
D. J. W.

Acknowledgements

We are most grateful to Dr J. McIntyre and Mr D. J. M. Rowe of our Department and to Dr M. B. Sparke of British Petroleum for their valuable assistance in revising Chapters 19 and 20, and to Dr C. J. Garratt, also of the University of York, for his help with revisions to Chapter 18.

Mr H. S. Pickering (Uppingham School), who made such a helpful contribution to the original drafts, has continued to give his valuable advice and we are also very grateful to Mr T. J. Harrington (Bradford Grammar School).

We have been fortunate, too, in the assistance we have been given by many teachers who have written to us with helpful suggestions.

We thank Mr J. Olive for the photographs used in Chapters 1, 2 and 15, and Mrs Ann Ferens and Mrs Morag Morgan who tried out new experiments that we wished to include and for the modifications they suggested.

We thank the Esso Petroleum Co. Ltd., Shell Petroleum Co. Ltd., British Petroleum Co. PLC, Imperial Chemical Industries PLC, and British Gas for permission to use photographs and for most helpful assistance with technical data

We acknowledge permission to us to use examination questions by the Colleges of the Universities of Cambridge and Oxford, the Local Examination Syndicate of the University of Cambridge, the Delegates of Local Examinations, University of Oxford, the Oxford and Cambridge Schools Examination Board, the Joint Matriculation Board, the Southern Universities' Joint Board, the Associated Examining Board, the Welsh Joint Education Committee, the Northern Ireland Schools Examination Council, and the University of London University Entrance and Schools Examinations Council. Those questions marked London (Nuffield) are those set for the Nuffield Science Teaching Project in Chemistry at A level and those marked London (X) are from papers taken by schools who were taking the London A examination following a Nuffield O course.

Nomenclature

We have followed, with two exceptions, those recommendations based on the I.U.P.A.C. nomenclature made by the Association for Science Education in their booklet 'Chemical nomenclature, symbols and terminology' (revised 1983) and accepted by the Examinations Boards.

The first exception is that we have retained the generic name 'ether'; the alternative—alkoxyalkanes, aryloxyalkanes and aryloxyarenes, as appropriate—is cumbersome. Secondly, we have used the trivial names for the important α-amino-acids, since these original names are still widely used in Biology and Biochemistry. Both these exceptions are accepted by I.U.P.A.C.

Safety

The experiments we have suggested at the end of chapters need safe handling. We commend to all readers the series of articles by the Association for Science Education that has appeared in *Education in Science* over the last few years and which has been brought together in *Topics in Safety* published in 1982. Copies may be obtained from the Association for Science Education, College Lane, Hatfield, Hertfordshire AL10 9AA, U.K.

Chapter 1

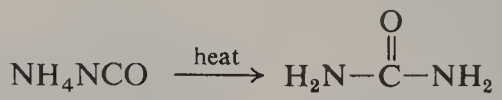
Introduction to organic chemistry

1.1 Introduction

Over two million compounds are known which contain the element carbon, and about 80,000 new carbon compounds are made each year. It is therefore convenient to study the compounds of carbon separately, and this branch of chemistry is known as **organic chemistry**.

Originally the word organic applied to those substances that were produced by living organisms. Berzelius wrote in 1815 that the essential difference between inorganic and organic compounds was that the formation of organic compounds could only be achieved by the influence of a 'vital force' which was present in nature. No organic material could be synthesised in the laboratory. Sugar, dyes, starch, oils, alcohol, known since the earliest times, could only be made by nature.

A conflicting point of view was put forward by Wöhler in 1828. He found that when an aqueous solution of ammonium cyanate is evaporated to dryness, carbamide (urea) is obtained:



$$\mathrm{NH_4NCO} \xrightarrow{\text{heat}} \mathrm{H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2}$$

Ammonium cyanate Carbamide

Ammonium cyanate is an inorganic compound whereas carbamide is present in the urine of all animals and was therefore particularly well known as an organic compound. It seemed, then, that 'vital force' was unnecessary. However, other scientists argued that, since the ammonia and cyanic acid from which Wöhler had made ammonium cyanate were both of animal origin, the true synthesis of an organic compound had not been achieved. It was not until 1845 that a final refutation of the 'vital force' idea was propounded, when Kolbe prepared the organic compound, ethanoic acid (acetic acid), from its constituent elements, carbon, hydrogen and oxygen.

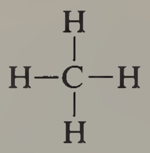
Today, the distinction between organic and inorganic chemistry is an arbitrary one. Organic chemistry is regarded as the chemistry of compounds of carbon other than its oxides, the metallic carbonates and related compounds.

1.2 Bonding

The bonds which carbon forms are covalent: that is, each bond is formed by the sharing of two electrons, one of which is provided by the carbon atom and one by the other atom. Carbon has four electrons available for sharing, so that it forms four bonds; a fuller description is given later (Chapter 4). It is convenient to represent each pair of electrons which constitutes a bond by a line, —; for example, a bond between carbon and hydrogen is shown as C—H.

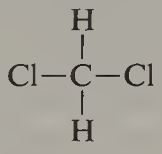
The bonds to a carbon atom have particular positions in space in relation to one another. For example, in methane, CH_4, the bonds are directed towards the corners of an (imaginary) regular tetrahedron of which the carbon atom is the centre; the angle between each pair of C—H bonds is 109° 28′.

For simplicity, a two-dimensional structure is usually drawn; for example, methane is written as

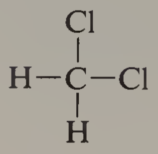


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

However, two-dimensional representations can be misleading and care must be exercised in their use. For instance, it might appear that there would be two compounds with the formula CH_2Cl_2:

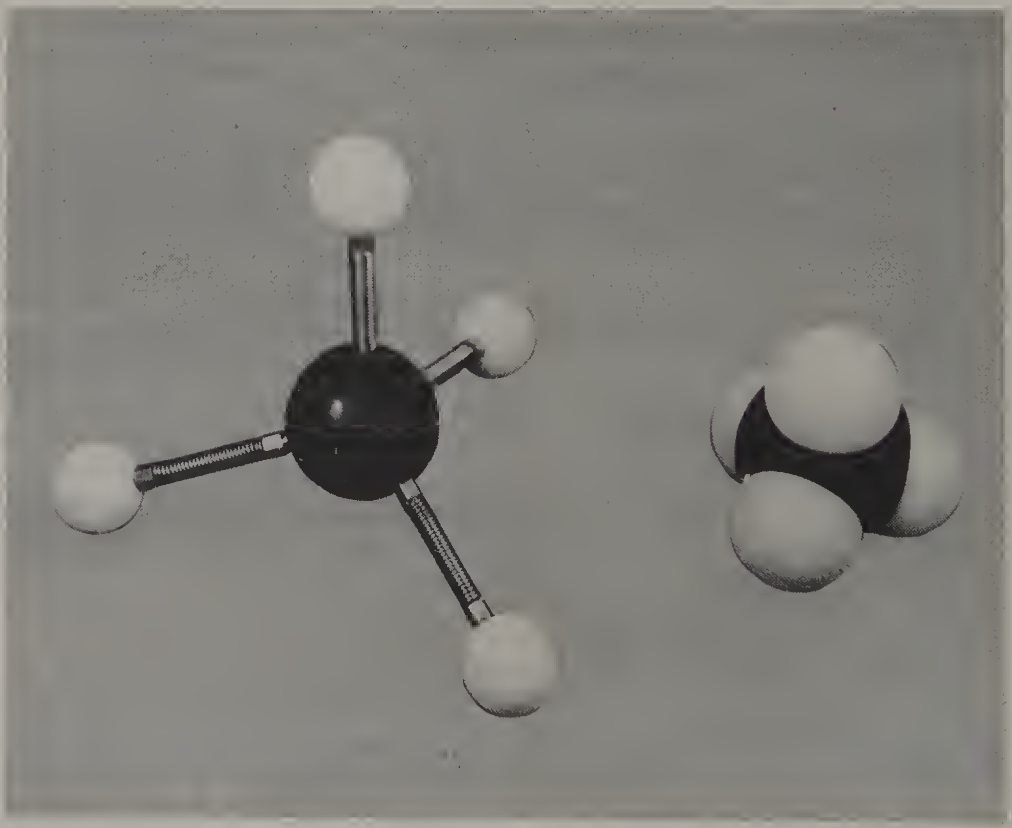


$$\begin{array}{ccc} & H & \\ & | & \\ Cl- & C & -Cl \\ & | & \\ & H & \end{array}$$



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

A three-dimensional representation shows that the two planar structures actually represent the same compound, and indeed only one compound of this formula exists.



(a) (b)

Plate 1.1. The tetrahedral arrangement of four atoms of hydrogen around a carbon atom in a molecule of methane: (a) ball and spring, (b) space-filling

It is useful to have a simple set of molecular models to consider problems like this; they can provide a quick means of translating the planar representations on paper into the more realistic three-dimensional structures.

The simplest models are called **ball and spring**. The balls are coloured differently to represent different atoms, and have holes drilled in them corresponding to the number of bonds they can form. The balls are joined together by means of stiff springs fitted into the holes which represent the bonds (Plate 1.1). **Space-filling** models are more useful when it is necessary to obtain a more accurate idea of how near together different atoms will be in the compound. In one sort, Stuart models, the atoms (generally constructed in a plastic) are made to scale according to the relative atomic radii of the elements they represent, and they are joined together by clips. The construction of the model for CH_2Cl_2 (Plate 1.2) shows at once that only one compound with this molecular formula exists.

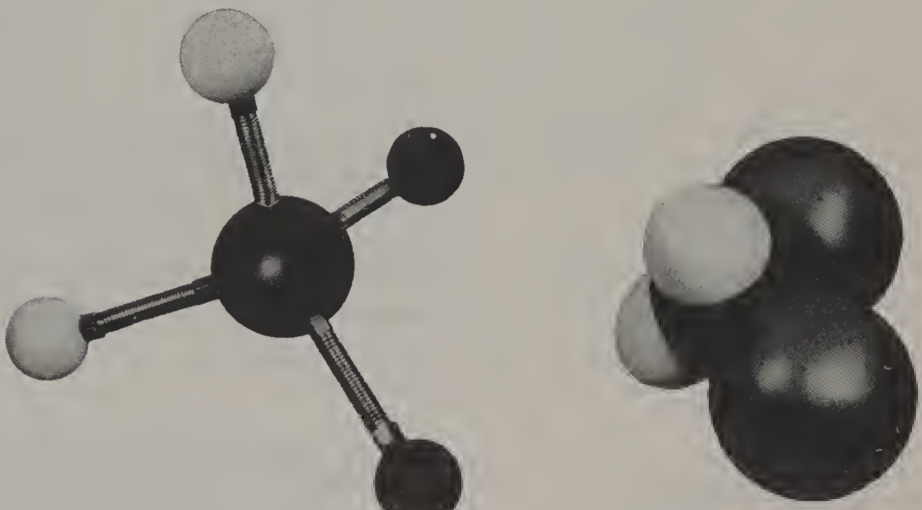
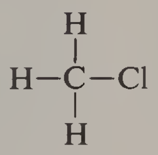

(a) (b)

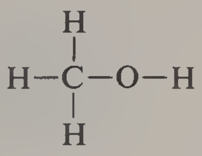
Plate 1.2. Molecular models of dichloromethane, CH_2Cl_2: (a) ball and spring, (b) space filling. The atoms are coloured black (carbon), white (hydrogen), grey (chlorine).

A carbon atom can be attached to monovalent atoms other than hydrogen. For example, one chlorine atom can replace one hydrogen atom to give chloromethane (also called methyl chloride):

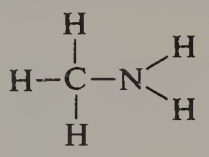

$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$$

Again for simplicity, some or all of the bonds are usually omitted in representing these compounds, so that chloromethane is written as $CH_3—Cl$ or CH_3Cl. Replacement of more than one of the hydrogen atoms by chlorine atoms gives the compounds dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4).

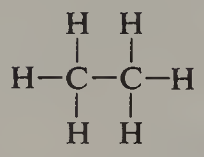
Carbon can be bonded to a divalent atom, as in methanol, CH_3OH:


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

to a trivalent atom, as in methylamine, CH_3NH_2:



or to another carbon atom, as in ethane, CH_3CH_3:



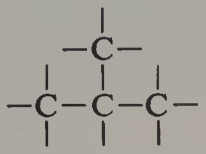
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Notice that ethane can be written as above or as C_2H_6, but not as CH_3; although the formula CH_3 describes the *relative* numbers of each kind of atom correctly, it does not give adequate information about the total number of atoms in the molecule. For this purpose, the **molecular formula** must be used, that is, a description of the *actual* number of each kind of atom present.

1.3
The unique nature of carbon

Why is it that carbon forms so many more compounds than all the other elements? The answer can be given in terms of bond energies. It can be shown that it requires about 1,652 kilojoules to break up one mole of methane into its carbon and hydrogen atoms. Since there are four C—H bonds in methane, the bond energy of one C—H bond is one-quarter of $1{,}652 = 413$ kilojoules per mole (abbreviated to $413\ \mathrm{kJ\ mol^{-1}}$). It can also be shown that it requires 2,823 kJ to break up one mole of ethane (CH_3—CH_3) into its constituent atoms. Since this compound contains six C—H bonds, each of which requires $413\ \mathrm{kJ\ mol^{-1}}$ for its rupture, the energy of the C—C bond is calculated to be $345\ \mathrm{kJ\ mol^{-1}}$. This is a very high value as compared with those for other elements joined by single bonds (e.g. $163\ \mathrm{kJ\ mol^{-1}}$ for N—N and $146\ \mathrm{kJ\ mol^{-1}}$ for O—O). Thus, whereas compounds containing O—O and N—N bonds are not very stable, very vigorous conditions—for example, the high temperatures produced in combustion—are necessary to destroy C—C bonds, and this underlies the occurrence of large numbers of stable compounds containing many C—C bonds. For example, in poly(ethene), a plastic (p. 328), many hundreds of carbon atoms are linked together in one molecule. The occurrence of chains of carbon atoms is known as **catenation**.

As well as forming long chains, carbon atoms can form branched chains, e.g.



There are also compounds in which some of the bonds between carbon atoms are double or triple bonds (1.5) or in which the atoms form rings (1.6). All these possibilities increase still further the number of carbon compounds which can be formed.

1.4
Homologous series and functional groups

The large number of organic compounds fall into a comparatively small number of series, known as **homologous series**. In a particular series, each member has similar methods of preparation and chemical properties to the other members. In the series of alkane hydrocarbons (Chapter 5), the simplest member is methane, CH_4. The next member is ethane, C_2H_6, then propane, C_3H_8, and so on; the general formula of the series is C_nH_{2n+2}. As the series is ascended, a **methylene group**, CH_2, is added to each successive member. As each methylene group is added, the physical properties change slightly. This is demonstrated in detail with the alkanes (Chapter 5).

We have seen already that there is a number of compounds which contain the grouping CH_3. This is called the **methyl group** (sometimes, the **methyl radical**). Other collections of atoms which occur frequently are the amino group, NH_2, and the hydroxyl group, OH. Each of these is able to bond to another group, as in methylamine, CH_3NH_2, and methanol, CH_3OH. They are examples of **functional groups**, which consist of an atom or group of atoms which determine the properties of the homologous series. For example, in the series of alcohols,

$CH_3{-}OH$
Methanol

$CH_3{-}CH_2{-}OH$
Ethanol

$CH_3{-}CH_2{-}CH_2{-}OH$
Propan-1-ol

$CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$
Butan-1-ol

there is a gradation of physical properties but the chemical properties are very similar.

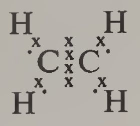
Several homologous series can be considered to be derived from the alkanes, C_nH_{2n+2}, a hydrogen atom being replaced by a functional group. The group formed from the alkane, C_nH_{2n+1}, is known as the **alkyl group**, and is often represented by the letter R.

The names of alkyl groups are related to the names of the corresponding alkanes:

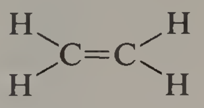
Alkane C_nH_{2n+2}(RH)	*Alkyl group* C_nH_{2n+1}(R)
Methane, CH_4	Methyl, CH_3
Ethane, C_2H_6	Ethyl, C_2H_5
Propane, C_3H_8	Propyl, C_3H_7
Butane, C_4H_{10}	Butyl, C_4H_9

1.5
Unsaturated compounds

The compounds we have described so far contain single covalent bonds, and these compounds are described as **saturated**. There are also **unsaturated** compounds in which two atoms share either four or six electrons. For example, the carbon atoms in ethene share four electrons (two originating from each atom); the bond is described as a **double bond**:



As can be seen from Plate 1.3, the carbon and hydrogen atoms are in a plane, with bond angles of 120° (compare the tetrahedral structure of methane). The molecule is described as *planar* and can be represented as



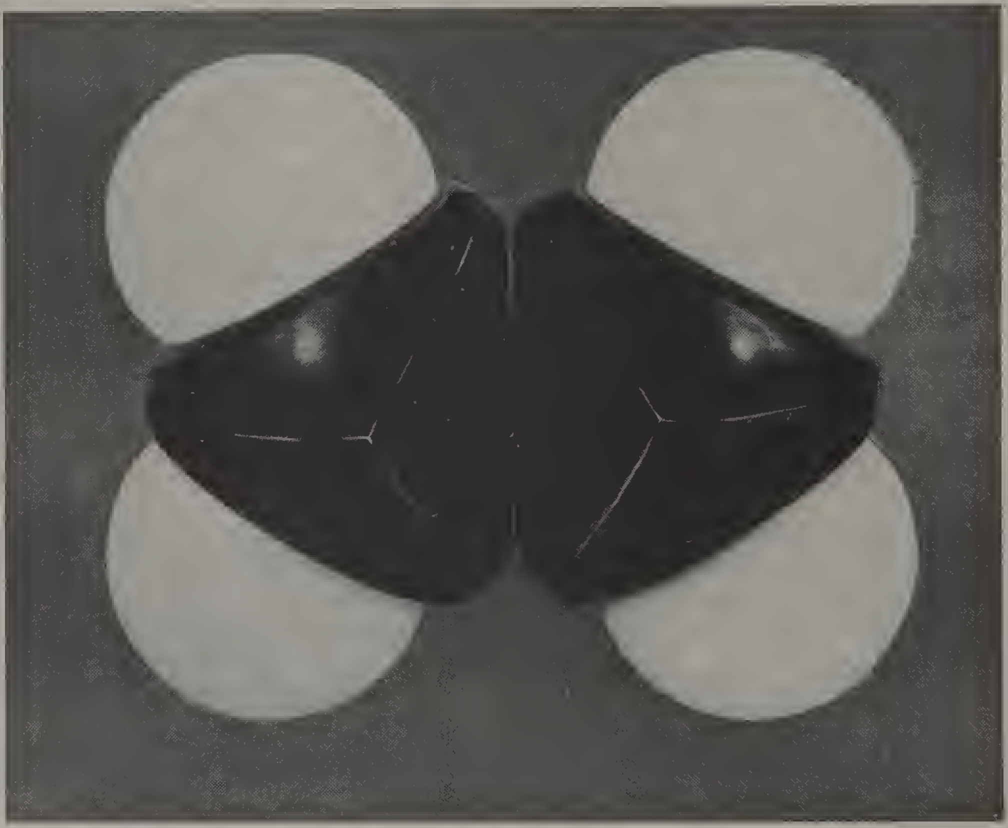
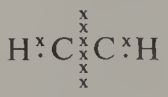


Plate 1.3. A space-filling molecular model of ethene

In ethyne, the carbon atoms share six electrons (three originating from each atom); the bond is described as a **triple bond**:



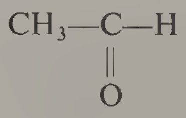
The carbon and hydrogen atoms lie in a straight line (Plate 1.4) and the molecule is described as *linear*. A simple representation is

$$H-C\equiv C-H$$

Other common unsaturated groups are $C\equiv N$, as in ethanenitrile, and $C=O$, as in ethanal and ethanoic acid.

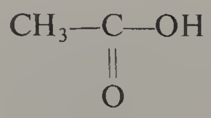
$CH_3-C\equiv N$

Ethanenitrile



$$CH_3-\underset{\underset{O}{\|}}{C}-H$$

Ethanal

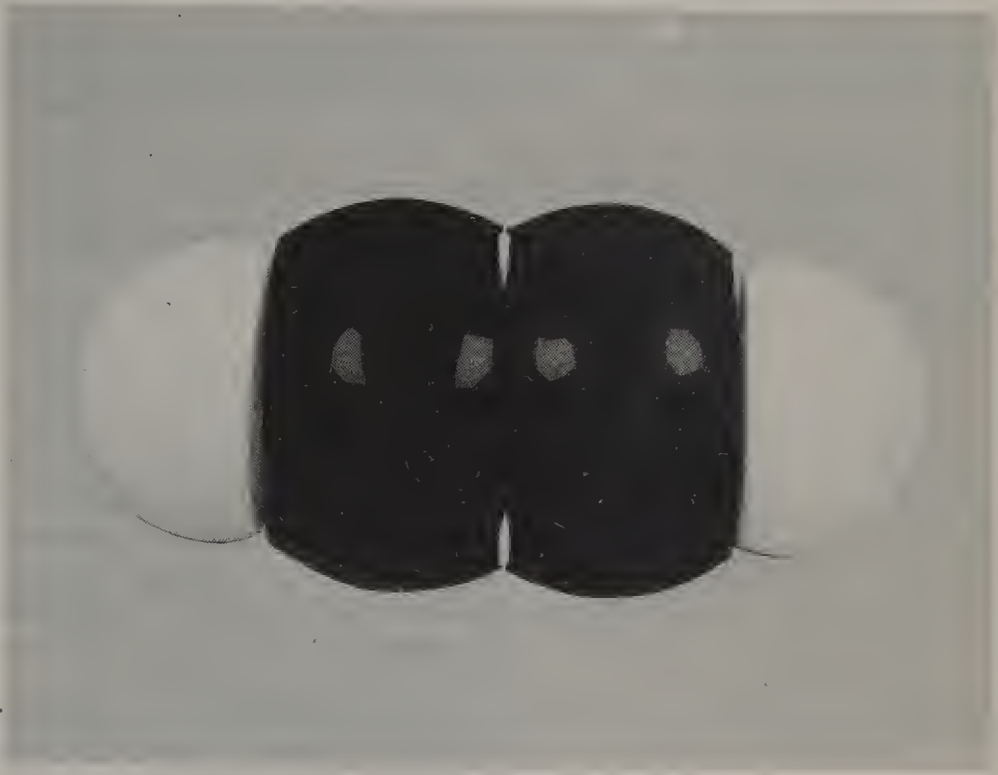


$$CH_3-\underset{\underset{O}{\|}}{C}-OH$$

Ethanoic acid

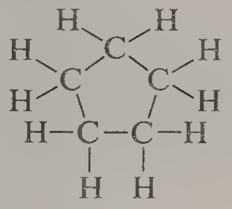
The groups $C{\equiv}N$, $C{=}O$ and CO_2H are called the nitrile, carbonyl and carboxylic acid groups, respectively.

Plate 1.4. A space-filling molecular model of ethyne



1.6 Aliphatic, alicyclic and aromatic compounds

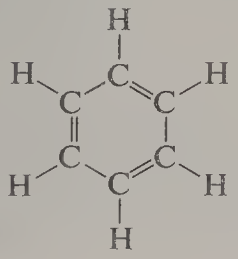
The compounds we have mentioned so far have had carbon atoms joined in straight chains or branched chains, and these are described as **aliphatic**. There are also compounds in which some of the atoms form a ring, e.g.



Cyclopentane

Rings with from three atoms to very large numbers are known, and these compounds are described as **alicyclic**.

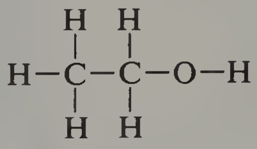
There is a special class of ring compound of which benzene is the parent:



A large number of compounds contain the same carbon ring but have atoms or groups other than hydrogen attached to it. For example, writing benzene as C_6H_6, chlorobenzene is $C_6H_5—Cl$. Compounds of this nature were originally termed **aromatic** because some of them have pleasant smells (Greek: *aroma*, fragrant smell). The term has been retained because it provides a useful classification; as we shall see, benzene has different properties from the simple unsaturated compound, ethene, and the differences arise because of the special nature of the bonding in benzene (8.2).

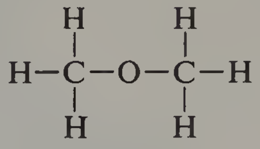
1.7 Isomerism

There are two compounds with the molecular formula C_2H_6O:



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

Ethanol



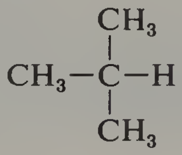
$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

Dimethyl ether

However, although both compounds have the same number of each kind of atom (two C, six H, one O), they have different physical and chemical properties. They are described as **isomers**, and the phenomenon is described as **isomerism**. Isomerism is said to occur when two or more compounds have the same molecular formula.

The existence of a large number of isomers is illustrated by the alkanes. There is only one compound of molecular formula CH_4 (methane), C_2H_6 (ethane) or C_3H_8 (propane). There are two of molecular formula C_4H_{10}:

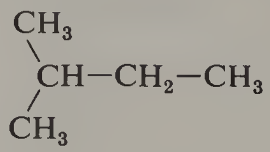
$CH_3-CH_2-CH_2-CH_3$

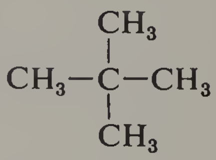


$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & H \\ & & | & & \\ & & CH_3 & & \end{array}$$

and three of molecular formula C_5H_{12}:

$CH_3-CH_2-CH_2-CH_2-CH_3$



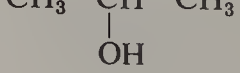


$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

Because carbon atoms can be joined in straight and in branched chains, the number of possible isomers increases very rapidly as the number of carbon atoms increases; for example, there are 5 isomers with molecular formula C_6H_{14} and 18 with molecular formula C_8H_{18}. When other atoms are introduced, the number of possible compounds with a particular molecular formula increases still further; e.g., there is only one compound with molecular formula C_3H_8 but three with molecular formula C_3H_8O, two being alcohols and one an ether:

$CH_3-CH_2-CH_2-OH$

Propan-1-ol



$$\begin{array}{ccccc} CH_3 & - & CH & - & CH_3 \\ & & | & & \\ & & OH & & \end{array}$$

Propan-2-ol

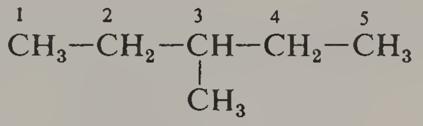
$CH_3-CH_2-O-CH_3$

Ethyl methyl ether

1.8
Nomenclature of carbon compounds

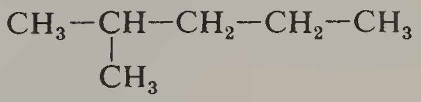
As organic chemistry developed, each new compound to be discovered was given its own name, so that a variety of unrelated names quickly grew up. It eventually became necessary to introduce a systematic form of nomenclature in order that the structure of a compound could be readily deduced from its name, and *vice-versa*. The nomenclature at present in use was laid down by the International Union of Pure and Applied Chemistry (I.U.P.A.C.), and the rules for naming some of the simpler compounds are given here.

Methane, as we have seen, is the simplest alkane, and each member of the homologous series of alkanes is given the suffix **-ane**. The first four retain the names originally given to them: methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). After that, the first part of the name is derived from the Greek for the number of carbon atoms in the molecule: pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), and so on. When the chain is branched, the name is taken from that of the longest straight chain of carbon atoms in the molecule; the carbon atoms are numbered from one end of the chain, and the position of the branch and the nature of the group there are indicated by the number of the carbon atom at which branching occurs and the name of the alkyl group which forms the branch. For example,



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\displaystyle CH_3}{\overset{3}{\underset{|}{C}}}H-\overset{4}{CH_2}-\overset{5}{CH_3}$$

is termed 3-methylpentane. The compound



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-CH_2-CH_3$$

might be called 2-methylpentane or 4-methylpentane, depending upon from which end the chain was numbered. The rule is to number from that end which gives the substituent the lower of the two possible numbers, so that the correct name is 2-methylpentane.

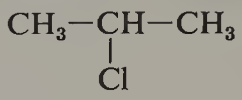
The unsaturated compounds with a C=C double bond which are often referred to as olefins are termed alkenes in the I.U.P.A.C. scheme. The number of carbon atoms is described in the same way as for the alkanes. Each member terminates in **-ene**, and the position of the double bond is determined by inserting the lowest possible number before the suffix to describe the carbon atom which forms one end of the double bond relative to its position in the chain; e.g.

$$CH_3—CH_2—CH_2—CH{=}CH_2$$

is pent-1-ene, not pent-2-ene or 4- or 5-ene.

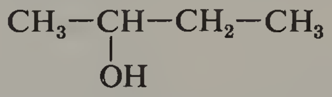
The unsaturated compounds with a C≡C triple bond, which are often described as acetylenes after the simplest member of the series, acetylene itself (CH≡CH), are termed alkynes in the I.U.P.A.C. scheme, and individual members are described as for the alkenes but with the termination **-yne**.

When an atom other than carbon or hydrogen is present, the name either begins or ends with a description of the type of group which contains this atom, preceded by the number of the carbon atom to which the group is bonded. The remainder of the name is that of the hydrocarbon with the same number of carbon atoms, the final **e** of this name being omitted when a suffix is employed for the substituents whose first letter is a vowel. For example, if chlorine is present, **chloro-** is used as a prefix, so that



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

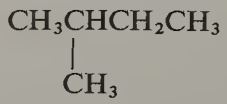
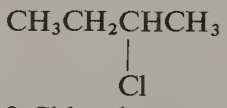
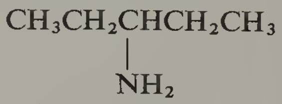
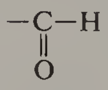
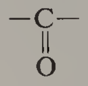
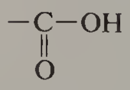
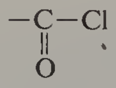
is 2-chloropropane. If a hydroxyl group is present, **-ol** is used as a suffix, so that



$$CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CH_2{-}CH_3$$

is butan-2-ol. Table 1.1 gives the names of some of the homologous series and their functional groups which are met early in this book.

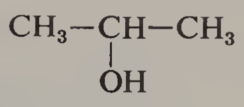
Table 1.1. Nomenclature of organic compounds

HOMOLOGOUS SERIES	FUNCTIONAL GROUP	PREFIX OR SUFFIX	EXAMPLE OF I.U.P.A.C. NOMENCLATURE
Alkanes	(—H)	-ane	 $CH_3\underset{\substack{|\\ CH_3}}{CH}CH_2CH_3$ 2-Methylbutane
Alkenes	$C=C$	-ene	$CH_3CH_2CH=CH_2$ But-1-ene
Alkynes	$C\equiv C$	-yne	$CH_3C\equiv CCH_3$ But-2-yne
Alcohols	—OH	-ol	$CH_3CH_2CH_2CH_2OH$ Butan-1-ol
Chloroalkanes (Alkyl chlorides)	—Cl	chloro-	 $CH_3CH_2\underset{\substack{|\\ Cl}}{CH}CH_3$ 2-Chlorobutane
Primary amines	$—NH_2$	amino-	 $CH_3CH_2\underset{\substack{|\\ NH_2}}{CH}CH_2CH_3$ 3-Aminopentane
Aldehydes	 $-\underset{\substack{\|\\ O}}{C}-H$	-al	CH_3CH_2CHO Propanal
Ketones	 $-\underset{\substack{\|\\ O}}{C}-$	-one	$CH_3COCH_2CH_2CH_3$ Pentan-2-one
Carboxylic acids	 $-\underset{\substack{\|\\ O}}{C}-OH$	-oic acid	$CH_3CH_2CO_2H$ Propanoic acid
Acid chlorides	 $-\underset{\substack{\|\\ O}}{C}-Cl$	-oyl chloride	$CH_3CH_2CH_2COCl$ Butanoyl chloride
Acid nitriles	—CN	-nitrile	CH_3CN Ethanenitrile

The nomenclature for each homologous series is described in detail in the Chapter concerned with that series. Where the older, or ‘trivial’, names are still often used, they are given, in brackets, after the I.U.P.A.C. name. Two commonly used prefixes in the older nomenclature are **n-**, which indicates an unbranched chain of carbon atoms, and **iso-**, which indicates the presence of the group $(CH_3)_2C$; for example:

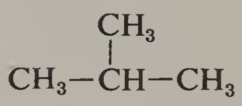
$CH_3-CH_2-CH_2-OH$

Propan-1-ol
(n-Propanol)



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

Propan-2-ol
(Isopropanol)



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

2-Methylpropane
(Isobutane)

1.9
Practical work

1. Make models for the following compounds: (a) ethane, (b) chloroethane, (c) ethanol.

2. Make models for compounds with the molecular formulae: (a) C_3H_8, (b) C_3H_6, (c) C_3H_4. Name the compounds.

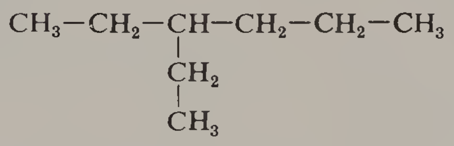
3. Make models for compounds with the molecular formulae: (a) C_4H_8, (b) C_4H_6. Name the compounds.

1.10
Questions

1 How many isomers would you expect with the following molecular formulae: CH_2Br_2; C_4H_6; $C_4H_{10}O$? How many isomers, each containing the group $C{=}O$, would you expect with the molecular formula $C_5H_{10}O$?

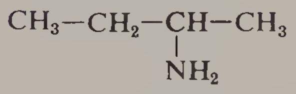
2 Write down the structures of the following compounds; 2-methylpentane; 2,2-dimethylpropane; hex-2-ene; 1-bromobutane; 2-methylpropan-2-ol; pentan-3-one.

3 Name the following compounds according to the I.U.P.A.C. rules:

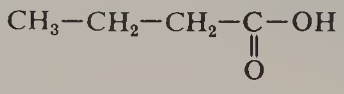


$CH_3-CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}-CH_2-CH_2-CH_3$

$CH_3-CH_2-CH{=}O$



$CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$



$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$

$CH_3-CH{=}CH-CH_2-CH_3$

$CH_3-CH_2-CH_2-C{\equiv}CH$

Preparation and purification of organic compounds

2.1 Introduction

There are three stages in the preparation of a pure organic compound. First, conditions are found under which the required product is formed in a relatively short time (that is, in a few minutes or at most a few hours, rather than days). Secondly, the product is separated from other materials. Finally, methods are employed to find out if the compound is pure.

The preparations of many organic compounds are described in detail in later chapters. In order to simplify the operations, the number of pieces of apparatus necessary has been kept as small as possible (a list is given in Appendix III). We describe below the more commonly used techniques in the preparation and purification of organic compounds.

2.2 Heating under reflux

Many organic reactions occur very slowly at room temperature. However, the rates of all reactions are increased by raising the temperature, and a reasonably rapid rate can often be achieved by carrying out the reaction at the boiling point of the mixture of reactants, or of the solution of the reactants if they are dissolved in a solvent. The apparatus for this purpose (Fig. 2.1) consists of a **water condenser** attached vertically to the reaction flask; when the mixture in the flask is boiled, its vapour condenses at the cold surface of the condenser and the liquid runs back into the flask. This is known as **heating under reflux**.

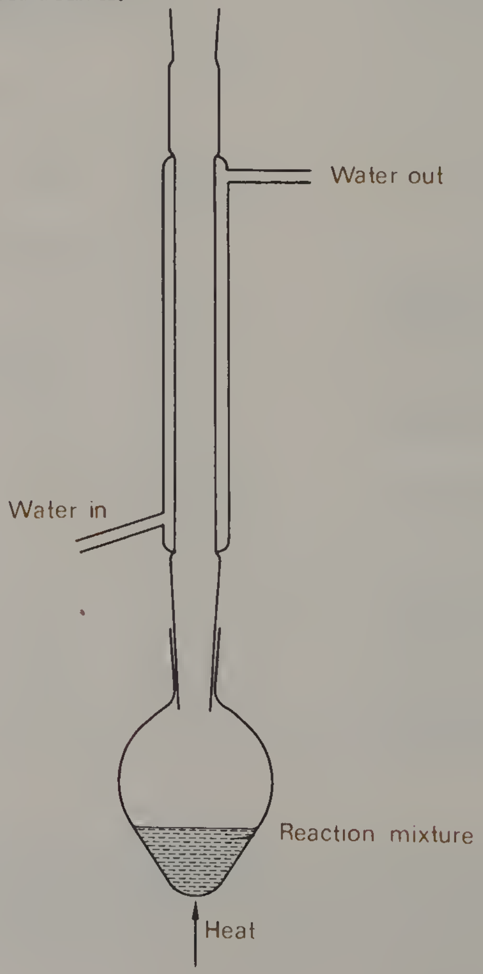
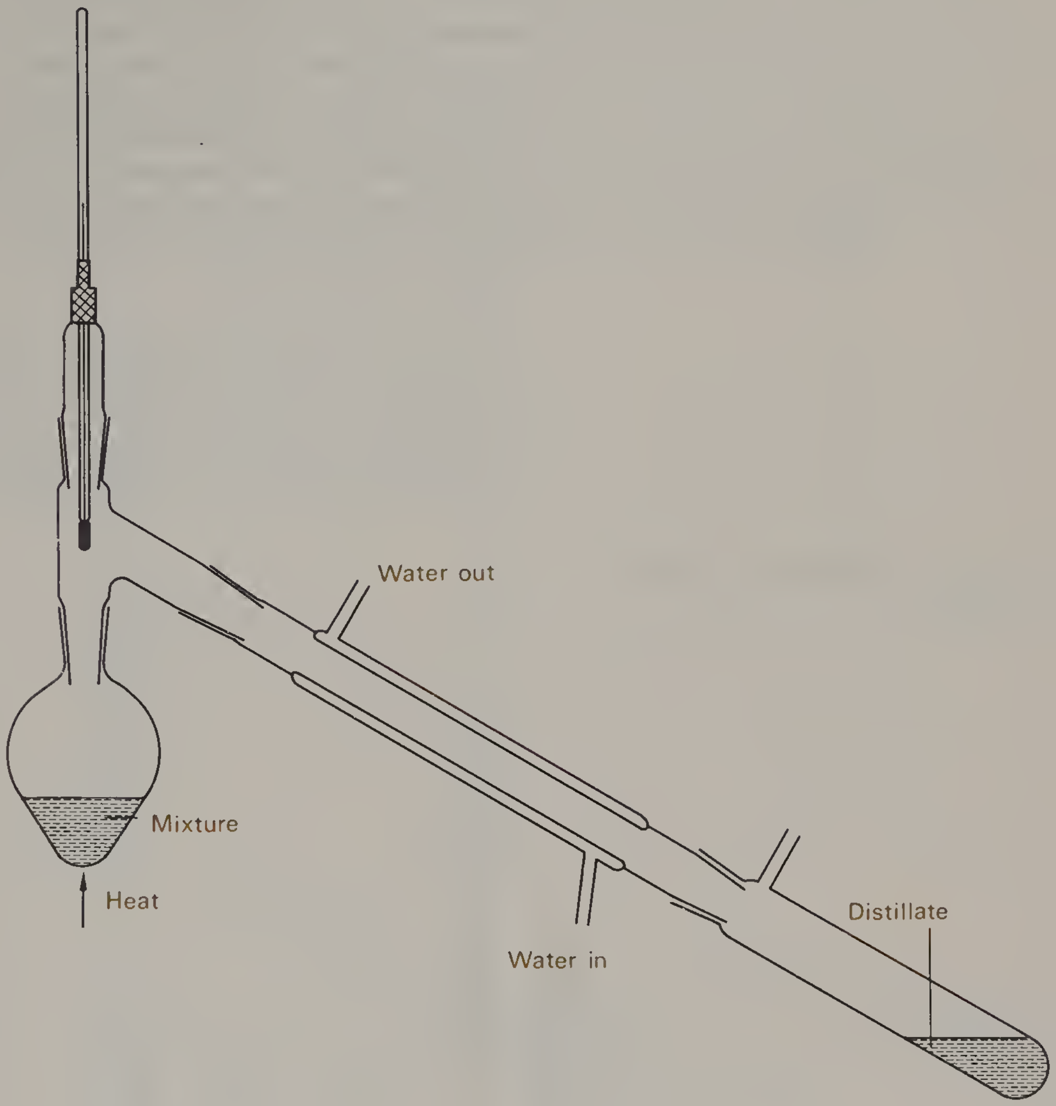


FIG. 2.1. *An apparatus for heating under reflux*

2.3 Distillation

When the product is a liquid or solid with a boiling point below about 250°C and no other such volatile compounds are present, the simplest method of purification is by **distillation**. The apparatus is shown in Figs. 2.2 and 2.3;

FIG. 2.2. *A distillation apparatus, with a water condenser*



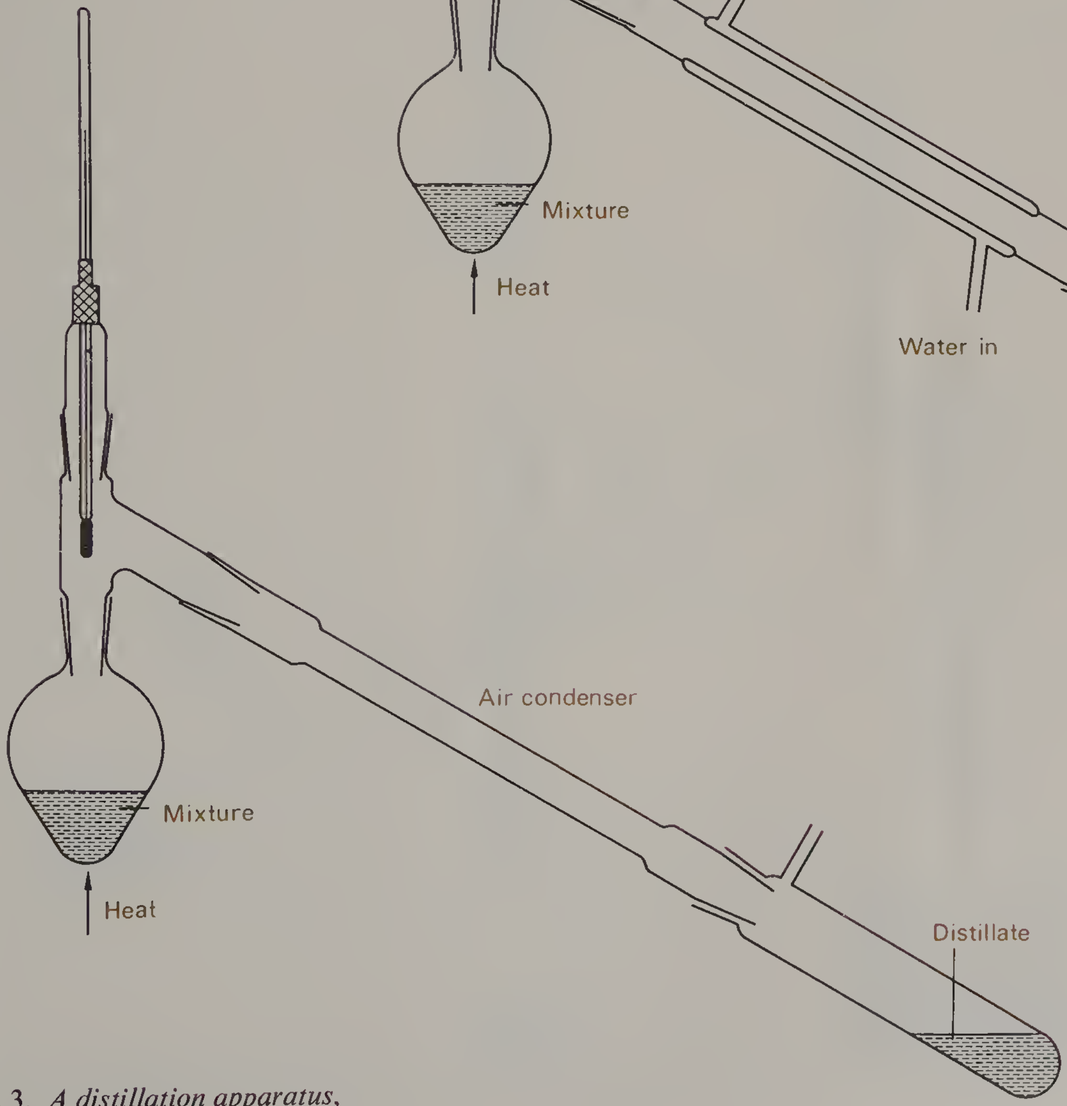
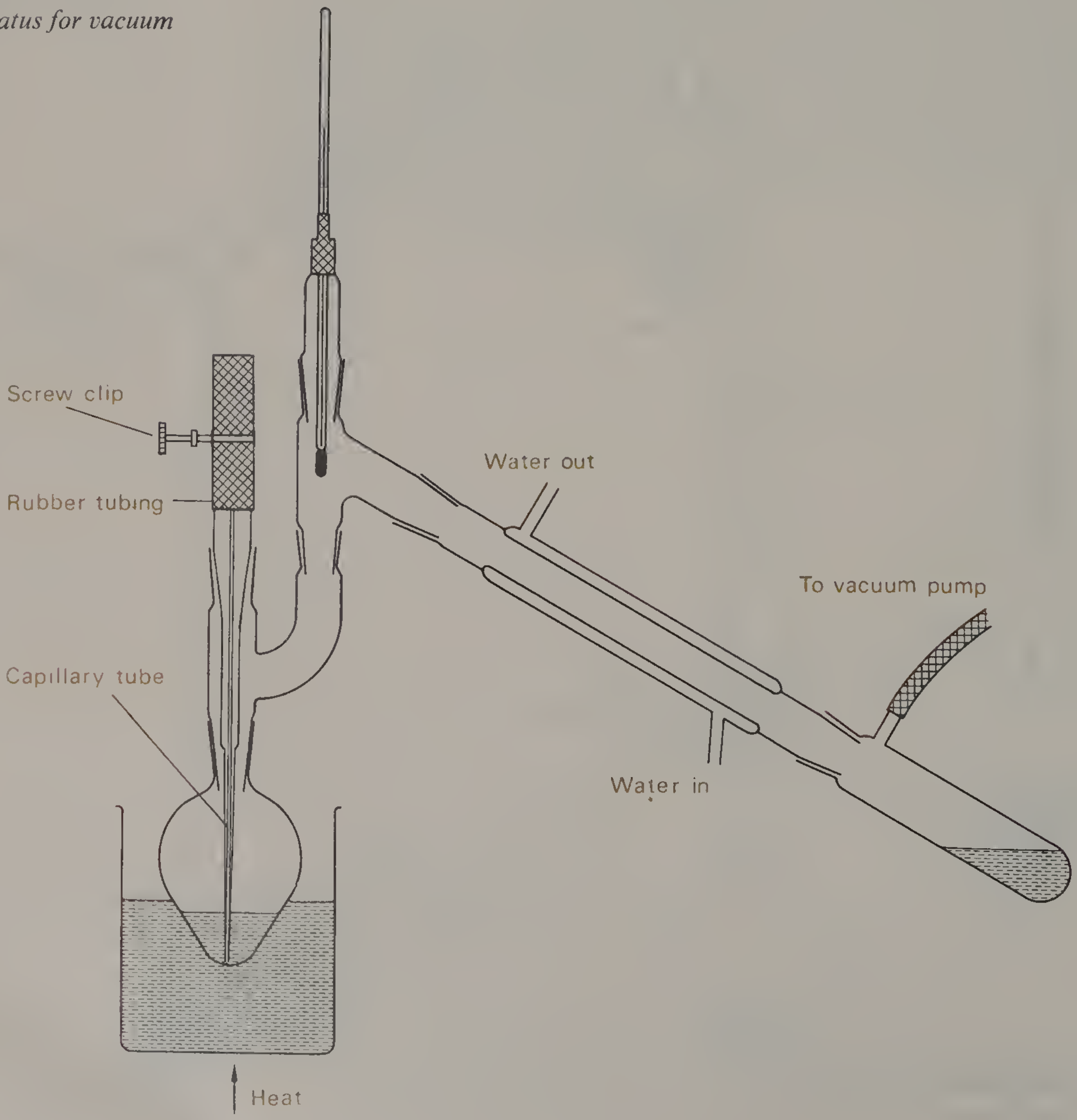


FIG. 2.3. *A distillation apparatus, with an air condenser*

the water condenser is used for compounds boiling up to about 180°C and the air condenser for compounds of higher boiling point. The mixture is heated to boiling and the vapour of the product liquefies in the condenser, the liquid collecting in a receiving flask at the end of the condenser. It is important to place the thermometer so that its bulb is fully immersed in the stream of vapour which is about to enter the condenser; the recorded temperature can then be compared with the quoted boiling point for the required compound. Since the boiling point of a liquid is dependent on the external pressure, the atmospheric pressure should also be measured and recorded when a boiling point is reported; e.g. ethanol, b.p. 78°C/760 mm Hg (the pressure in S.I. units is 101·33 kN m^{-2}). Unless the pressure is stated, you may assume that the reported boiling point was measured at a pressure of 760 mm Hg.

Although some organic liquids decompose before they have a chance to boil at atmospheric pressure, they can still be purified by distillation by reducing the external pressure until their boiling points are below their decomposition temperatures. This is known as **vacuum distillation**. The receiving flask is attached to the condenser and to a thick-walled rubber tube through which air can be withdrawn from the apparatus (Fig. 2.4). By

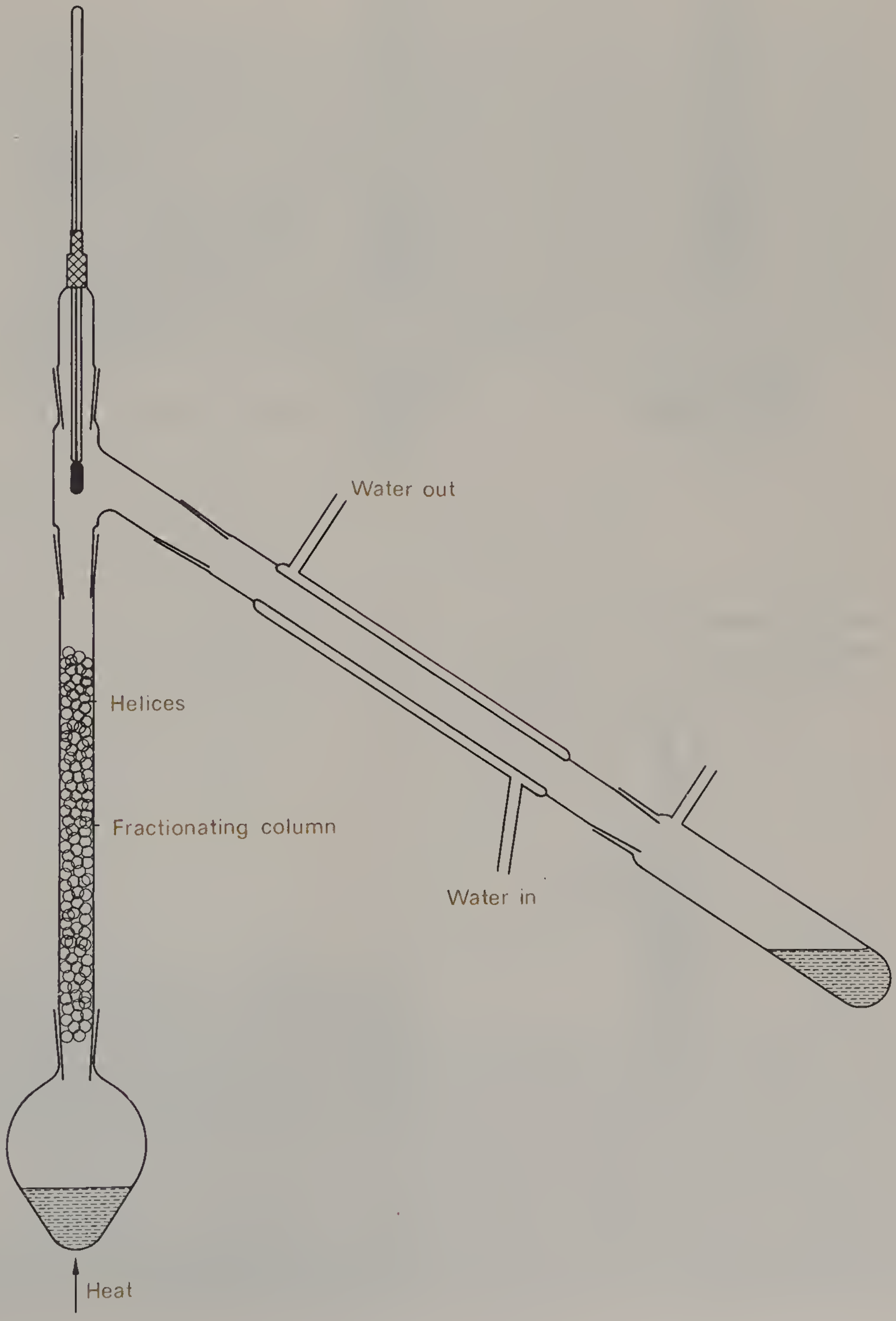
FIG. 2.4. *An apparatus for vacuum distillation*



attaching this tube to a water pump, the pressure can be reduced to a value equal to the vapour pressure of water, which is about 12 mm Hg at room temperature. Much lower pressures can be obtained with a rotary oil pump.

When the required product is accompanied by one or more other compounds of similar boiling point, **fractional distillation** must be carried out. A glass column containing glass or stainless steel coils or beads (Fig. 2.5) is attached to the boiling flask and, at its top outlet, to the condenser. In the apparatus shown, liquids boiling at least 30°C apart (e.g. benzene, b.p. 80°C, and methylbenzene, b.p. 111°C) can be separated successfully but as the difference in boiling points becomes smaller the efficiency of separation decreases and longer columns are necessary. The theoretical basis for fractional distillation is discussed in physical chemistry textbooks.

FIG. 2.5. *An apparatus for fractional distillation*



If a liquid of high boiling point is immiscible with water it can be purified by **distillation in steam**. This method is particularly useful when separation from inorganic and other non-volatile materials is necessary. The apparatus is shown in Fig. 2.6: steam is passed through the heated mixture, and the required liquid and water are collected in the conical flask.

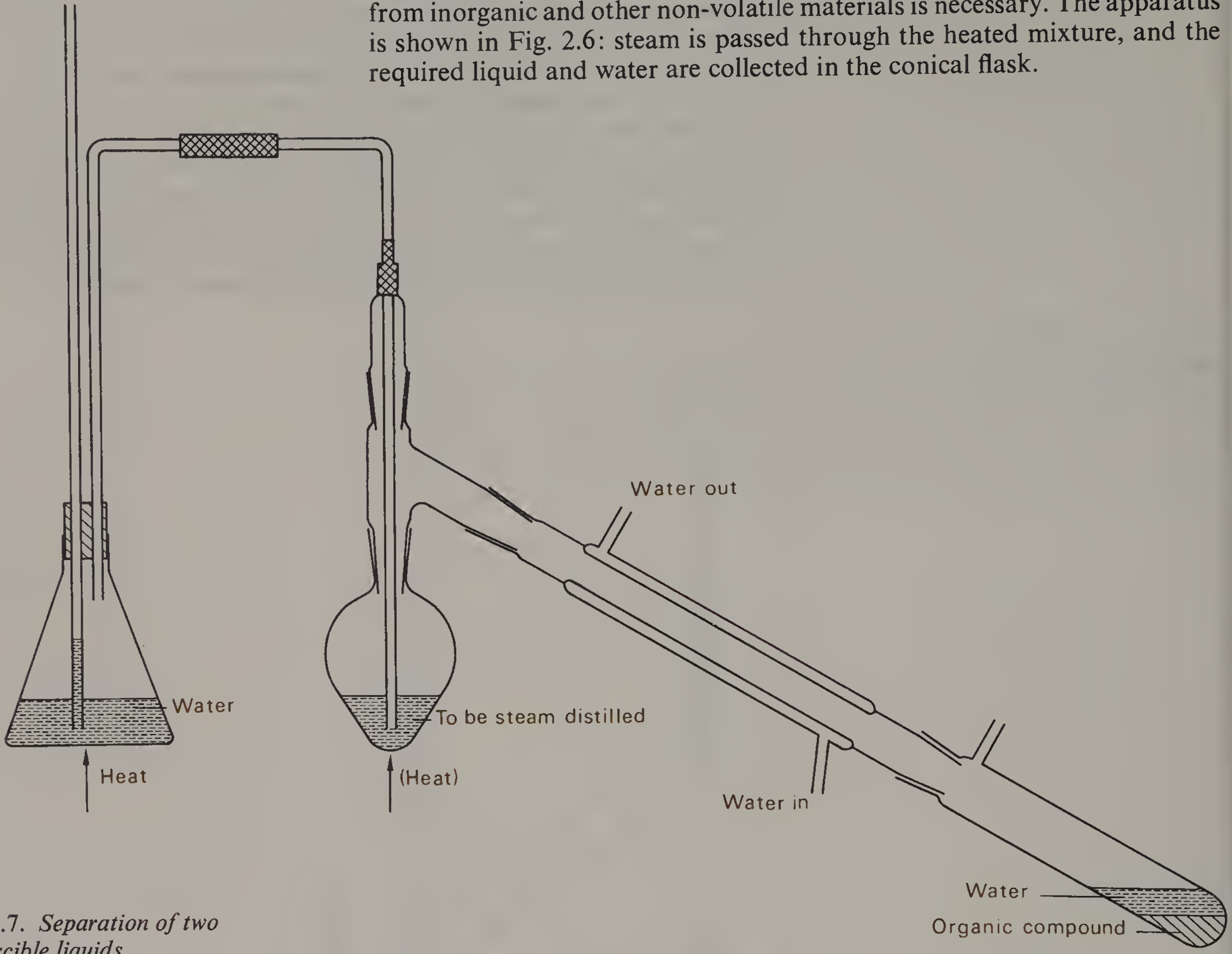


FIG. 2.6. *An apparatus for distillation in steam*

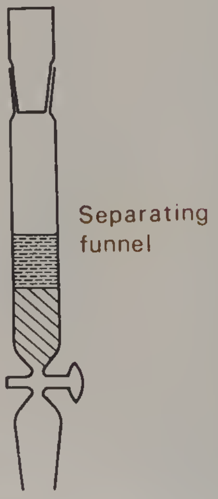


FIG. 2.7. *Separation of two immiscible liquids*

For example, nitrobenzene boils at 210°C. At 98°C, its vapour pressure is about 50 mm, while that of water is 710 mm. The total vapour pressure is equal to the atmospheric pressure, and the mixture boils. Thus, nitrobenzene is distilled at 112°C below its boiling point. It is separated from water by using a separating funnel (Fig. 2.7) from which the denser liquid (in this case nitrobenzene) is run off first.

2.4 Extraction

If the material to be purified is soluble in one solvent, while the impurities are not, the mixture can be partitioned between two immiscible solvents.

For example, sometimes an organic compound is obtained as an aqueous solution, which is contaminated with inorganic materials. The aqueous solution is shaken with diethyl ether (often referred to simply as ether) in a separating funnel. Only the organic compound is soluble in ether, and the residue remains in the aqueous layer. The two layers are separated, and the ether solution is shaken in the presence of a solid drying agent such as anhydrous magnesium sulphate to remove the small amount of water which will have dissolved in it. The solution can then be filtered from the drying agent and the organic compound can be separated from the ether by distillation.

Extraction is more efficient if several small quantities of ether are used, rather than one large quantity. This is considered theoretically in many physical chemistry textbooks.

2.5 Recrystallisation

This is the commonest method for purifying a solid. It is based on the fact that the solubility of organic compounds in a particular solvent increases as the temperature is raised. The solvent is heated with that amount of the solvent which gives a nearly saturated solution at the boiling point. The solution must then be filtered very rapidly, and this is done using a fluted filter paper, contained in a glass funnel from which the stem has been removed, through which the filtrate runs into a conical flask; insoluble impurities are thereby removed. The solution is then allowed to cool, and crystals of the solid continue to be deposited until the solution has reached room temperature. The crystals are filtered off in a Buchner funnel (a porcelain funnel with a large number of holes in its base on which a filter paper rests), which is attached to the filter flask (a Buchner flask) whose side-tube is connected to a water-pump. When filtration is complete, the crystals are washed with a small quantity of the pure solvent to remove any impurities which might have deposited on the surface. The crystals are then dried on a watch-glass to remove the solvent; drying may be at room temperature if the solvent is a particularly volatile one; but it is usually quicker to place the watch-glass in an oven, taking care that the temperature of the oven is below the melting point of the solid.

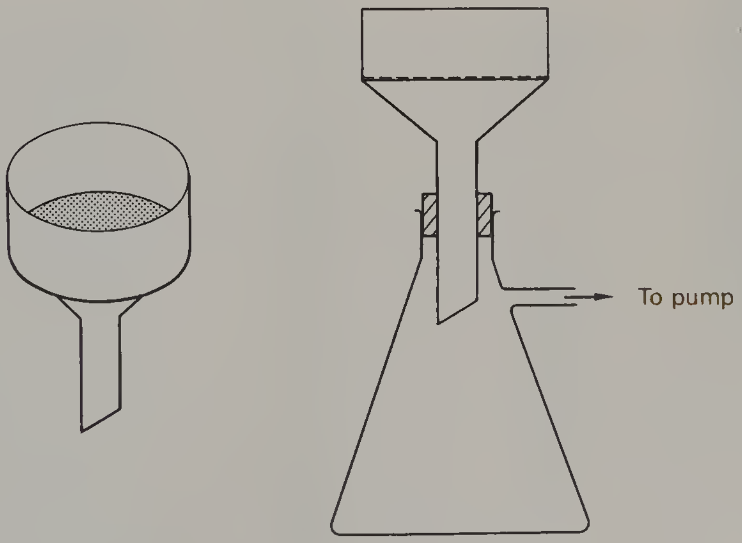


FIG. 2.8. *A Buchner funnel and flask*

If one recrystallisation does not yield a pure material, further recrystallisations, preferably with different solvents, should be carried out.

2.6 Chromatography

The chromatographic methods of separation are particularly important for complex mixtures of substances which are not otherwise readily separated. The principal methods are:

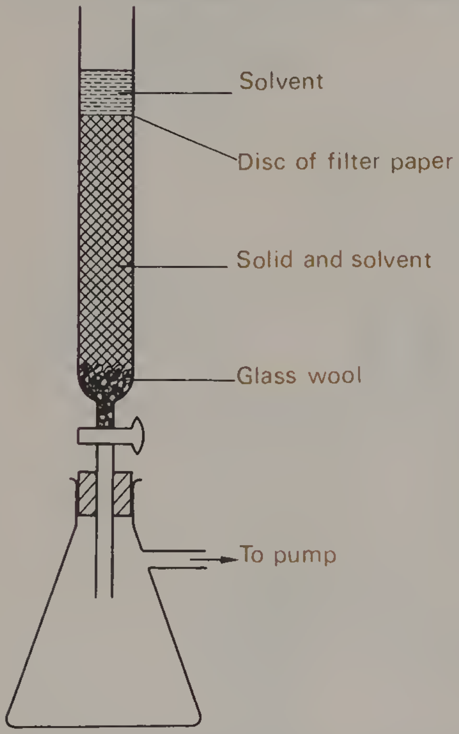
(a) Column chromatography
(b) High pressure liquid chromatography
(c) Thin-layer chromatography
(d) Paper chromatography
(e) Gas chromatography

(a) Column chromatography

This is a method for the separation of solids, and can be successful even when the solids have very similar solubilities, when recrystallisation would not be effective.

A glass column about 30 cm long and 2 cm in diameter, which narrows at one end to an outlet tube, is used. A pure liquid such as benzene is run in until the column is about half-full, and then a slurry of a solid adsorbent (such as alumina) in the same solvent is added. The solid sinks to the bottom, forming an evenly packed column immersed in the solvent; a pad of glass wool at the bottom prevents the solid running out, and a disc of filter paper is added at the top of the column to avoid disturbance of the solid when a solution or solvents are added later. The solvent above the column of damp solid is run off, care being taken that the column of solid remains wetted, for otherwise cracks and channels appear and the solution to be added does not run evenly through the column.

FIG. 2.9. *Column chromatography*



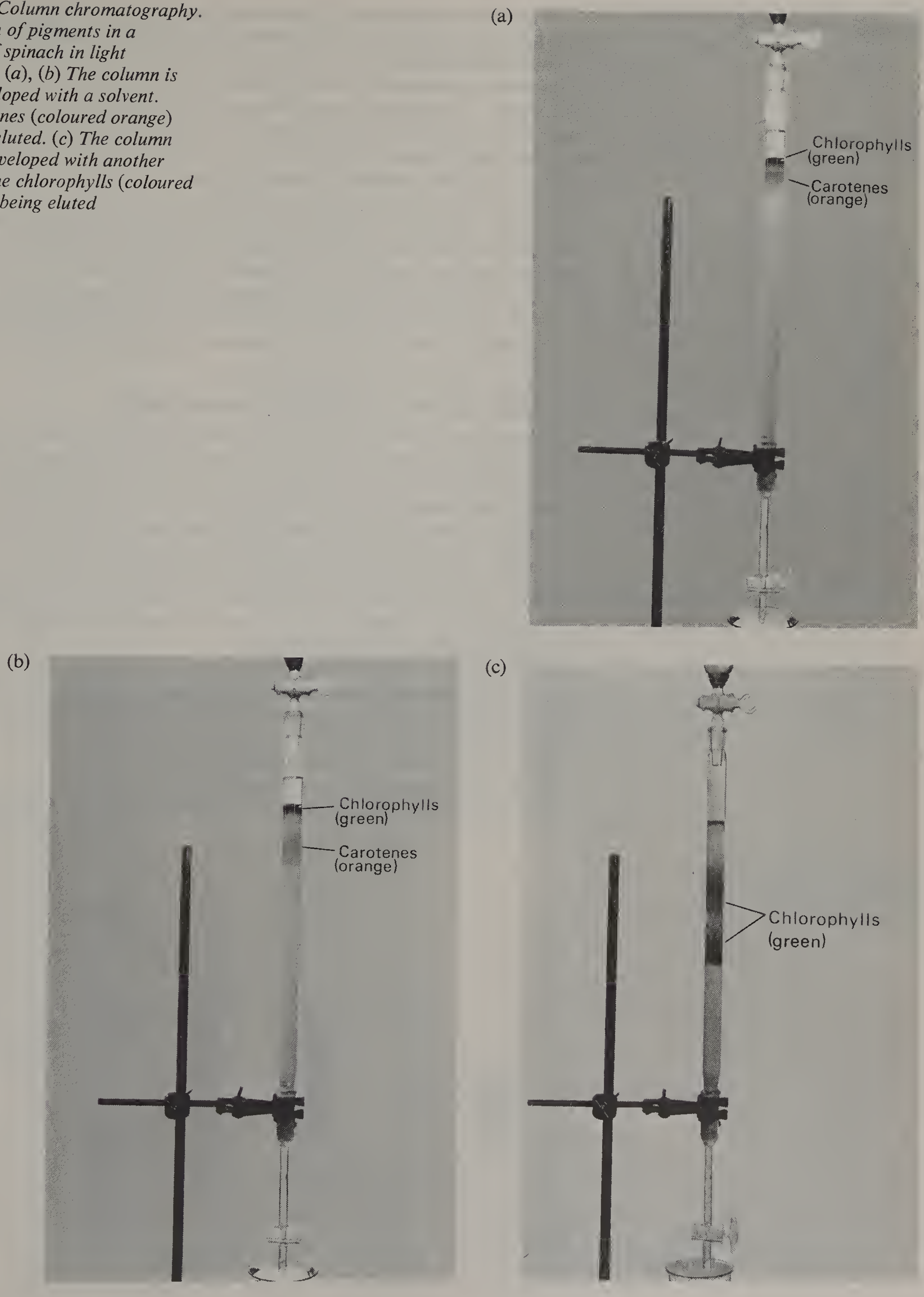
A solution of the mixture in the same solvent is then added at the top of the column and the liquid emerging at the bottom is collected; by attaching the receiver to a pump, the rate of passage through the column can be increased (Fig. 2.9). Following addition of the solution, further quantities of the solvent are added, and after a while solutions of the components of the mixture will emerge successively. This process is known as **elution**. Each solution is collected in a separate flask, and the solvent is then removed by distillation to leave the pure compound.

If the solutes are coloured, they are seen as they pass down the column. If they are colourless, a physical property, such as fluorescence under ultraviolet light, can be employed to find out how each compound is moving down the column so that a fresh flask can be inserted at the bottom just when the solution of the compound is about to emerge.

The principle of the method is that each compound in the mixture has a particular solubility in the solvent and a particular tendency to be **adsorbed** by the solid in the column; no two compounds behave exactly alike in these respects. Thus, compounds which are readily soluble and not strongly adsorbed move rapidly down the column in the stream of solvent; those which are not so soluble and are more strongly adsorbed are held on the column for longer periods.

In some cases a particular solvent causes one component of a mixture to be eluted rapidly while another component does not travel down the column at a significant speed. It is then helpful to use a second solvent after the first compound has been eluted. Plate 2.1 shows a column packed with alumina in which a solution obtained from spinach is being separated.

Plate 2.1. Column chromatography. Separation of pigments in a solution of spinach in light petroleum. (a), (b) The column is being developed with a solvent. The carotenes (coloured orange) are being eluted. (c) The column is being developed with another solvent. The chlorophylls (coloured green) are being eluted



A recent development in column chromatography has been in the way the column is packed with the solid adsorbent. This is the dry pack method. Nylon tubing (about 20 cm in length and 2 cm in diameter) is used instead of glass. It is sealed at one end (by pressing the end with a hot iron). Sand is poured in to a depth of 1 cm, followed by the adsorbent and finally by a little more sand, to a depth of 0·5 cm. The packed column is then stood in a measuring cylinder. A sample of the solution of the mixture is added, followed by small portions of the eluting solvent. Elution is stopped when the solvent reaches the end of the column.

The nylon column is then taken out of the cylinder, lain sideways and sliced with a sharp knife. The sections containing the solutes are placed in different beakers and each is extracted with a solvent. The extracts are filtered and evaporated, leaving samples of the pure compounds.

While this method is often not as efficient in separating closely related compounds, it is very quick and convenient and is becoming widely used.

(b) High pressure liquid chromatography

The separations achieved by column chromatography can be improved by reducing the size of the particles of adsorbent and ensuring that they are of uniform size. However, this results in the solvent moving very slowly through the column, and for practical purposes it is necessary to use a high pressure to speed up the process. This is the basis of high pressure (sometimes called high performance) liquid chromatography (HPLC).

There were practical difficulties in developing HPLC, since the materials used to make the columns must be able to withstand the high pressures, the solvent should flow at constant rate and a special system must be used to inject the mixture into the column.

The difficulties have been overcome. The columns are made of thick-walled glass (8 mm diameter with 2 mm bore) or stainless steel. Pressures of 200–300 atmospheres are generally used and, with the use of valves, the flow-rate of solvent can be kept constant. The sample is injected on to the column *via* a special valve or syringe (Fig. 2.10).

Many column packings have been developed. One is a polymer (often poly(phenylethene) is used) which is prepared so that it is porous. Small

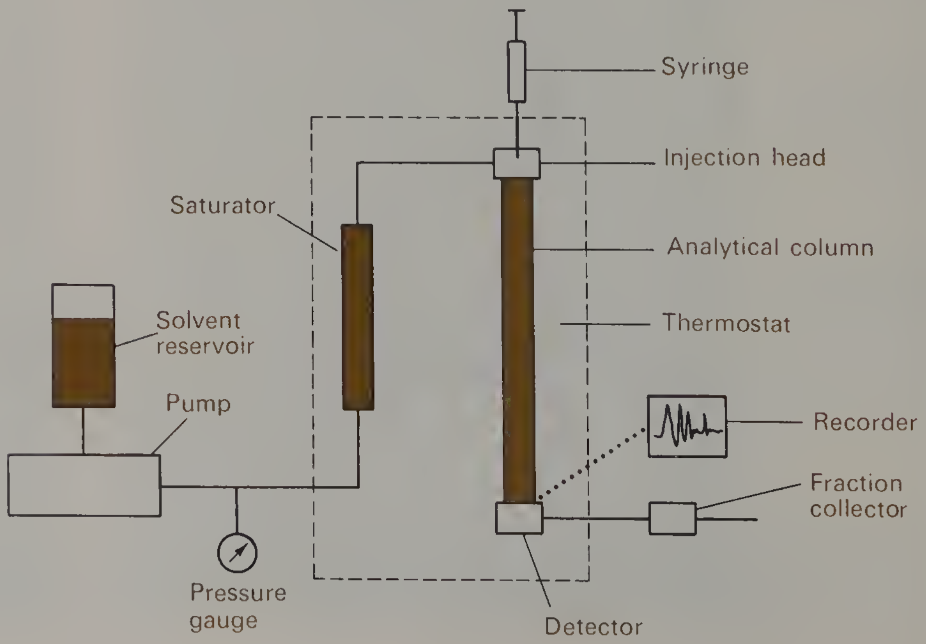


FIG. 2.10. *Outline of a high-pressure liquid chromatograph*

molecules tend to be trapped in the pores, while larger molecules are excluded. Thus the larger molecules elute first, the smaller molecules later. This is known as **gel permeation chromatography**. Solutions containing a polymer whose molecules have different chain lengths can be separated into fractions with more or less similar lengths.

Ion-exchange resins are used as packing materials to separate mixtures of amino-acids, a particularly useful technique in the elucidation of protein structure (Chapter 18) and in the analysis of protein hydrolysates in medical diagnosis.

Other column packings include silica and alumina, similar in chemical nature to those used for column chromatography above but with particles which are much smaller and of more even diameter. Another development has been to produce column materials composed of a liquid coated on an inert solid. The compounds in the mixture are partitioned between the liquid on the inert solid (known as the stationary phase) and the eluting solvent. The liquid tends to be washed off the column by the solvent, and to avoid this the solvent is first saturated in the liquid before it is pumped through the column. Another interesting development is to 'sew' the liquid onto the column by chemical reaction so that it cannot wash off.

When the solvent emerges from the column it passes through a detector which usually measures either refractive index or ultraviolet absorption and can thereby show whether the solvent is pure or contains a solute; as each of the latter fractions emerges, it is collected separately and the solution is then evaporated to obtain the pure compound.

The detector is used in conjunction with a pen-recorder. The result of a typical experiment is shown in Fig. 2.11. The sample was injected at time A.

The time taken for each solute to pass through the column [for phenylethanone, time (B − A)]—its **retention time**—is characteristic of the compound and the conditions of the experiment (the rate of flow of solvent, the nature and concentration of the stationary phase and the temperature). Provided that the conditions are constant, an unknown compound can be identified by comparison of its retention time with those for samples of known compounds.

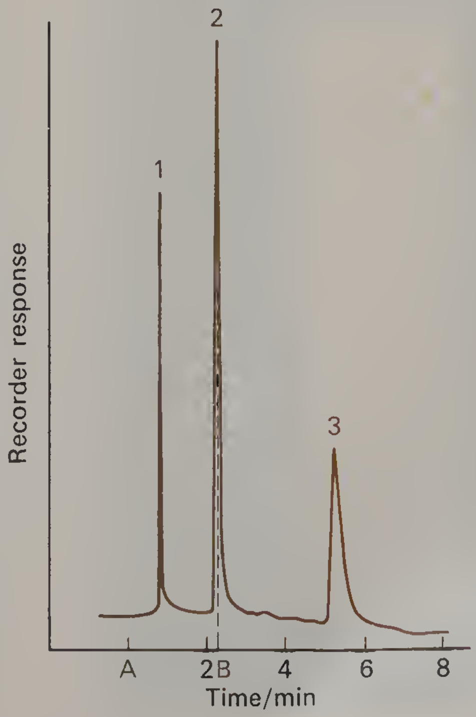


FIG. 2.11. *Separation of a mixture of compounds by high pressure liquid chromatography: 1, benzene; 2, phenylethanone; 3, methyl benzoate. The retention time for phenylethanone is (B − A) min.*

The column used was a silicone 'sewn' on to an inert solid support and the solvent was a mixture of propan-2-ol, dichloromethane and hexane.

The area under the peak of the chromatogram depends on the amount of the material present, so that the amount in a mixture can be measured by calibrating the chromatogram with injections of measured quantities of the compound and comparison of the resulting areas with that from the mixture.

(c) Thin-layer chromatography

This method is similar to column chromatography but on a much smaller scale. It is generally used for the identification of components in a mixture rather than as a method of purification in preparative work.

Plate 2.2 (colour) faces p. 22

A solid adsorbent such as silica gel or alumina is spread as a thin, even layer on a glass plate [Plate 2.2(a)]. A solution of the sample to be analysed is placed as a spot on the surface of the plate and near one end. When the solvent has evaporated from the spot, the plate is put in a tall beaker or jar containing the same solvent, so that the spot is a little way above the level of the liquid. The beaker is covered to reduce evaporation. The solvent rises slowly up the plate by capillary action, and after it passes the spot, the components in the mixture begin to move with the solvent at different rates, just as in column chromatography [Plate 2.2(b)].

When the solvent has almost reached the top of the plate, the plate is removed from the beaker and the solvent is allowed to evaporate. If the components of the mixture are coloured, each will be seen as a coloured area [Plate 2.2(c) and (d)]. If they are colourless, the plate is **developed** by being stood in a beaker containing some crystals of iodine. After a few minutes, a dark spot will appear where each compound is held on the plate.

The distances from the original spot to the solvent front and the position of each compound are measured. It is convenient to calibrate the distance travelled by the solvent from 0–1, and the fraction of this distance travelled by each compound is described as its R_F value. For example, in Fig. 2.12,

FIG. 2.12. *R_F values*

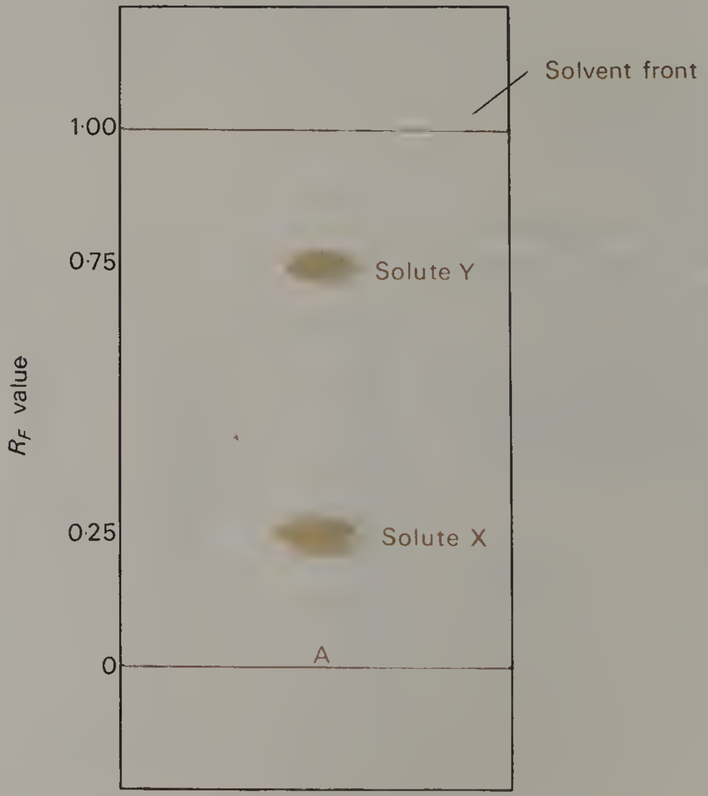
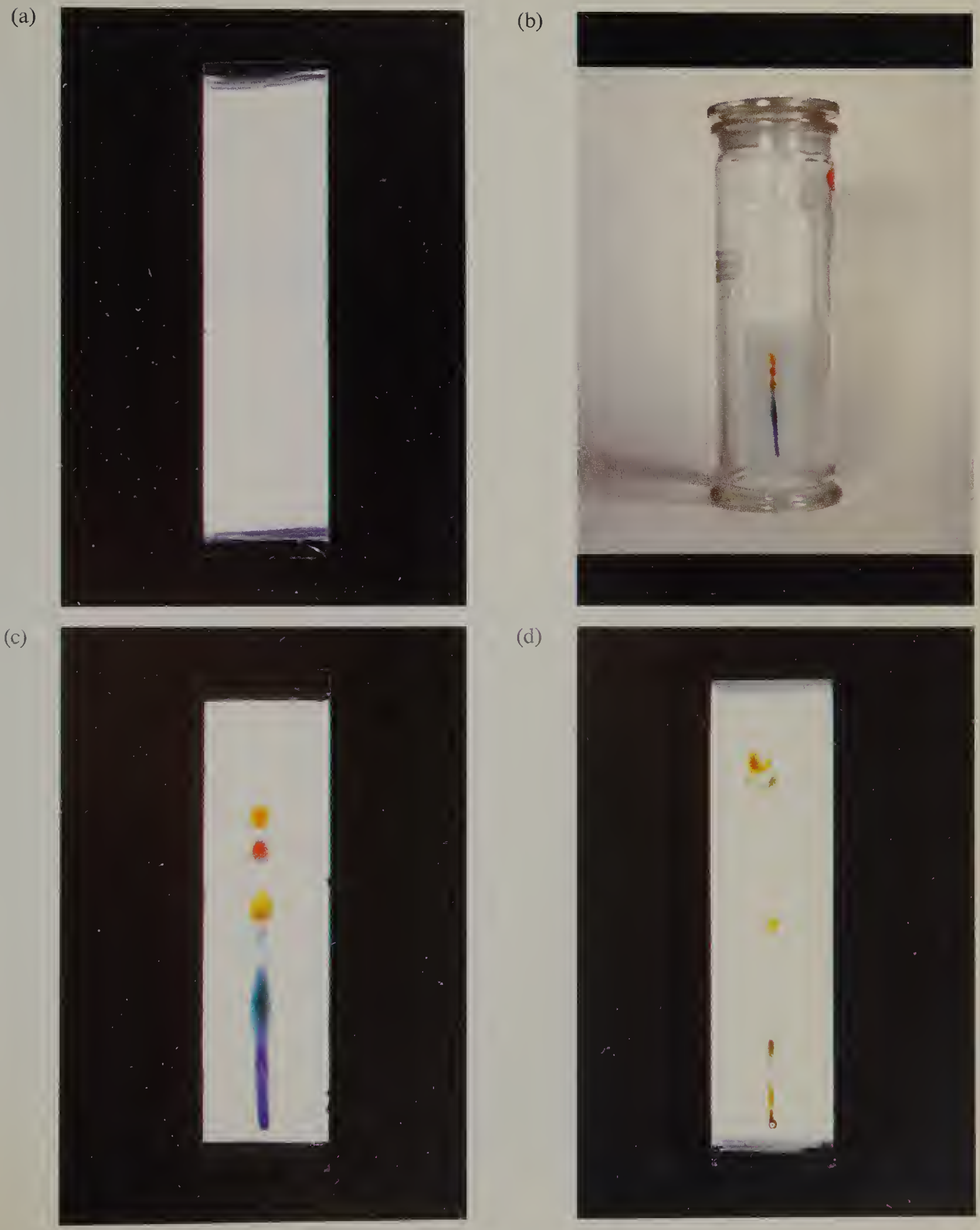


Plate 2.2. Thin-layer chromatography. (a) A thin-layer plate. (b) The development of a thin-layer plate. (c) Separation of black ink using butan-1-ol, ethanol and 2M ammonia solution (3:1:1 by volume) as solvent.
(d) Separation of pigments in a solution of spinach in light petroleum



see p. 20

the mixture was placed on the plate at A, and thus solute X has an R_F value of 0·25 and solute Y has an R_F value of 0·75.

Different substances have different R_F values for the particular conditions of the experiment, so that comparison of the values from the mixture with those from authentic samples of pure compounds enables the components of the mixture to be identified. It is essential that comparison is made for the same solvent and temperature, for the R_F value depends on these as well as on the nature of the compound.

(d) Paper chromatography

This method is like thin-layer chromatography in being suitable for the identification of the components of a very small sample of a mixture. The procedure is similar except that a large rectangular piece of filter paper mounted in a glass tank (Fig. 2.13) is used instead of solid adsorbent on a glass plate.

A pencil line is drawn across the paper near the bottom and a drop of the solution (which contains, for example, a mixture of amino-acids) is placed on the paper at this line by means of a fine glass pipette. Samples of solutions of the compounds believed to be in the mixture are placed alongside so that a direct comparison of R_F values can be made. Solvent is then poured into the tank so that the pencilled line is just above the surface.

When the solvent reaches almost the top of the paper, the paper is removed from the tank and the solvent is allowed to evaporate. If the components are coloured, they are easily seen, but if not, a physical or chemical property must be employed to reveal their positions. In Plate 2.3, a chemical reagent, ninhydrin, was used to form a coloured compound with each of the amino-acids.

FIG. 2.13. *Apparatus for paper chromatography*

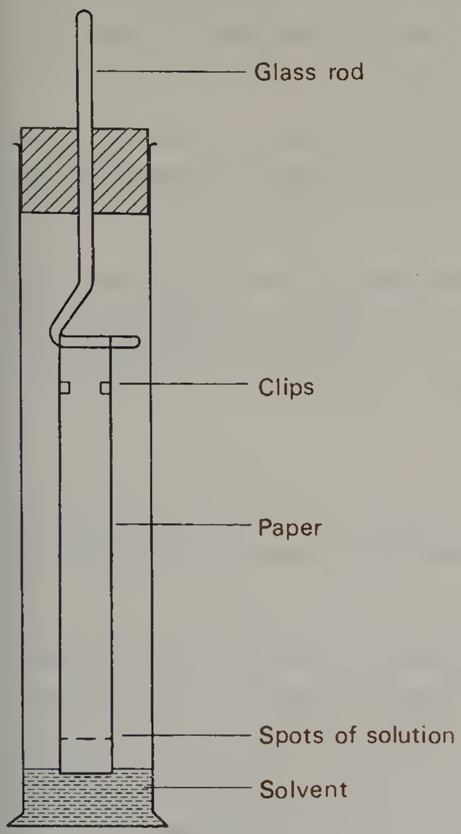
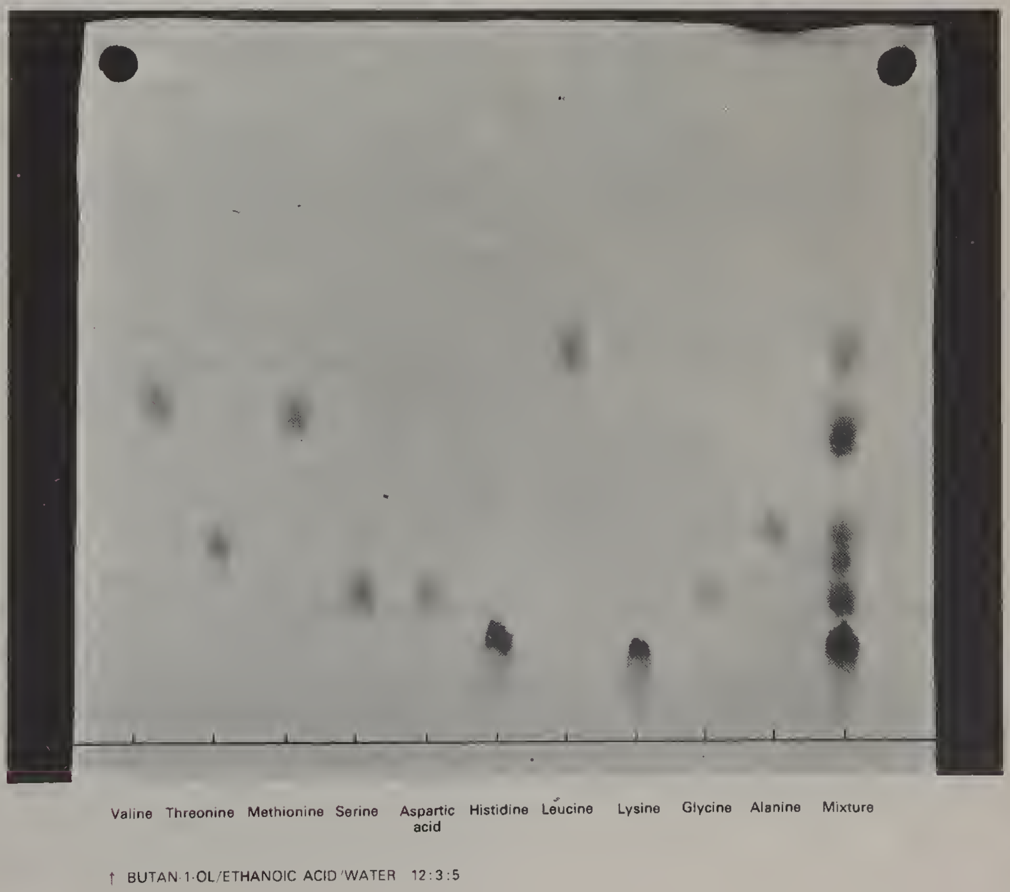


Plate 2.3. Paper chromatography. Separation of some amino-acids with a mixture of butan-1-ol, ethanoic acid and water as solvent. The paper has been developed with ninhydrin solution. On the extreme right-hand side, a mixture of amino-acids has been separated, and the R_F values can be compared with those for pure amino-acids developed at the same time



The underlying principle in paper chromatography is the **partition** of a solute between two solvents. One solvent is the one which travels up the paper (the eluting solvent), and the other is water, the molecules of which are adsorbed on the cellulose which constitutes the filter paper. Compounds which are relatively more soluble in the eluting solvent travel faster (i.e. have larger R_F values) than the less soluble ones.

In some cases, two or three components in a complex mixture are not separated completely in this way. It is an advantage to elute with one solvent, remove the paper, dry it, turn the paper through 90° and elute with a second solvent.

Thin-layer chromatography is a more rapid method than paper chromatography. However, for compounds which are only slightly soluble in organic solvents but moderately soluble in water, thin-layer chromatography is unsuitable whereas paper chromatography is successful.

(e) Gas chromatography

There are two types of gas chromatography: gas-liquid chromatography and gas-solid chromatography. Each is suitable for separating mixtures of gases, liquids and volatile solids.

In **gas-liquid chromatography**, as in paper chromatography, the compounds in the mixture are partitioned between two solvents. One solvent is fixed in position and is known as the **stationary phase** (cf. water in paper chromatography); it consists of a non-volatile liquid (such as a long-chain alkane) which is coated on an inert solid. The other solvent is a gas which travels through the column containing the stationary phase (cf. the eluting solvent in paper chromatography). It is known as the **carrier gas**, and must be one which does not react with the components of the mixture. Nitrogen is often used.

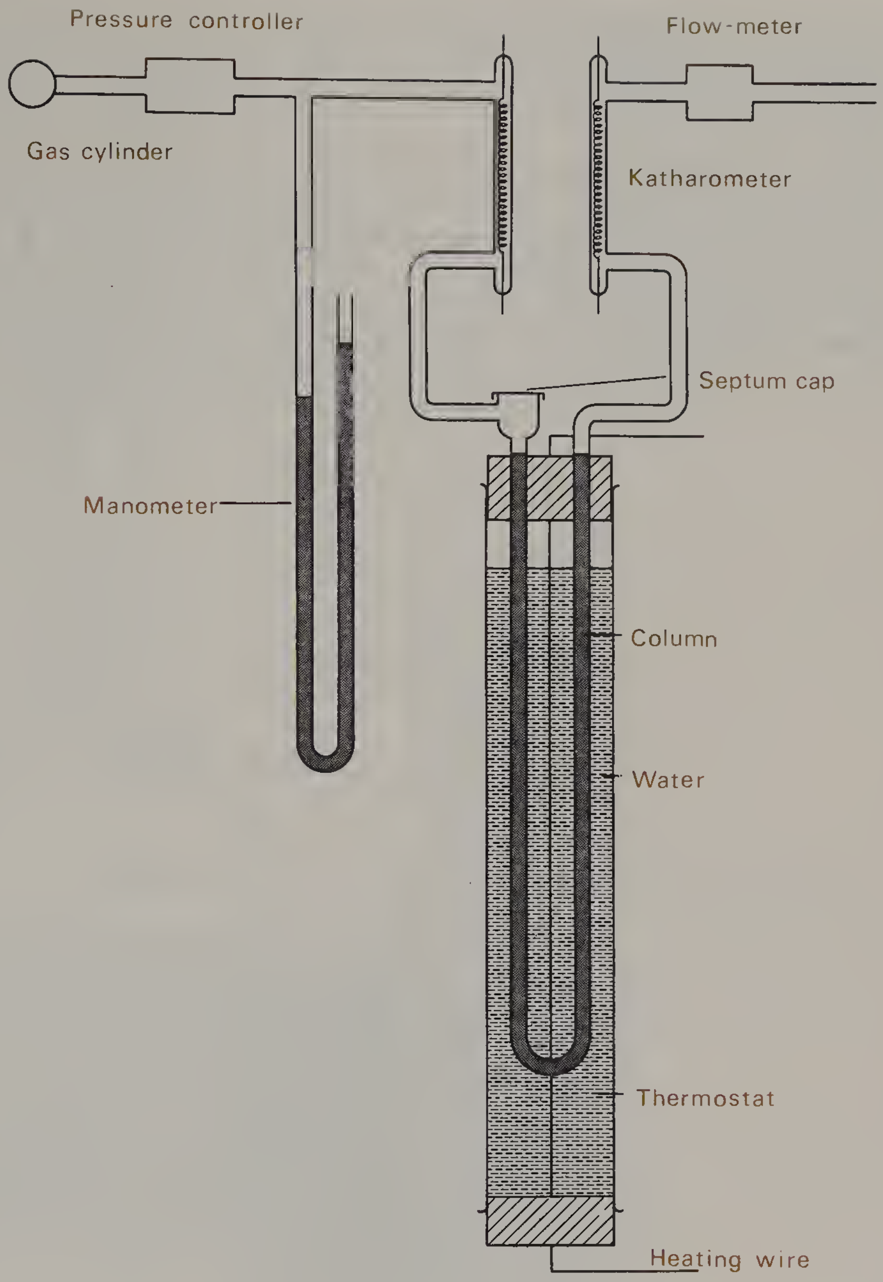
Gas-solid chromatography differs in employing a solid as the stationary phase. The principle of separation is like that of column chromatography save that the eluting solvent is a gas and not a liquid. The solids generally used are silica gel or alumina.

The gas chromatograph consists of: (i) a supply of carrier gas at constant pressure; (ii) a flow-meter to measure the rate at which the carrier gas passes through the column; (iii) the column, in a thermostat; and (iv) a detector, to determine when each component of the mixture is eluted. At the top of the column is a rubber septum cap through which the solution for analysis is introduced by means of a hypodermic syringe; the cap is self-sealing so that when the syringe is withdrawn the sample and carrier gas cannot escape. Figure 2.14 gives an outline of a gas chromatograph with a column 2 m long and 4 mm in diameter.

The detector makes use of a physical or chemical property of the compounds in the mixture. Two detectors commonly employed are the katharometer and the flame-ionisation detector. The **katharometer** (Fig. 2.14) measures the change in the thermal conductivity of the emerging gas which occurs when an organic compound is eluted in a stream of carrier gas. The **flame-ionisation detector** measures the concentration of ions in a flame. Hydrogen is mixed with the carrier gas as it emerges from the end of the column and is burned at a jet, and the ions formed in the flame are collected on a charged plate above it. While only hydrogen is being burnt, the concentration of these ions remains steady, but when an organic compound is eluted there is a change in the concentration.

These detectors are used in conjunction with a device which enables the changes to be observed. A galvanometer is suitable, but it is helpful to have

FIG. 2.14. *A gas chromatograph*



a permanent record, and a pen-recorder is generally used. The result of a typical gas chromatography experiment is shown in Fig. 2.15. There were six compounds in the mixture.

In Figure 2.16 a gas chromatogram of a sample of one of the fractions from the primary distillation of a crude oil is shown. It illustrates the remarkable power of the technique. Although in this example the separation took three hours, it is more usual to allow the temperature of the oven containing the chromatographic column to rise at a uniform rate. This speeds up the separation and it is possible to complete an analysis such as this in 10–20 minutes.

A recent development has been to connect the gas chromatograph to a mass spectrometer. As the vapour of each solute is eluted at the end of the column, part of it is channelled into the spectrometer, and by analysis of the mass spectrum the structure of the materials can be deduced (3.7). Such a system would be used to identify, for example, all the hydrocarbons in the sample of the crude oil (Fig. 2.16).

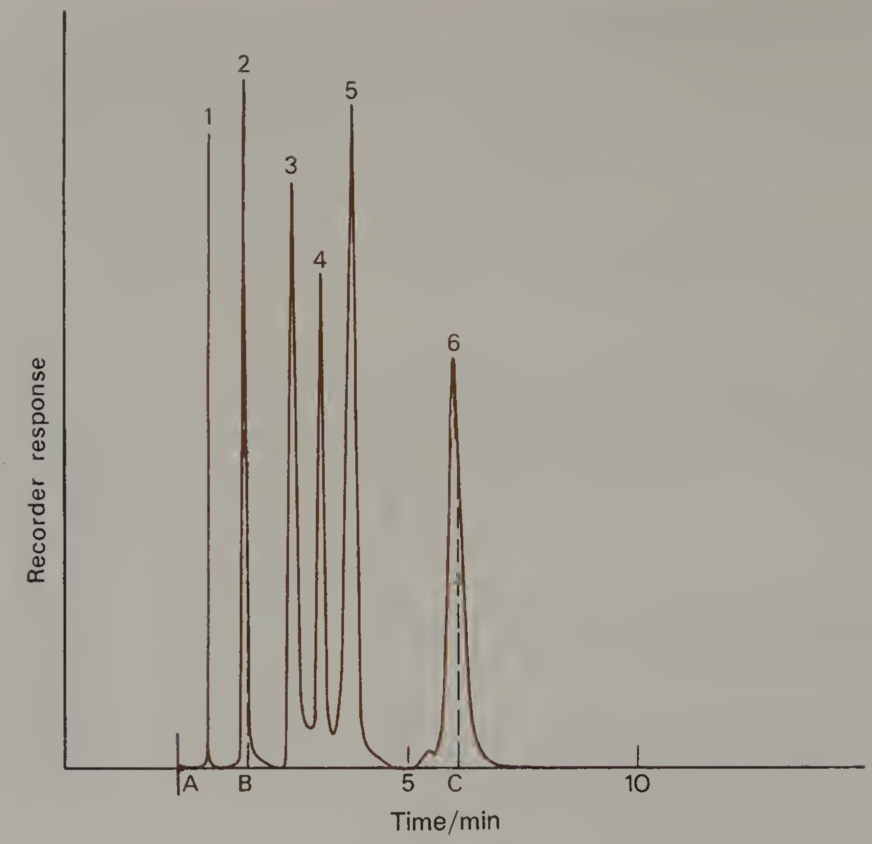


FIG. 2.15. *A gas chromatogram. The separation of a mixture of six substances: 1, diethyl ether; 2, propanone; 3, methanol; 4, ethanol; 5, pentan-3-one; 6, propan-1-ol. The retention time for propanone is (B − A) min, and for propan-1-ol, (C − A) min. The area under each curve is a measure of the amount of the compound in the mixture.*

The gas chromatograph described above is suitable only for analytical purposes, since the quantity of a mixture injected into the column is only about one-hundredth of a gramme. However, it is also possible to use columns of larger diameter which enable several grammes of a sample to be introduced, so that each component can be isolated as well as identified. For this purpose, the emerging gas is divided into two streams, the smaller of which passes into the detector and the larger of which flows through a U-tube surrounded by a freezing mixture. After each peak is registered, a fresh U-tube is inserted to collect the next compound.

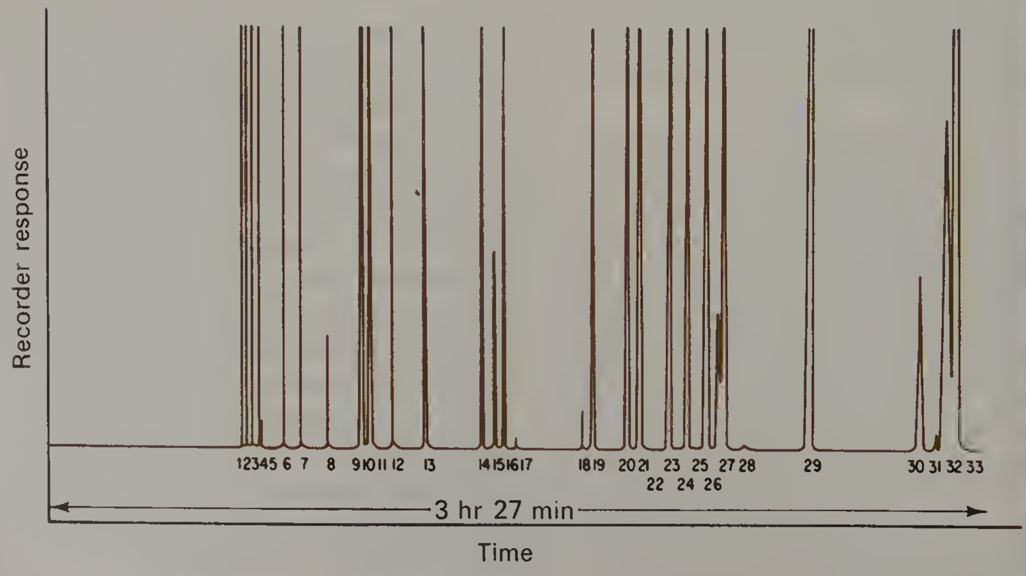


FIG. 2.16. *A gas chromatogram of a sample of a low boiling fraction (up to 150°C) of crude oil, showing the relative abundances of the lighter hydrocarbons. There are 33 separate peaks, all of which have been identified. Of these are 1, methane; 2, propane; 4, butane; 7, pentane; 13, hexane; 16, benzene; 19, cyclohexane; 29, heptane; 33, 2,2,3,3-tetramethylbutane. The others are isomers of these compounds.*

The column was packed with a C_{30} alkane, known as squalane, coated on a solid support. Nitrogen was the carrier gas.

2.7
Criteria of purity

Pure solids melt over a very small temperature range (approximately 1–2°C), whereas the presence of even 1 per cent of an impurity can increase the range to several degrees. The melting point therefore provides a very good criterion of purity.

A small sample of the solid is placed in a glass capillary tube which is sealed at its lower end. The tube is attached to a thermometer so that the sample is level with the bulb and the thermometer is suspended in a small beaker of paraffin oil (Fig. 2.17). The oil is heated slowly (not more than 2° per minute near the melting point of the solid) and is stirred at the same time. The temperature at which melting is first observed and that at which it is complete are both noted, and the melting point is then recorded by quoting both temperatures, e.g. ethanamide, m.p. 81–82°C.

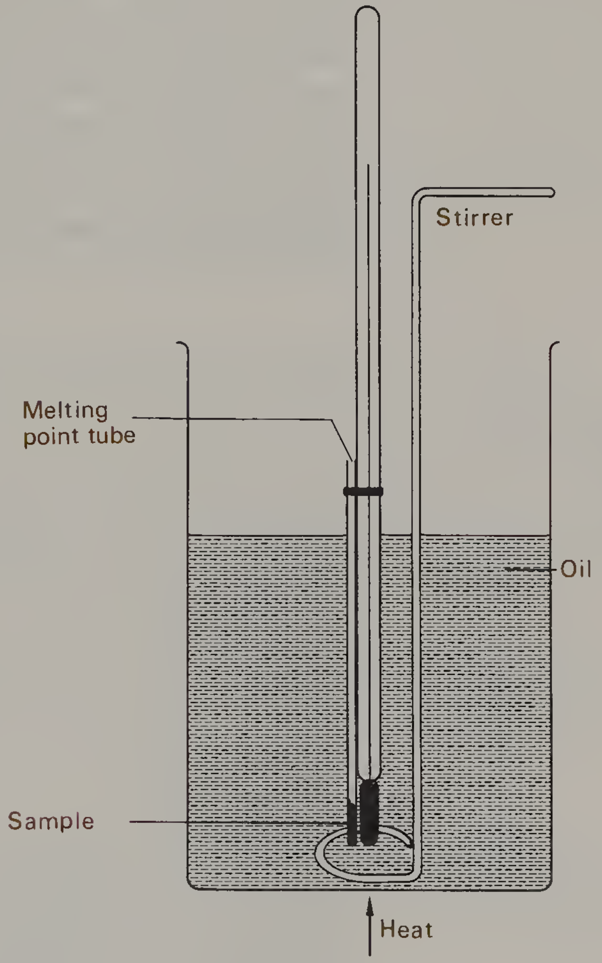


FIG. 2.17. *A simple melting point apparatus*

A melting-point method can also be used to confirm the identity of a compound. Suppose that a compound has been isolated which is thought to be ethanamide and which has the expected melting point for ethanamide of 81–82°C. A small amount is mixed with about the same quantity of a sample from an authentic source of ethanamide. The mixture is ground up and its melting point determined. If the first compound is in fact ethanamide, the melting point of the mixture will still be 81–82°C, but if it is not, then melting will begin at a lower temperature and extend over a wider range of temperature than that for a pure compound. This is known as the **mixed melting point** method.

A second criterion of purity for a solid is that it should give only one spot on a thin-layer or paper chromatogram. Small quantities of impurities can be revealed in this way, but unfortunately it sometimes happens that an impurity has the same R_F value as the required compound and is therefore not revealed. Thus, observation of a single chromatographic spot is a necessary but not a sufficient criterion for purity.

Pure liquids boil within a range of about 1°C. If the temperature recorded during a distillation covers a wider range, the resulting liquid cannot be pure. However, the converse is not necessarily true, because sometimes a distillate which boiled at a constant temperature is found to contain small quantities of other materials. In this respect, the boiling point of a liquid is a less satisfactory criterion of purity than the melting point of a solid, while even fractional distillation of a liquid is not so successful at removing impurities as recrystallisation of a solid.

Two other criteria for the purity of liquids are available. One is the refractive index, which can be measured to five significant figures with a modern refractometer and which is very sensitive to impurities. The second is the combination of the gas chromatogram and the mass spectrum. The chromatogram of a pure compound shows only a single peak, and gas chromatography is so sensitive a method that it is possible to detect less than 1 per cent of an impurity even when only about 1 mg of the compound is available. However, an impurity with the same retention time as that of the compound is not revealed on the chromatogram, and to test for this possibility the eluting compound is fed into the mass spectrometer; an impurity is revealed by the resulting spectrum.

2.8
Summary of the use of chromatographic methods

Between them, the various types of chromatography provide methods for (i) the separation of the components of a mixture on a preparative scale,

Chromatographic method	*Separation*	*Identification*	*Purity*
Column	+		
High pressure	+	+	+
Thin-layer		+	+
Paper		+	+
Gas (small scale)		+	+
Gas (large scale)	+		

Type	*Mobile phase*	*Stationary phase*	*Principle of separation*
Column	Liquid	Solid	Adsorption
High pressure liquid	(a) Liquid (b) Liquid	Solid Involatile liquid on solid	Adsorption Partition
Thin-layer	Liquid	Solid or water adsorbed on solid	Adsorption and/or partition depending on conditions
Paper	Liquid	Water adsorbed on paper	Partition
Gas	(a) Gas (b) Gas	Involatile liquid on solid Solid	Partition Adsorption

(ii) the identification of unknown compounds in a mixture, even when only minute quantities (e.g. 1 mg) are available, and (iii) testing the purity of a material.

2.9 Practical work

Column chromatography

Preparation of a column for the separation of dyes

Place a plug of glass wool in the narrow neck of the bottom of a glass tube (about 12 cm long and 1 cm in diameter; Fig. 2.9). Fill the column half-full of water and pour a slurry of alumina and water into it, tapping the tube. The solid will sink to the bottom, giving a uniform column; there must be no cracks or channels in the solid. Liquid is run out of the column until the solid is just covered. Place a small piece of filter paper on top of the solid to prevent it from being disturbed when the solution is added.

Pipette (carefully, so that the solid is not disturbed) 3 cm^3 of an aqueous solution of two dyes (0·1 per cent w/v of malachite green and methylene blue). Elute with water and, when one dye has passed through, elute with ethanol until the second dye has run off. Make sure that the solid is always covered with solvent, and adjust the water pump so that solvent passes through the column at 5–10 cm^3 per minute.

Preparation of a column for the separation of pigments in spinach

(a) *Preparation of a solution of pigments from spinach*

Crush about 20 g of frozen spinach with about 20 cm^3 of methanol. Filter off the methanol and crush the spinach with 50 cm^3 of a mixture (2:1 by volume) of light petroleum (b.p. 60–80°C) and methanol. Filter the mixture, collect the solvents in a flask and transfer them to a separating funnel. Run off the methanol layer, and then pour the petroleum layer into a conical flask. Add about 2 g of anhydrous sodium sulphate and shake for a few minutes to dry the solution.

Decant the solution into a flask and evaporate off the solvent using a hot water bath (cf. Fig. 2.2) until about 5 cm^3 of solution remain. Allow the solution to cool, stoppering the flask to prevent further evaporation of the solvent.

(b) *Preparation of a column of alumina*

Prepare a column of alumina as described above, using dry methylbenzene instead of water. The empty column should be half-filled with methylbenzene and the slurry made with alumina and methylbenzene.

(c) *Separation of the solution from spinach*

Place 2 cm^3 of the solution from spinach on the column of alumina, and develop the column with methylbenzene until the first band, which are carotenes and coloured orange, passes into the flask. Change the receiver and develop the column with a second solvent containing butan-1-ol, ethanol and water in the ratio of 3:1:1 by volume. This separates the chlorophylls, coloured green, from the xanthophylls, coloured pink-brown.

Preparation of a dry-pack chromatography column

Cut a piece of nylon tubing, of about 2 cm diameter, to a length of 20 cm. Seal the end, either with a hot iron or in the edge of a bunsen flame.

Using a small filter funnel, pour fine sand in the bottom to a depth of about 1 cm, then alumina to a depth of about 12 cm, tapping the sides of the tube to ensure even distribution of the solid, and then more fine sand to a depth of about 0.5 cm.

Prick the bottom of the column with a pin (this will prevent rising air bubbles from breaking up the column when solvent is added).

Stand the packed column in a 50 cm^3 measuring cylinder or similar container (Fig. 2.18).

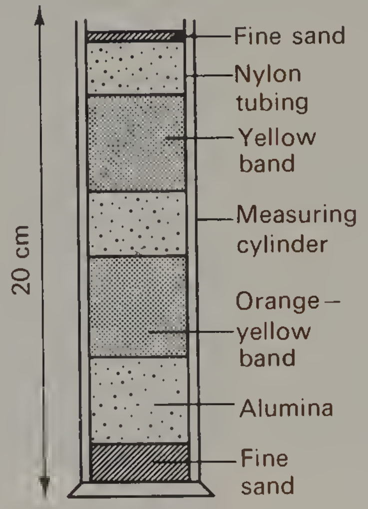


FIG. 2.18. *Dry-pack chromatography*

Separation of the isomeric nitrophenylamines

Dissolve ca. 0.1 g of 2-nitrophenylamine and 4-nitrophenylamine in 2–3 cm^3 of propanone and, with a dropping pipette, run about 1 cm^3 of the solution into the sand. Add propanone, dropwise, on to the sand until the solvent almost reaches the bottom of the column. You will need about 15 cm^3 of solvent.

The nitrophenylamines are toxic. You should wear protective gloves when handling them.

If there is time, slice up the column with a sharp scalpel and put the sliced sections containing the solutes in separate beakers. Add a few cm^3 of propanone to each, filter, collect the solutions and evaporate the solvent to obtain pure samples of solutes. Determine their melting points. The melting points of the 2- and 4-isomers are 72° and 147°C, respectively.

You may wish to compare the efficiency of separation using this method with the older method described above. You will need to make the slurry of alumina in propanone when preparing the column.

Thin-layer chromatography

Preparation of thin-layer plates

Make a slurry of silica gel (20 g) in 1,1,1-trichloroethane (50 cm^3) in a beaker. Dip two microscope glass slides (15 × 2 cm) back-to-back in the slurry and withdraw them slowly but at a constant rate. Separate the slides and, holding them horizontally, wave them gently while the solvent evaporates. It is important to wipe the back and edges of the slide free of solid.

Scratch a line across the slide about 2 cm from the bottom, leaving spaces where the solution to be analysed is to be placed. Apply the solutions using a fine glass capillary tube; the spot should be no wider than 3–4 mm. Place the slide in a beaker containing solvent; the level of the solvent should be just *below* the level of the line drawn across the slide. When the solvent has risen over three-quarters of the way up the slide, remove the slide and allow the solvent to evaporate.

As trichloromethane is used, teachers may prefer to do the next two experiments as class demonstrations.

Separation of pigments from spinach

Prepare a solution of pigments as described on p. 29. Develop the slide with trichloromethane. Note the number of spots developed, measure their R_F values and describe their colours. Place the slide in a beaker in which there are two or three crystals of iodine. Cover the beaker with a watch-glass and note whether any additional spots are developed.

Separation of products from the nitration of phenol

Place 3 spots on a thin-layer plate: (a) a solution of 2-nitrophenol in ethanol, made up by dissolving a few crystals of the solid in 5 drops of ethanol; (b) a solution of 4-nitrophenol in ethanol; (c) a solution of the reaction products from the nitration of phenol (p. 278) (or an artificial mixture of 2- and 4-nitrophenol) in ethanol.

Develop the plate using trichloromethane.

Separation of dyes in black ink

Apply a small spot of black ink (for example, Quink) to a thin-layer plate and develop it using a mixed solvent, butan-1-ol, ethanol and 2M ammonia solution in the ratio of 3:1:1 by volume.

Paper chromatography

Apparatus for paper chromatography (ascending solvent front)

A gas jar can be used as a chromatograph tank (Fig. 2.13). The paper is held in position by a piece of glass rod and clips.

Cut strips of Whatman No. 1 filter paper about 4 cm wide and 30 cm long. Draw a pencil line across the paper near the bottom and apply the solutions with a fine capillary tube (a melting-point tube is useful). To prevent the spot spreading, it should be dried quickly (with a hair dryer, for example).

Pour about 40 cm^3 of solvent in the cylinder and place the end of the paper just below the level of the solvent.

Separation of amino-acids

Make up 100 cm^3 of solvent by shaking together 40 cm^3 of butan-1-ol and 50 cm^3 of water in a separating funnel for about 10 minutes and then adding 10 cm^3 of ethanoic acid. Shake the mixture again. On standing, the mixture will separate into two layers. The top layer should be used as the solvent.

Make up solutions of (a) 0·1 g of glycine in 10 cm^3 of water, (b) 0·1 g of proline in 10 cm^3 of water, (c) a mixture of 0·1 g of glycine and 0·1 g of proline in 10 cm^3 of water.

Place 3 spots, (a), (b), and (c) on the paper, set up the chromatography apparatus and allow the solvent front to move at least three-quarters of the way up the paper. Dry the paper (preferably in an oven at 100°C) and spray it with a solution of ninhydrin (0·2 g of ninhydrin in 99 cm^3 of butan-1-ol and 1 cm^3 of ethanoic acid). If no spray is available (a cheap scent spray is useful), draw the paper through a shallow bath of ninhydrin solution. Dry the paper for about 2 minutes at 100°C.

Glycine and proline react with ninhydrin to form a blue and a yellow compound, respectively. The R_F values of the spots formed in the control experiments (a) and (b) may be compared with those formed by the mixture.

Gas chromatography

Several types of apparatus which can be constructed in a school laboratory are described in *Organic Chemistry Through Experiment* (p. 173–184).

2.10 Further reading

Organic Chemistry Through Experiment. D. J. Waddington and H. S. Finlay (4th ed. 1977). Bell and Hyman Ltd.

Thin-layer chromatography. D. A. Stephens, *School Science Review*, Vol. 48, p. 376 (1967).

Simple chromatographic demonstrations. M. Taylor, *School Science Review*, Vol. 45, p. 75 (1963).

2.11 Videotape

Chromatography (V) I.C.I.

2.12 Questions

1 Summarise the various methods available for the purification of an organic compound and discuss the physico-chemical principles underlying any **two** of these methods. (W(S))

2 When an organic compound is nitrated under certain conditions, the solid mononitro and a small proportion of solid dinitro derivatives are formed. Describe how the mononitro compound is obtained in the pure state by recrystallisation from ethanol explaining the *reasons* for all the techniques employed.

A melting-point determination is carried out after four successive recrystallisations (a), (b), (c) and (d) with the following results:

	m.p.	
(a)	120°	Melting-point *not sharp*
(b)	125°	
(c)	127°	Melting point *sharp*
(d)	127°	

Describe, with the aid of a diagram, how the determination is carried out and explain the significance of the results quoted. (S)

Chapter 3

Determination of the structure of an organic compound

3.1
Introduction

The determination of the structure of an organic compound necessitates the following steps:

1. The purification of the compound. Methods of purifying organic compounds, and of testing their purity, are described in Chapter 2.
2. Determination of which elements are present: qualitative analysis (3.9).
3. Determination of the molecular formula. This can be achieved by combination of quantitative analysis to find the proportions of each element in the compound (3.3) and measurement of the formula weight (3.5). In recent years it has become possible to find the molecular formulae of some compounds directly by mass spectrometry (3.6).
4. Determination of the way in which the atoms are arranged in the molecule. Both chemical methods and physical methods (spectroscopy) are used.

3.2
Qualitative analysis

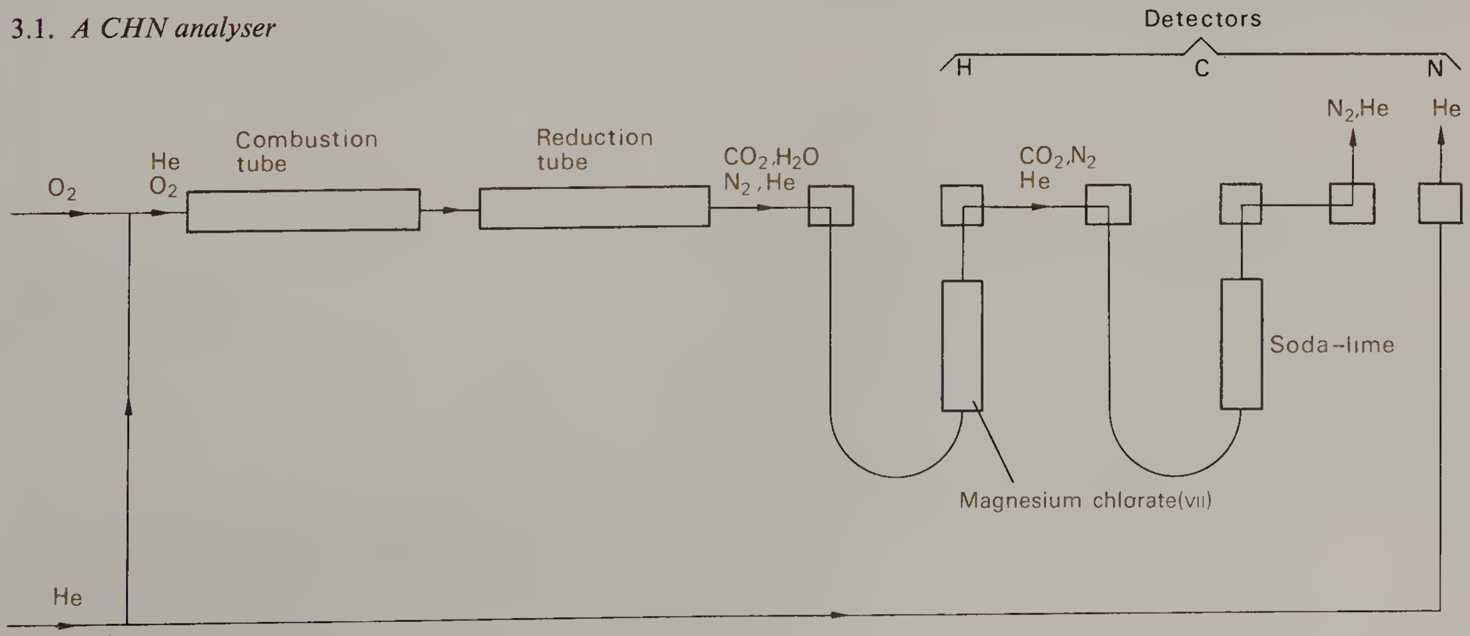
Practical details for the detection of carbon and hydrogen are given in Section 3.9, together with the Lassaigne test for nitrogen, sulphur and the halogens.

3.3
Quantitative analysis

Carbon, hydrogen and nitrogen

A known weight of the compound is heated to a high temperature in an excess of dry oxygen. The compound burns to form carbon dioxide and water. If nitrogen is present in the organic compound, a mixture of nitrogen oxides (and sometimes nitrogen gas) is also produced; the oxides of nitrogen are subsequently reduced by copper to nitrogen. The weights of carbon dioxide, water and nitrogen are then found and the percentage composition of carbon, hydrogen and nitrogen can be calculated.

FIG. 3.1. *A CHN analyser*



Recently, analysers (known as CHN analysers) have been introduced which enable the compound to be analysed automatically. In one of these (Fig. 3.1), the sample (about 1–3 mg) is weighed in a platinum boat placed in a stainless steel **combustion tube** (Fig. 3.2). The tube is heated in a furnace at about 900°C in a stream of dry oxygen and a carrier gas (helium). The compound burns, and the products pass along the tube. They first pass over three materials which are present to remove elements which would otherwise interfere with the analysis for C, H and N: silver removes halogens as involatile silver halides, and silver tungstate(VI) and silver vanadate(V) remove elements such as phosphorus and sulphur with which they combine to form involatile inorganic salts. The gases then pass through a second tube, the **reduction tube**, which is filled with copper and heated to 650°C. This causes the oxides of nitrogen to be reduced to nitrogen and removes oxygen by formation of copper(II) oxide. The gas, which now contains only carbon dioxide, water, nitrogen and helium, then passes through three

FIG. 3.2. *The combustion and reduction tubes used for analysis of carbon, hydrogen and nitrogen. The combustion and reduction tubes are in different furnaces*

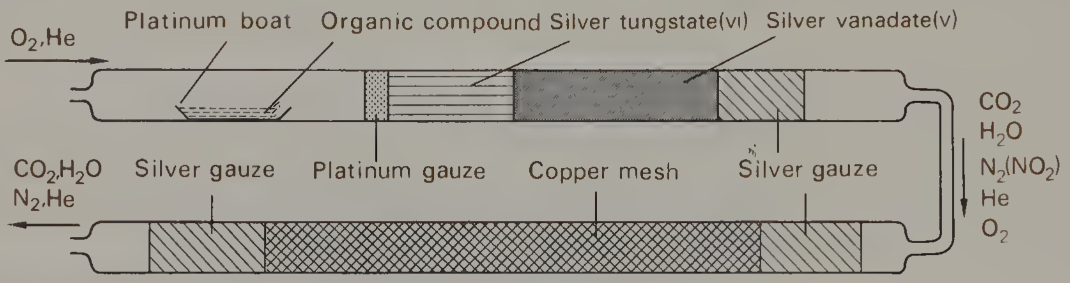
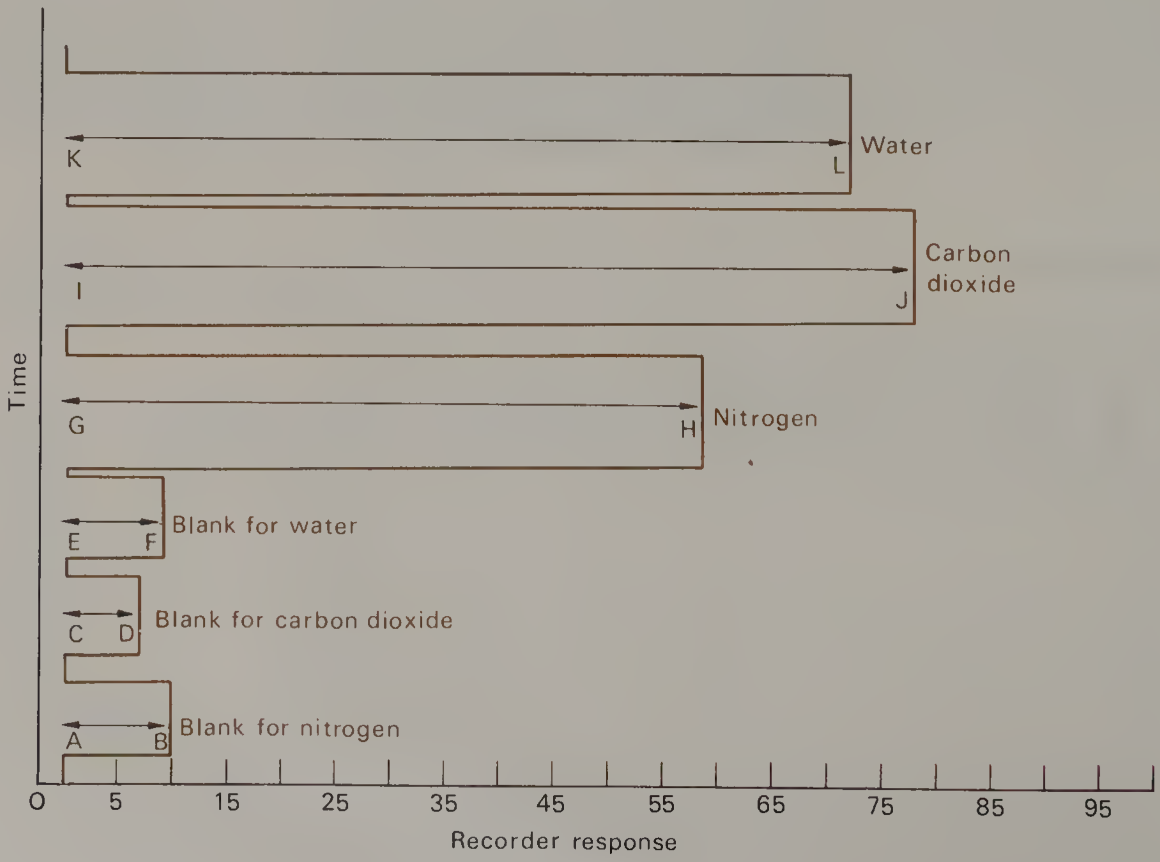


FIG. 3.3. *Analysis of a compound containing C, H, N. The percentage composition of the elements is found from the heights of the peaks, subtracting values for the blanks (values obtained when the boat is empty). The height for carbon dioxide is (IJ – CD)*



katharometers (p. 24); each of these consists of two thermal conductivity cells which contain heated platinum wires, the two wires forming two arms of a balanced Wheatstone bridge circuit. The gases pass through the first cell of the first katharometer, then through a tube of magnesium chlorate(VII) to absorb the water vapour, and then through the second cell of the same katharometer. The conductivity of the gases in the two cells is therefore different, so that the Wheatstone bridge circuit becomes out of balance and a current flows; the current, which is proportional to the weight of water absorbed, is recorded automatically (Fig. 3.3) so that the weight of water, and hence the percentage composition of **hydrogen** in the compound, can be calculated. The cells of the second katharometer are separated by a tube of soda-lime which absorbs the carbon dioxide; thus, the percentage of **carbon** can be calculated from the Wheatstone bridge current in the same way as that of hydrogen. The remaining mixture of nitrogen and helium passes into one cell of the third katharometer while a second stream of helium, at the same flow-rate as in the mixture of gases, passes through the second cell. The current in the Wheatstone bridge circuit is proportional to the concentration of nitrogen, so that the percentage composition of **nitrogen** can be calculated.

Nitrogen by Kjeldhal's method

Another method for determining the percentage composition of nitrogen in an organic compound is to boil a weighed sample with concentrated sulphuric acid and anhydrous potassium sulphate (to raise the boiling point of the acid). A catalyst (for example, mercury to which a little selenium is added) is sometimes used. The resulting solution of ammonium sulphate is diluted, excess of sodium hydroxide is added and the liberated ammonia is distilled into excess of standard acid. The acid is then titrated against standard sodium hydroxide to determine the amount of acid originally neutralised by ammonia.

Halogens by Carius's method

A weighed quantity of the compound is heated strongly with concentrated nitric acid and solid silver nitrate in a sealed tube for some hours. The tube is cooled and then broken under water. The silver halide is filtered, washed, dried and weighed.

3.4
Calculation of the empirical formula

Once the percentage composition of each element is known, the ratio of the numbers of atoms of each element present in the compound can be calculated. This is the **empirical formula**.

The method is to divide the percentage composition of each element by its relative atomic mass and to factorise the resulting numbers so as to obtain simple whole numbers. For example, a compound *X*, a white solid, was found by analysis to contain 23·30 per cent carbon, 4·85 per cent hydrogen and 40·78 per cent nitrogen. It was known to contain no other elements except oxygen, so that the composition of oxygen was

$$100 - (23{\cdot}30 + 4{\cdot}85 + 40{\cdot}78) = 31{\cdot}07 \text{ per cent.}$$

Then:

Element	% *Composition*	*Relative atomic mass*	*Atomic ratio*	*Simplest atomic ratio*
Carbon	23·30	12	1·94	2
Hydrogen	4·85	1	4·85	5
Nitrogen	40·78	14	2·91	3
Oxygen	31·07	16	1·94	2

The empirical formula of X is $C_2H_5N_3O_2$. To determine the molecular formula, the relative molecular mass must be found.

3.5 Determination of a relative molecular mass

The determination of relative molecular masses of compounds is described in detail in texts on Physical Chemistry. Those of **gases** are generally determined by the limiting density method, using a gas density balance, while those for **volatile liquids and solids** are found by an adaptation of the traditional Victor Meyer's method in which the volume of vapour from a known weight of compound is determined. The relative molecular mass of an **involatile liquid or solid** is often found from the depression of the freezing point of a solvent.

In many cases, the relative molecular mass can be found quickly and with a very high degree of precision by **mass spectrometry**. The vapour of the substance, at a low pressure (10^{-5}–10^{-6} mm Hg), is bombarded by a stream of electrons. This causes the loss of one electron from a molecule of the substance, giving the **molecular ion** (sometimes called the **parent ion**):

$$M + e \rightarrow M^{+\cdot} + 2e$$

These positive ions are accelerated in an electrostatic field and pass through a slit in the negatively charged plate into an electrostatic analyser. This causes them to be deflected by amounts depending on their kinetic energies, and only one component of the beam of ions, with a well defined kinetic energy, can emerge from the slit at the other end of the analyser. This component then enters a magnetic field in which it is again deflected, and the strength of the field is altered until the ions impinge on a detector; this generates an electrical signal which is shown on an oscilloscope and/or recorded on photographic paper.

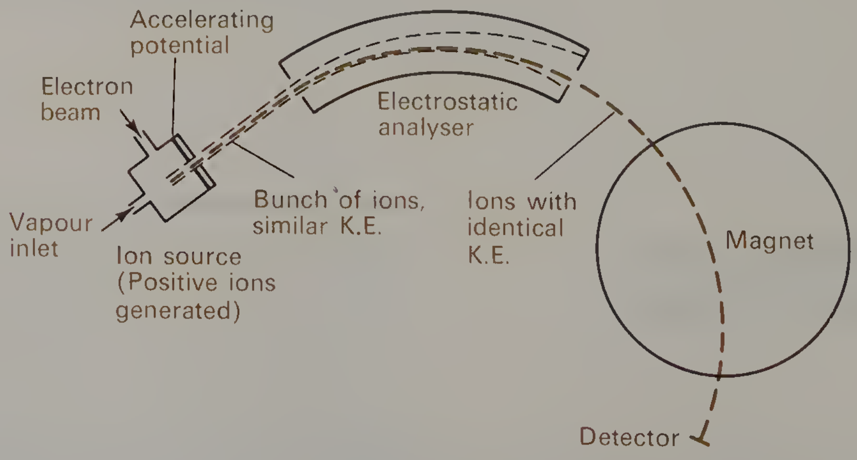


FIG. 3.4. *A mass spectrometer*

The radius of the deflection, r, depends upon the strength of the magnetic field, B, and the kinetic energy of the ions; and the latter depends on the accelerating voltage, V, and the relative molecular mass of $M^{+\cdot}$. Therefore, by finding the value of B for selected values of r and V, the relative molecular mass can be calculated.

With modern spectrometers, the relative molecular mass can be measured to the fourth decimal place.

For some compounds, the molecular ion decomposes so rapidly into smaller particles (p. 38) that it cannot be detected. The relative molecular mass cannot be determined by mass spectrometry for these compounds, although important information about their structures can still be obtained from identification of the fragments (3.7).

3.6
Determination of the molecular formula

The molecular formula of a compound—the **actual** number of each kind of atom in the molecule—can be determined from the empirical formula and the relative molecular mass.

For example, the empirical formula of the compound *X* in Section 3.4 was found to be $C_2H_5N_3O_2$. The formula weight (determined, for example, by freezing-point depression) is 103. In this case, therefore, the empirical formula is also the molecular formula. On the other hand, if the relative molecular mass had been found to be 206, the molecular formula would have been $C_4H_{10}N_6O_4$.

If a molecular ion is formed in the mass spectrometer, the molecular formula can be found without determination of the empirical formula or any other study of the compound. Thus, the molecular ion of the compound *X* was measured as 103·0382. Its molecular formula must therefore be $C_2H_5N_3O_2$ since no other possible combination of elements corresponds to this mass. (Table 3.1 lists compounds of formula weights between 103·0170 and 103·0494, based on $^{12}C = 12{\cdot}000000$; see Appendix VI.)

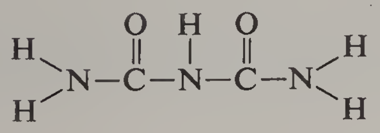
Table 3.1. Organic compounds of relative molecular mass ca. 103

MASS	NUMBER OF ATOMS IN THE MOLECULE			
	C	H	N	O
103·0170	5	1	3	–
103·0269	3	5	1	3
103·0382	**2**	**5**	**3**	**2**
103·0427	7	5	1	–
103·0494	1	5	5	1

3.7
Determination of the structural formula

The structural formula shows us which atoms are joined to which in the molecule. Strictly speaking, a structural formula requires a three-dimensional representation, but planar, two-dimensional representations are usually more convenient (1.2).

In elucidating the structural formula, it is usual to consider the possible structures based on the molecular formula. For example, the compound *X* has the molecular formula $C_2H_5N_3O_2$; a possible structural formula is:



In order to confirm this structure, we examine both the physical and the chemical properties of the compound. By studying the chemical reactions, the presence or absence of the functional groups can be determined. For example, for X, we would test for the presence of the groups $-NH_2$, $-NH-$, and $C=O$. There is also a special chemical test for the $-NH-$ group which is adjacent to $C=O$ (p. 229).

However, in more complex molecules, physical methods for the determination of structure are always used as well, in particular three spectroscopic techniques: mass spectroscopy, infrared spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

Mass spectroscopy

When molecules, M, are bombarded by electrons in the mass spectrometer, molecular ions, $M^{+\cdot}$, are usually formed (p. 36). A proportion of these fragment into smaller species, one of which carries a positive charge and the other of which is a neutral radical:

$$M^{+\cdot} \rightarrow X^{+} + Y$$

These fragments can in turn break down into smaller ones. Each of the positively charged fragments is recorded by the spectrometer, so that its mass can be determined. The resulting array of detected ions is described as the **fragmentation pattern**.

The abundances of the different positively charged fragments vary widely. For convenience in interpreting the spectrum, the relative abundances of the fragments are plotted against their masses, the most abundant ion being given an arbitrary value of 100 units (the **base peak**); the plot is known as a **stick diagram**. The molecular ion is rarely the most abundant one; indeed, with some compounds, the molecular ion is not detected and the formula weight cannot then be determined (3.5).

The fragmentation pattern of a compound depends on its structure. The presence of particular groupings is associated with specific fragmentation patterns, and so the determination of the fragmentation pattern for a compound of unknown structure can often enable the structure to be deduced.

For example, the stick diagram for hexadecane is shown in Fig. 3.5. The molecular ion is at 226, and the principal fragments are at 29, 43, 57, 71, 85, 99, 113, 127. This difference of 14 units between fragments is characteristic of the behaviour of linear alkanes. It occurs because the molecular ion can break in two ways: by losing a methyl radical, $\cdot CH_3$, or an ethyl radical, $\cdot CH_2CH_3$. Each new ion can then lose molecules of ethene successively.

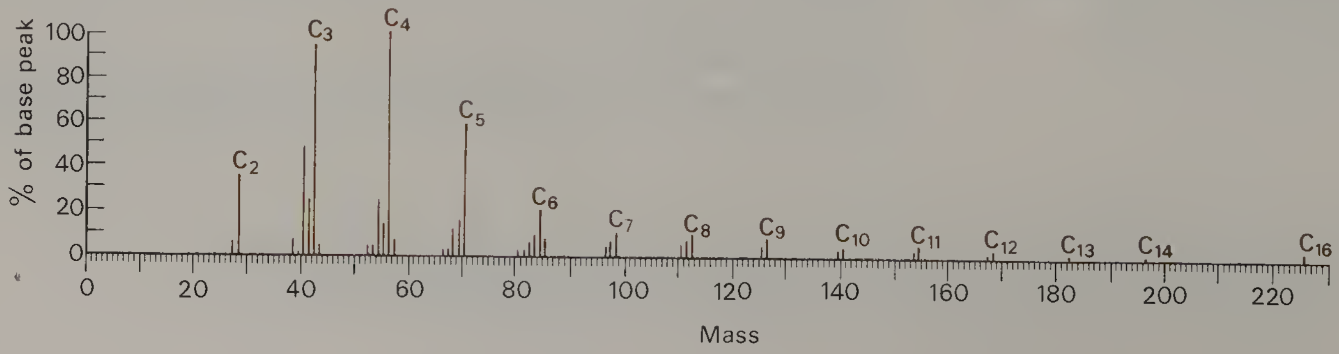
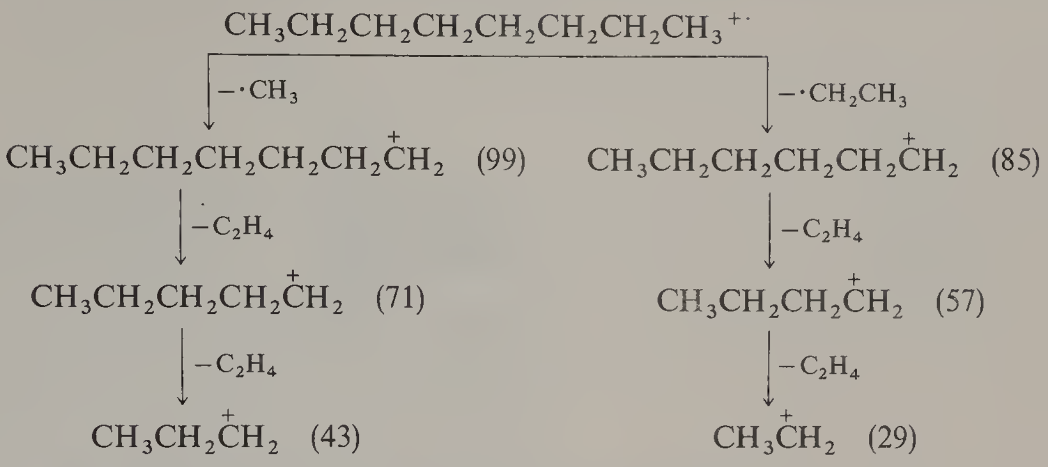


FIG. 3.5. *The mass spectrum of hexadecane (formula weight 226)*

For example, fragmentation of the molecular ion from octane occurs as follows:



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3{}^{+\cdot}$$

$$\xrightarrow{-\cdot CH_3} CH_3CH_2CH_2CH_2CH_2CH_2\overset{+}{C}H_2\ (99) \xrightarrow{-C_2H_4} CH_3CH_2CH_2CH_2\overset{+}{C}H_2\ (71) \xrightarrow{-C_2H_4} CH_3CH_2\overset{+}{C}H_2\ (43)$$

$$\xrightarrow{-\cdot CH_2CH_3} CH_3CH_2CH_2CH_2CH_2\overset{+}{C}H_2\ (85) \xrightarrow{-C_2H_4} CH_3CH_2CH_2\overset{+}{C}H_2\ (57) \xrightarrow{-C_2H_4} CH_3\overset{+}{C}H_2\ (29)$$

If there had been branching in the carbon chain, fragmentation would have occurred preferentially at the branch [as a more stable, secondary carbonium ion is formed (p. 67)]. For example, 2-methylheptane has a molecular ion at 114 and a significant fragment is at 99 (Fig. 3.7).

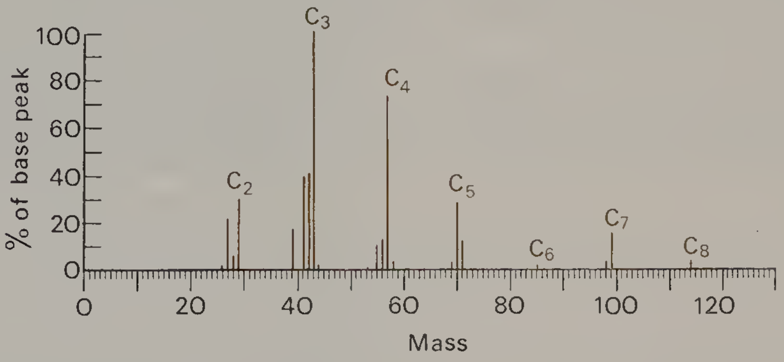
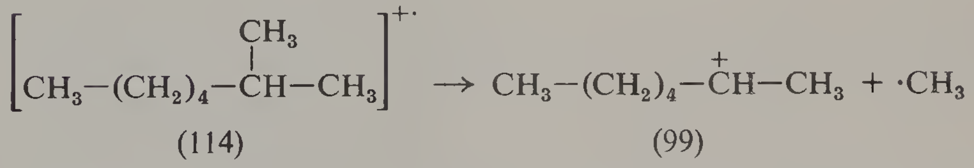


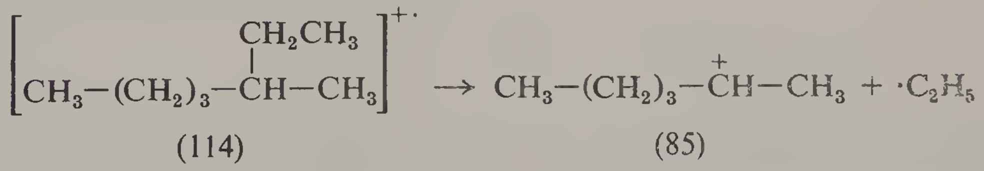
FIG. 3.6. *The mass spectrum of 2-methylheptane (formula weight 114)*



$$\left[CH_3{-}(CH_2)_4{-}\overset{\overset{\textstyle CH_3}{|}}{C}H{-}CH_3\right]^{+\cdot} \rightarrow CH_3{-}(CH_2)_4{-}\overset{+}{C}H{-}CH_3 + \cdot CH_3$$

(114) (99)

In contrast, for the isomer, 2-ethylhexane, there is a major fragment at 85:

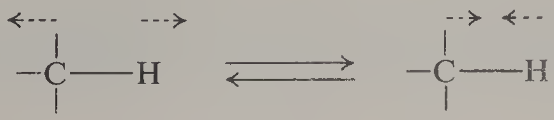


$$\left[CH_3{-}(CH_2)_3{-}\overset{\overset{\textstyle CH_2CH_3}{|}}{C}H{-}CH_3\right]^{+\cdot} \rightarrow CH_3{-}(CH_2)_3{-}\overset{+}{C}H{-}CH_3 + \cdot C_2H_5$$

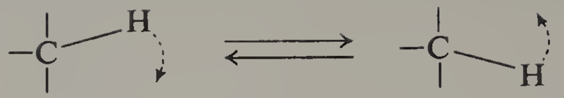
(114) (85)

Infrared spectroscopy

The bonds in organic compounds undergo various types of vibration. For example, a C—H bond can stretch:



or bend:



For a particular bond, only a particular set of vibrational frequencies is possible. Suppose a bond is vibrating at frequency ν_1, and its next available higher frequency is ν_2; then, if electromagnetic radiation with frequency $(\nu_2 - \nu_1)$ is incident on the compound containing this bond, some of the radiation is absorbed and some of the bonds then vibrate at the higher frequency. The appropriate radiation to excite the bonds in organic compounds in this way corresponds to the infrared region of the spectrum, that is, to frequencies in the region of 10^{13} Hz (1 Hz = 1 cycle per second). (The frequency is usually quoted in reciprocal cm (cm^{-1}); a frequency of ν Hz corresponds to $1/\lambda$ cm^{-1} where λ is the wavelength of the radiation and is related to ν by the expression $\lambda\nu = c$, the velocity of light (3×10^{10} cm s^{-1}). For example, a frequency of 6×10^{13} Hz corresponds to 2000 cm^{-1} or a wavelength of 5×10^{-4} cm.)

The excitation frequency for a particular bond is, to a first approximation, independent of the other bonds in the compound. Therefore, determination of the frequencies in the infrared region which are absorbed by a compound gives information about the types of bond which are present.

The apparatus for this purpose—an **infrared spectrophotometer**—consists of a cell (usually made of rock salt as glass absorbs infrared radiation) which contains the organic compound, a source of infrared radiation such as a Nernst glower (a rod made of metal oxides which is heated at 1500°C), a means of separating the infrared beam into its constituent frequencies (a prism or diffraction grating) and a detector for infrared light (a sensitive thermocouple). The infrared light is passed through the separator and a particular emergent frequency then passes through the cell; behind the cell is the detector. By rotating the prism or grating, all the infrared frequencies are passed in turn through the cell and, by coupling the detector to a pen recorder, a record of the behaviour of the compound towards each frequency—the **infrared spectrum**—is obtained.

The characteristic frequencies for various types of bonds in organic compounds are in Table 3.2. Thus, a compound which is found to absorb in the region 1700–1750 cm^{-1} can be deduced to contain the carbonyl group, C=O (for example, propanone, the infrared spectrum of which is in Fig. 3.7).

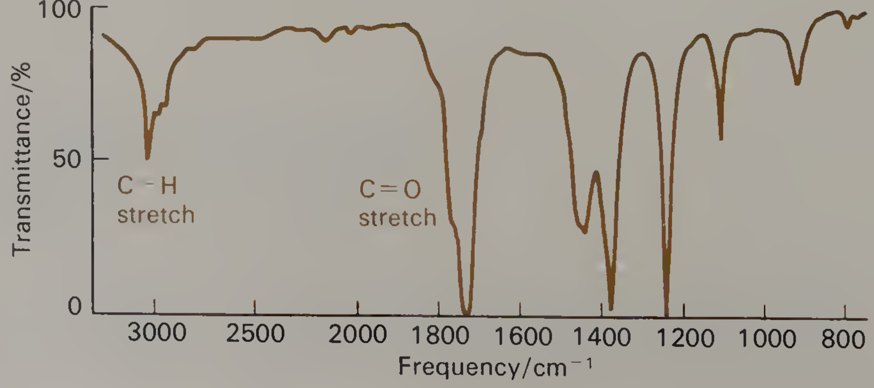


FIG. 3.7. *The infrared spectrum of propanone*

Table 3.2. Characteristic infrared frequencies for organic bonds

BOND	COMPOUND	FREQUENCY/CM^{-1}
C—H	Alkane	2850–2960
C—H	Alkene	3075–3095
C—H	Alkyne	3300
C—O	Alcohol, ether	1050–1200
C=O	Aldehyde, ketone, carboxylic acid	1700–1750
O—H	Alcohol, phenol	3590–3650
N—H	Amine	3300–3500

Nuclear magnetic resonance spectroscopy

The atoms of some of the elements have a nuclear structure which causes them to behave like small magnets. In organic compounds, the commonest of these elements is hydrogen; the hydrogen nucleus—the proton—when placed in a magnetic field, aligns itself so that its magnetic moment (sometimes referred to as its 'spin') is either in the same direction as the applied field or in the opposite direction.

The energies of these two possible states differ. The protons whose spins are aligned *with* the field have a lower energy than those aligned *against* the field; the energy difference, ΔE, is proportional to the strength of the field, B:

$$\Delta E = \frac{\gamma h B}{2\pi}$$

where γ is a constant for a particular nucleus and h is Planck's constant.

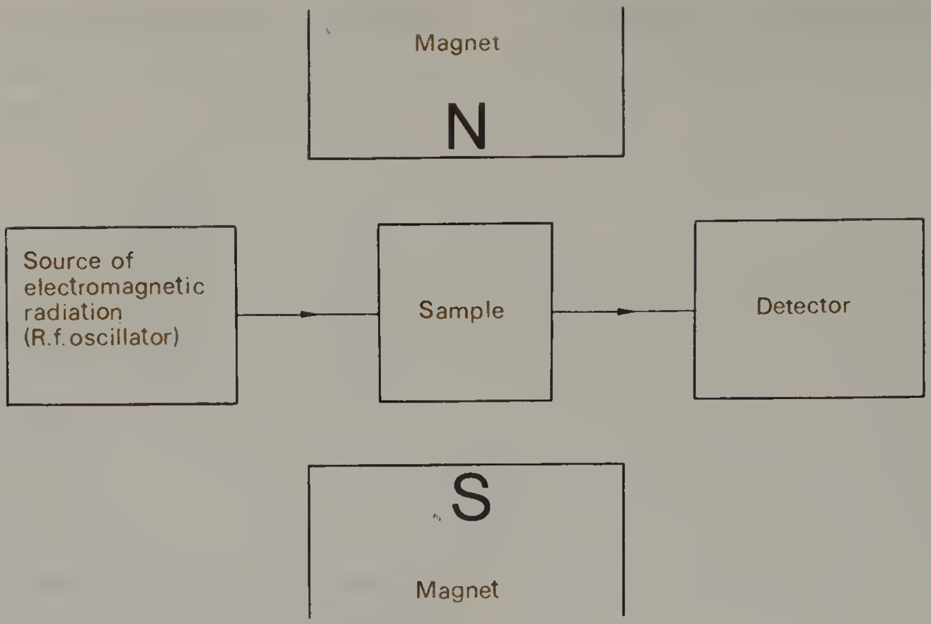
If electromagnetic radiation is incident on the protons, then, providing that its frequency ν is such that its energy, $h\nu$, is exactly equal to the energy difference, ΔE, for the proton's two orientations, some of the radiation will be absorbed and some of the protons in the orientation of lower energy will 'flip' over to the orientation of higher energy; the total energy of the system remains constant. Thus, the condition for absorption of radiation (the **'resonance' condition**) is

$$\nu = \frac{\gamma B}{2\pi}$$

This phenomenon can be studied with a **nuclear magnetic resonance spectrometer**, shown schematically in Fig. 3.8. A sample of the compound containing hydrogen atoms is placed in a cell between the pole pieces of a magnet and is irradiated; a detector records whether a particular frequency of the radiation is absorbed or not. For the proton, the size of γ is such that, with a magnetic field of about 1·5 T, the frequency absorbed is 60 MHz, which is within the range of radio waves; it is usual to keep this frequency constant and to vary the magnetic field (e.g. by varying the current in an electromagnet) while searching for absorption of the radiation.

So far, we have considered only the resonance condition for a proton which experiences the applied field. What makes NMR spectroscopy so

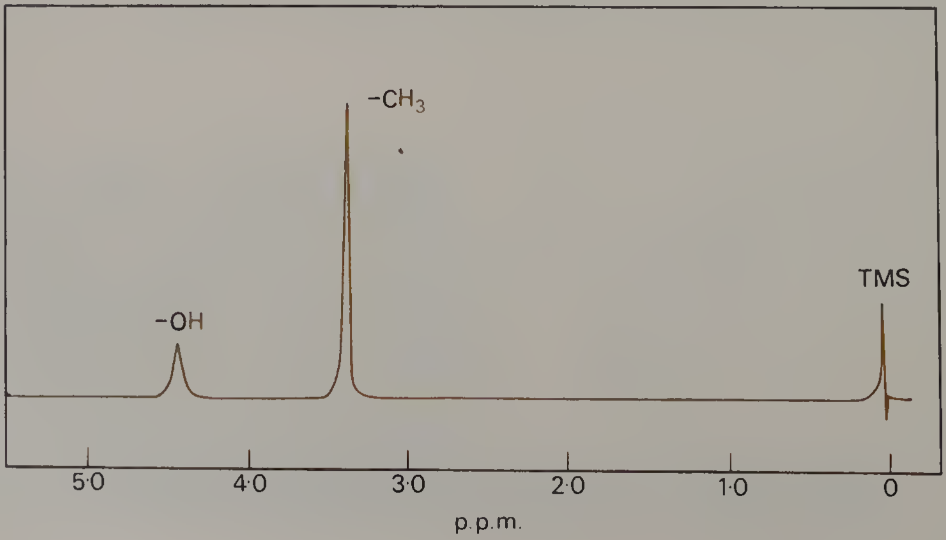
FIG. 3.8. *An NMR spectrometer*



useful in organic chemistry is the fact that, in any compound containing hydrogen, the magnetic field to which a particular proton is subjected is not the same as the field which is applied. This is because the applied field induces a circulatory motion of the electrons in the bond to the hydrogen atom and this motion in turn produces a small magnetic field which opposes the applied field. Thus, the magnetic field experienced by the proton is slightly *less* than the applied field. Consequently, for the resonance condition to be fulfilled, the applied field must be increased slightly.

The magnetic field induced at the proton by the bonding electrons decreases as the electrons are moved away from the proton. Now, the average position of the pair of electrons in a bond relative to each nucleus depends on the nature of the atoms concerned (4.8); for example, the electrons are relatively further from the proton in the O—H bond than in the C—H bond. Therefore, the applied magnetic field at which the resonance condition is met is smaller for a proton in an O—H bond than for one in a C—H bond. This is shown in the NMR spectrum of methanol (Fig. 3.9); the area under

FIG. 3.9. *The NMR spectrum of methanol. Methanol has been dissolved in tetrachloromethane and TMS added as an internal reference standard*



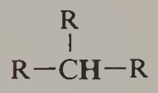
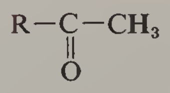
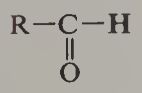
the peak corresponding to resonance for the C—H protons is three-times that for the O—H proton since there are three times as many protons in the former environment.

Since the NMR characteristics of protons in a wide variety of environments are known, the measurement of the NMR spectrum of a compound of unknown structure reveals the bonds present between hydrogen and other groups and also, from their relative peak areas, the relative numbers of these bonds. It is convenient to measure the NMR spectrum relative to a standard; tetramethylsilane (TMS), $(CH_3)_4Si$, is usually chosen since, having only one type of proton, it gives only one absorption peak and so causes minimum interference with the peaks from the unknown compound. Suppose that, for a given frequency, the protons in tetramethylsilane come into resonance at an applied field B_1 and the proton in another bond comes into resonance at an applied field B_2. Then the **chemical shift**, δ, for the latter proton is defined as

$$\delta = \frac{B_1 - B_2}{B_1}$$

To obtain simple numbers for δ, the value is usually multiplied by 10^6 and then expressed as parts per million (p.p.m.). Since chemical shifts are ratios, they are independent of the frequency used for the NMR measurements and therefore provide a common scale. Values for protons in environments which occur commonly in organic compounds are in Table 3.3.

Table 3.3. Chemical shifts for protons

TYPE OF PROTON	CHEMICAL SHIFT/P.P.M.
$R-CH_3$	0·9
$R-CH_2-R$	1·3
 $R-\overset{R}{\overset{\vert}{C}}H-R$	1·5
 $R-\underset{O}{\underset{\Vert}{C}}-CH_3$	2·1
$R-O-CH_3$	3·3
$R_2C=CH_2$	4·7
$R-O-H$	1–5
 $R-\underset{O}{\underset{\Vert}{C}}-H$	9·7

Still further information can be obtained from the NMR spectrum by increasing the resolution of the spectrometer. Figures 3.10 and 3.11 show the spectrum of bromoethane. The former spectrum has two peaks, corresponding to the CH_2 and CH_3 protons (relative areas 2:3). In the latter spectrum, measured at higher resolution, the CH_2 and CH_3 peaks are split into four lines and three lines, respectively.

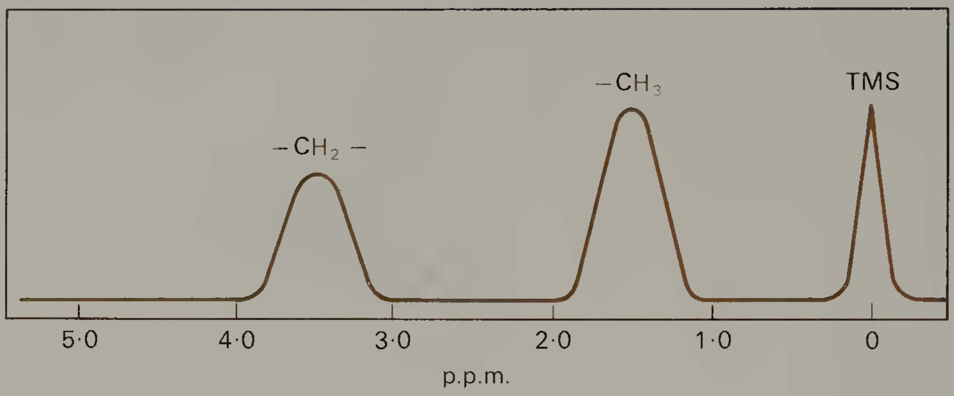


FIG. 3.10. *The NMR spectrum of bromoethane at low resolution. Bromoethane has been dissolved in tetrachloromethane and TMS added as an internal reference standard*

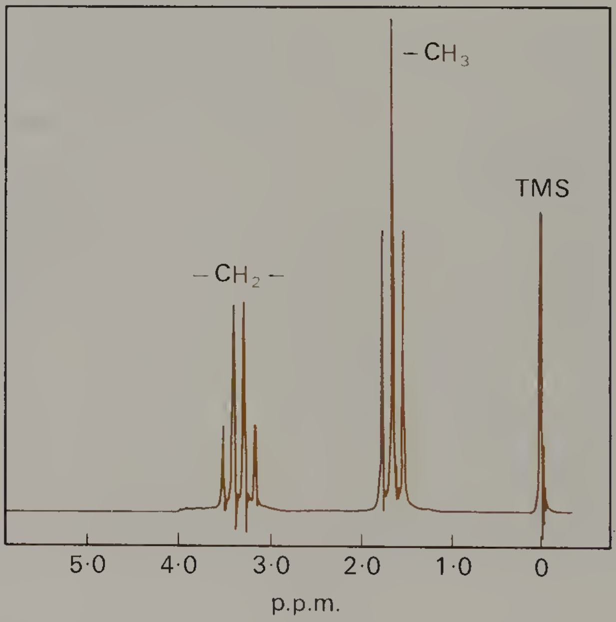
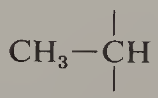


FIG. 3.11. *The NMR spectrum of bromoethane at high resolution showing spin-spin coupling. Bromoethane was dissolved in tetrachloromethane and TMS added as an internal reference standard*

The splitting is the result of **spin-spin coupling** and has the following basis. Consider the conditions for resonance of the protons in the methyl group in a compound of the type

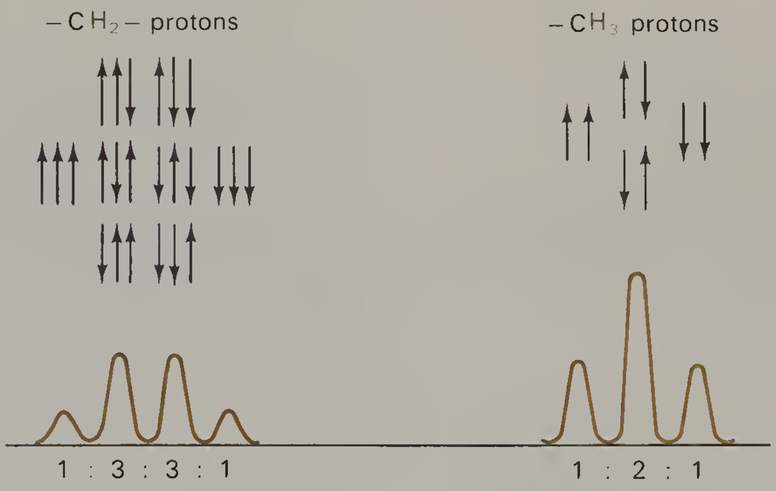


$$CH_3{-}\overset{|}{\underset{|}{C}}H$$

The magnetic moment of the single proton on the adjacent carbon atom can be aligned either with or against the applied magnetic field. For the former orientation, the protons in the methyl group experience a magnetic field slightly *greater* than the applied field, and for the latter orientation they experience a magnetic field correspondingly slightly *less*. Consequently, there are *two* values of the applied field at which the resonance condition for the methyl protons is met; one is slightly less than would be the case in the absence of the single adjacent proton, and the other is correspondingly slightly greater. Thus, the methyl group appears as a **doublet**.

Consider now the condition for resonance of the single proton. The magnetic moments of the protons in the methyl group can all be aligned with the applied field; two can be aligned with, and one against, the applied field; one can be aligned with and two against, the applied field; and all three can be aligned against the applied field. There are therefore four possible magnetic arrangements for the methyl protons, and so there are four values of the applied field at which resonance occurs; the CH group appears as a **quartet**. However, the resulting four peaks in the spectrum do not have equal areas. If we designate as → or ← a proton whose magnetic moment is aligned respectively with or against the applied field, then we see that there are three times as many ways in which two are aligned with the field and one against it (→→←, →←→, ←→→) or the converse (←←→, ←→←, →←←) as there are ways in which all three are aligned either with (→→→) or against (←←←) the field. Therefore the four peaks have relative areas 1:3:3:1. Likewise, it can be shown that two protons interact to give a 1:2:1 **triplet** pattern. Thus, in the spectrum of bromoethane, the quartet corresponding to the CH_2 group results from coupling with the three methyl protons, and the triplet corresponding to the CH_3 group results from coupling with the two CH_2 protons (Fig. 3.12).

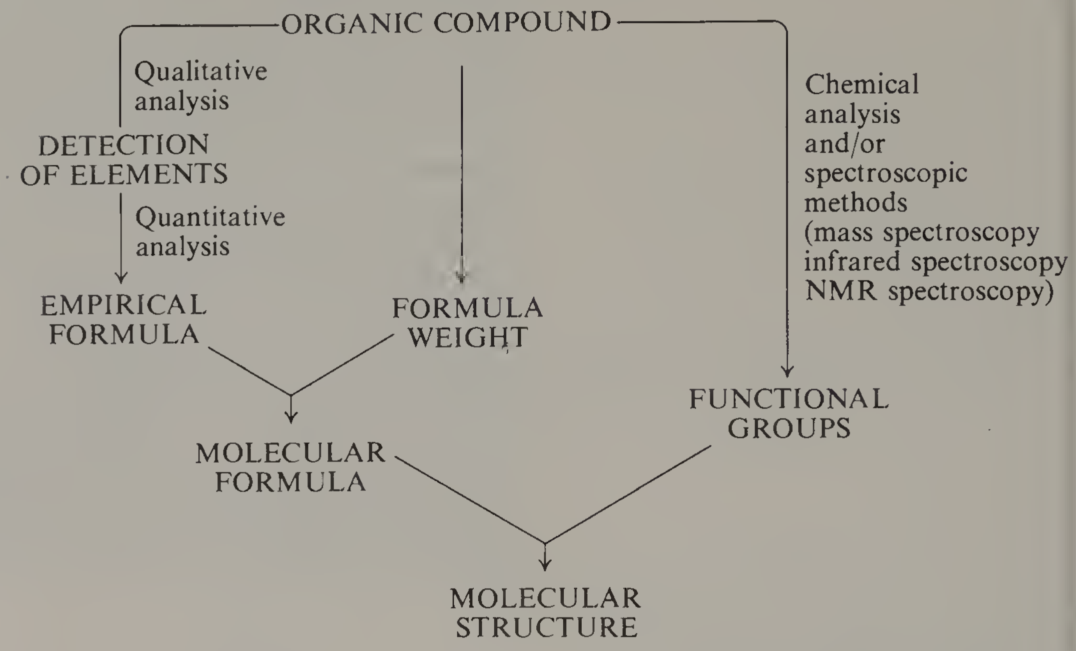
FIG. 3.12. *Possible orientations of nuclear spins of the protons in an ethyl, CH_3–CH_2, group and the expected spin-spin coupling*



In summary, while the chemical shift of a proton gives information about the nature of the group containing that proton, the spin-spin coupling pattern gives information about other protons in adjacent groups.

Recently, ^{13}C NMR spectroscopy has become important. Although the commonest isotope of carbon, ^{12}C, does not possess a magnetic moment, ^{13}C does so, just like the proton. The γ-value for ^{13}C is about one-quarter that for ^{1}H, so that, for the same magnetic field, the resonance frequency for ^{13}C is about a quarter that for ^{1}H (e.g. 15 MHz and 60 MHz, respectively, in a field of about 1·5 T). This also means that the sensitivity is much smaller (about 1/64th) for ^{13}C compared with ^{1}H. Moreover, since the abundance of ^{13}C in naturally occurring carbon compounds is only 1·1 per cent, resonances in a ^{13}C spectrum are only about one six-thousandth as intense as those in a ^{1}H spectrum. Consequently, special measures must be adopted to record a ^{13}C NMR spectrum. One way is to scan the spectrum repeatedly, accumulating the resonances in a computer, but this means that days or even weeks are necessary to obtain a reasonable spectrum. A much better method is to use an electronic pulse which excites all the ^{13}C nuclei in a molecule simultaneously; a computer then accomplishes a *Fourier transform* analysis of the electronic output, and a complete, though still very weak, spectrum is obtained in about a second. Repeated pulses, with computer accumulation, then give a reasonable spectrum in minutes or, at the most, hours. ^{13}C spectra display chemical shifts and spin-spin coupling (normally with protons) just as do ^{1}H spectra.

3.8
Summary



3.9
Practical work: Qualitative analysis of an organic compound

Carbon and hydrogen

Heat a mixture of the compound and an excess of dried copper(II) oxide in a pyrex test-tube. Pass the gases evolved into a solution of lime-water (Fig. 3.13). If the solution turns milky, **carbon** is present in the compound.

If a liquid forms on the side of the tube, test it with anhydrous copper(II) sulphate. If it turns blue, the liquid is probably water and the compound contains **hydrogen**.

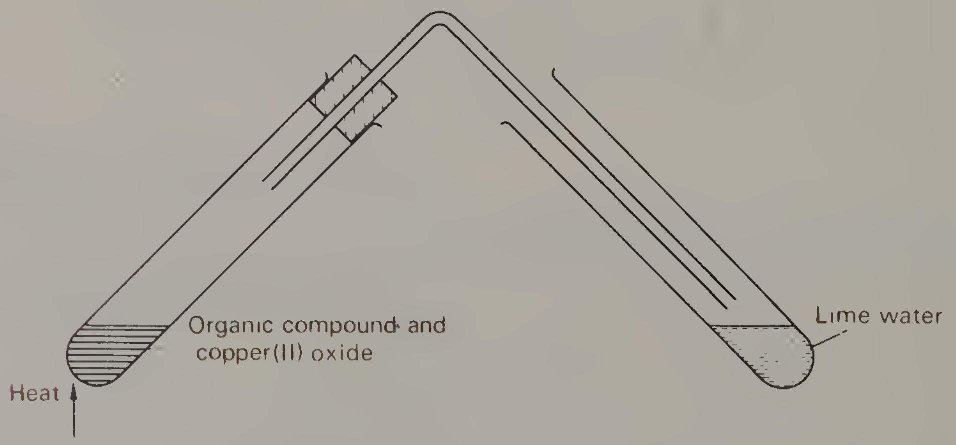


FIG. 3.13. *Testing for carbon and hydrogen in an unknown compound*

Lassaigne sodium test for nitrogen, halogens and sulphur

Take great care and wear safety glasses.

Place about 0·2 g of the compound in an ignition tube together with a small pellet of sodium. Hold the tube in an almost horizontal position and warm it gently so that the metal becomes molten. Then hold the tube vertically and heat it strongly. Plunge the tube into a small beaker containing about 3 cm^3 of water. Boil the mixture for a few minutes, filter it and divide the filtrate into three parts.

Some of the elements in the organic compounds have now been converted into inorganic salts of sodium. If nitrogen is present in the compound, it will have formed cyanide ions, the halogens will have formed halide ions and sulphur will have formed sulphide ions.

Sulphur

To one part of the filtrate, add a drop of an aqueous solution of disodium pentacyanonitrosylferrate(III) ('sodium nitroprusside'). A purple colour indicates the presence of **sulphur**.

Nitrogen

To the second part of the filtrate, add an equal volume of a fresh solution of iron(II) sulphate. The mixture now contains a green precipitate of iron(II) hydroxide. Boil the mixture for a few minutes, then add 2 or 3 drops of iron(III) chloride solution and acidify the mixture with dilute hydrochloric acid. Centrifuge (or filter) the mixture. A residue of Prussian blue indicates the presence of **nitrogen** in the compound:

$$Fe^{2+} \xrightarrow{6\,CN^-} Fe(CN)_6{}^{4}$$

$$4Fe^{3+} + 3Fe(CN)_6{}^{4-} \longrightarrow \underset{\text{Prussian Blue}}{Fe_4[Fe(CN)_6]_3}$$

Halogens

(a) *If nitrogen is present.* Cyanide ions interfere with the test for halide ions and must therefore be removed. If it has already been shown that nitrogen is present, acidify the third part of the filtrate with dilute nitric acid and evaporate it to about a quarter of its original volume. Add a few drops of silver nitrate solution.

A white precipitate which is soluble in an excess of dilute ammonia solution indicates the presence of **chlorine** in the compound:

$$Ag^+ \xrightarrow{Cl^-} AgCl\downarrow \xrightarrow{2NH_3} Ag(NH_3)_2{}^+ + Cl^-$$

A pale yellow precipitate which is soluble in an excess of concentrated ammonia solution indicates the presence of **bromine**.

A yellow precipitate which is insoluble in an excess of concentrated ammonia solution indicates the presence of **iodine**.

(b) *If nitrogen is not present.* Acidify the third portion of the filtrate from the sodium fusion with dilute nitric acid, add a few drops of silver nitrate solution and proceed as in (a).

3.10
Further reading

The Physics of Chemical Structure. R. J. Taylor (1968). Unilever Educational Booklet. Advanced Series.
Investigation of Molecular Structure. B. C. Gilbert (1976). Bell and Hyman Ltd.
Organic Chemistry: a problem solving approach. M. J. Tomlinson and M.C.V. Cane (1977). Bell and Hyman Ltd.
Molecular Identification and Bonding (1980). Open University. S246 4–6

3.11
Film and Videotape

Analysis by Mass (F) A.E.I.-G.E.C. Film. Guild Organisation Ltd.
Spectroscopy (V) Open University. 246/05V

3.12 Questions

1 A compound **P** contains 85·7 per cent carbon and 14·3 per cent hydrogen. After reaction with trioxygen and then with water, two of the compounds formed, **Q** and **R**, were distilled and purified. Both compounds absorbed infrared radiation at about 1700 cm^{-1}. Mass spectra were obtained for **Q** and **R**:

Q	Mass	29	44	43	42
	Abundance (%)	100	89	50	15
R	Mass	43	58	15	
	Abundance (%)	100	33	30	

What are **P**, **Q** and **R**? Describe carefully how you elucidated the structures of **Q** and **R** from the evidence given.

2 Two hydrocarbons, **X** and **Y**, contain 82·8 per cent carbon and 17·2 per cent hydrogen. They have the following mass spectra:

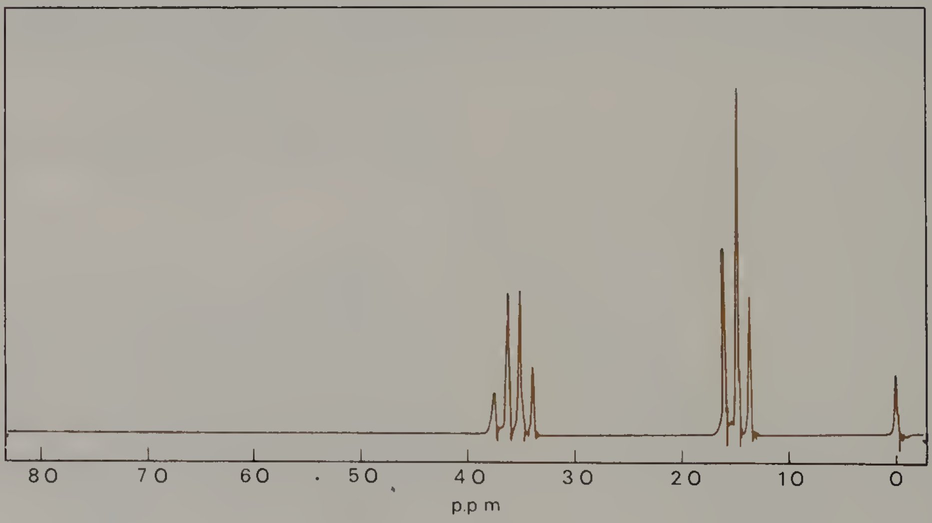
X	Mass	43	41	42	27	15	29	57
	Abundance (%)	100	39	32	17	7	6	3
Y	Mass	43	29	27	28	41	39	42
	Abundance (%)	100	43	39	32	29	14	12

Write down the structural formulae for **X** and **Y**, giving reasons for your choice.

3 Compound **A** contains 22·2 per cent carbon, 4·6 per cent hydrogen and 73·2 per cent bromine. The mass spectrum for compound **A** was:

Mass	108	110	29	79	81
Abundance (%)	100	97	51	4	4

The following NMR spectrum (with TMS as standard) was obtained for **A**:



How do you account for the physical evidence given?

4 The chemical shift, δ, for the CH_2 protons for the following compounds are:

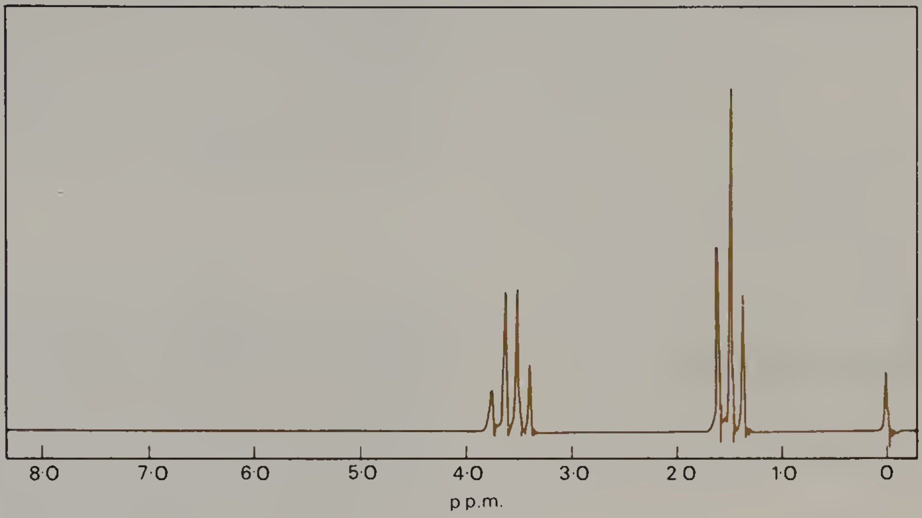
$CH_3—CH_2—Cl$	3·57 p.p.m.
$CH_3—CH_2—Br$	3·43 p.p.m.
$CH_3—CH_2—I$	3·20 p.p.m.

How do you account for these results?

5 A compound, **F**, contains 38·2 per cent carbon, 4·9 per cent hydrogen and 56·9 per cent chlorine. On reduction with hydrogen, it forms **G** which has the following mass spectrum:

Mass	64	28	29	27	66	26	49	51
Abundance (%)	100	90	84	75	32	29	25	8

The NMR spectrum of **G** (with TMS as standard) is shown below. Give the structural formulae for **F** and **G** and account for the physical data given.



6 Two compounds, **P** and **Q**, contain carbon, hydrogen and oxygen and have a precise relative molecular mass, as determined by mass spectrometry, of 58·0419. Their mass spectra are:

P	Mass	43	15	58	27	42	26
	Abundance (%)	100	31	28	7	7	4
Q	Mass	29	58	28	27	57	18
	Abundance (%)	100	83	82	57	26	8

(i) Using the precise data in Appendix VI, determine the molecular formulae of **P** and **Q**.
(ii) What are the possible structural formulae for **P** and **Q**?
(iii) Using the data from the mass spectra, determine the structural formulae of the two compounds.

Chapter 4

Bonding in organic compounds

4.1 Introduction

Chemistry is concerned with the making and breaking of bonds between atoms, and the bonds are associated with the electrons that surround the nucleus. Present ideas of the nature of chemical bonding are based on both experiments and mathematical theory. We are only able to describe the conclusions in a non-mathematical way, but this is still a valuable exercise because many experimental observations can be rationalised if we understand the principles of the theory.

4.2 Atomic orbitals

Our understanding of the behaviour of the electrons in atoms and molecules has evolved from quantum theory. Four especially important principles are involved.

First, an electron can only possess particular energies; for example, it might have energy *a*, *b*, *c*, etc., but could not have an energy intermediate between *a* and *b* or between *b* and *c*. That is, it has various **quanta** of energy.

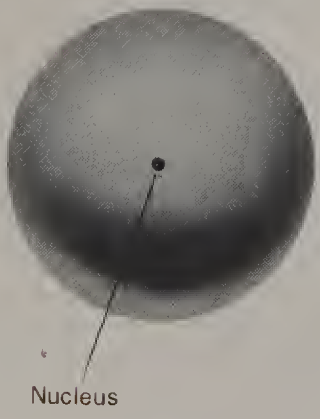
Secondly, the behaviour of electrons can be described by the same equations as describe a wave motion. This is not to say that electrons *are* waves, but only that they behave in the same way as waves. An electron of mass m and velocity v has a wave-length, λ, defined by de Broglie's equation: $\lambda = h/mv$, where h is a constant (Planck's constant).

Thirdly, it is not possible to describe simultaneously both the precise position and the momentum of an electron (Heisenberg's *Uncertainty Principle*); if the momentum is determined with a high degree of precision, then the position is known only approximately, and *vice-versa*.

Consider an electron in an atom. It can possess one of various specific energies, each of which, because of de Broglie's relationship, is associated with a particular wave-length. Thus, the energy of an electron can be defined by a series of equations which describe wave motion—**wave functions**—and it is customary to refer to these wave functions as **orbitals**. Now, because the energy of the electron is defined precisely, it follows from the Uncertainty Principle that its position cannot be known with certainty. It is possible only to say that there is a particular probability of finding the electron at a given point, or to describe a volume of space in which there is, say, 99 per cent probability that the electron will be found.

The fourth principle is that a particular orbital can be associated with a maximum of two electrons (*Pauli's Principle*); they are described as having opposite spins, and are sometimes represented as ↑ and ↓. When two electrons are present, they are described as **paired**; when only one is present it is described as **unpaired**. Now, since systems tend to adopt states in which their potential energy is minimised, it follows from Pauli's principle that the electrons in an atom are associated with the orbitals of lowest energy, each orbital being associated with not more than two electrons.

FIG. 4.1. *The 1s atomic orbital*



The hydrogen atom has one electron. It is associated with the orbital of lowest energy, which is spherically symmetrical about the nucleus. A contour diagram is shown in Fig. 4.1; if lines are drawn from the nucleus, the electron is as likely to be found at a particular distance along one line as at the same distance along any other. However, the probability that the electron will be found at a particular distance from the nucleus varies with the distance, rising to a maximum at a distance of 50 picometres (pm) (1 pm = 10^{-12}m) and then decreasing again.

It must be noted that the diagram in Fig. 4.1 represents an orbital (wave function) and not the volume in which the electron is most likely to be found. However, the probability of finding the electron at a given point is related to the wave function (it is actually proportional to the square of the wave function), so that the diagram gives an indication of the likely 'distribution' of the electron. It must also be emphasised that, strictly, it is incorrect to describe an electron as 'occupying an orbital'; it is simply a useful short-hand notation to describe it in this way, remembering that an orbital, as a wave function, is not like the orbit which describes the motion of a planet.

The orbital shown in Fig. 4.1 is described as the 1*s* orbital; the electron in the hydrogen atom which occupies it is unpaired. In the next element, helium, there are two electrons in the 1*s* orbital, with their spins paired. The next element, lithium, has three electrons. Two are in the 1*s* orbital and the third is in the next lowest orbital in the energy scale. This is the 2*s* orbital, and it is also spherically symmetrical about the nucleus (as are all orbitals of *s* type). However, it is larger than the 1*s* orbital, and the distance from the nucleus at which the electron has the maximum probability of being found is greater for the 2*s* than for the 1*s* orbital. The next element, beryllium, has two electrons in the 1*s* and two electrons in the 2*s* orbital, each of which is therefore complete.

Of the five electrons in the next element, boron, four are in the 1*s* and 2*s* orbitals and the fifth is in an orbital of different symmetry, namely, a 2*p* orbital. There are three 2*p* orbitals which are mutually perpendicular and are described as $2p_x$, $2p_y$ and $2p_z$ orbitals (Fig. 4.2); their shapes are identical and are illustrated in Fig. 4.3. The electron is as likely to be found on one side of the nucleus as on the opposite side, but there is zero probability of its being found at the nucleus (known as the **node**).

The three 2*p* orbitals have the same energy, so that the choice between the $2p_x$, $2p_y$ and $2p_z$ orbitals for the fifth electron in boron is an arbitrary one. However, with the next element, carbon, a different choice is available: the sixth electron could either go into the same 2*p* orbital as the fifth or into one of the other two 2*p* orbitals. The latter is found, and moreover the spins of the two 2*p* electrons are the same (*Hund's rule*) (Fig. 4.4). With the next element, nitrogen, the third 2*p* orbital is occupied. In successive

FIG. 4.2. *The directions of the three* 2p *atomic orbitals*

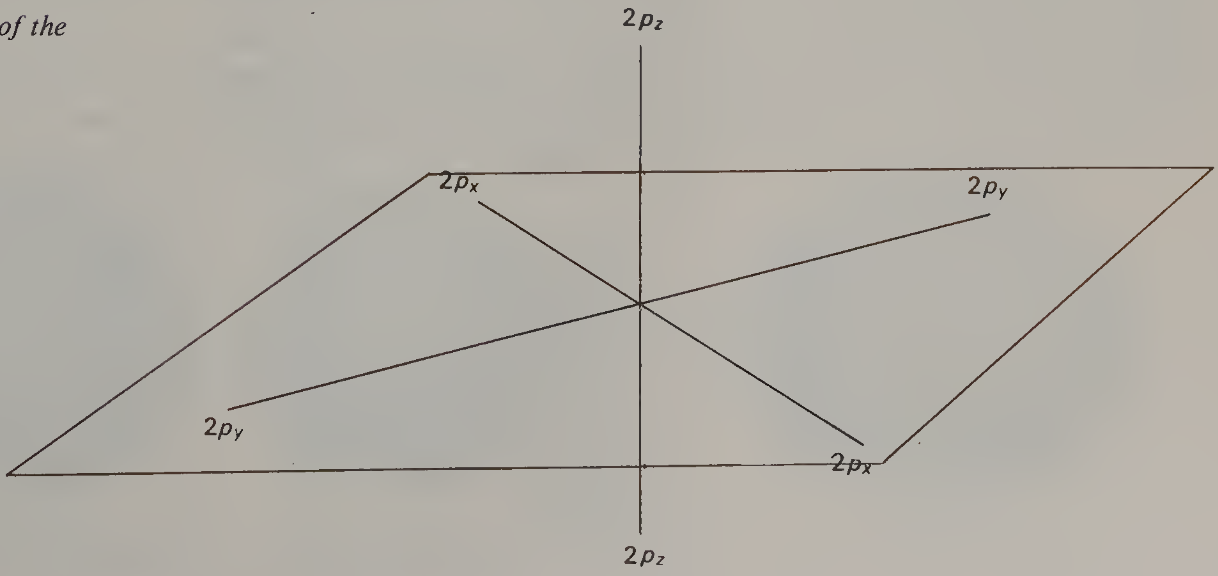
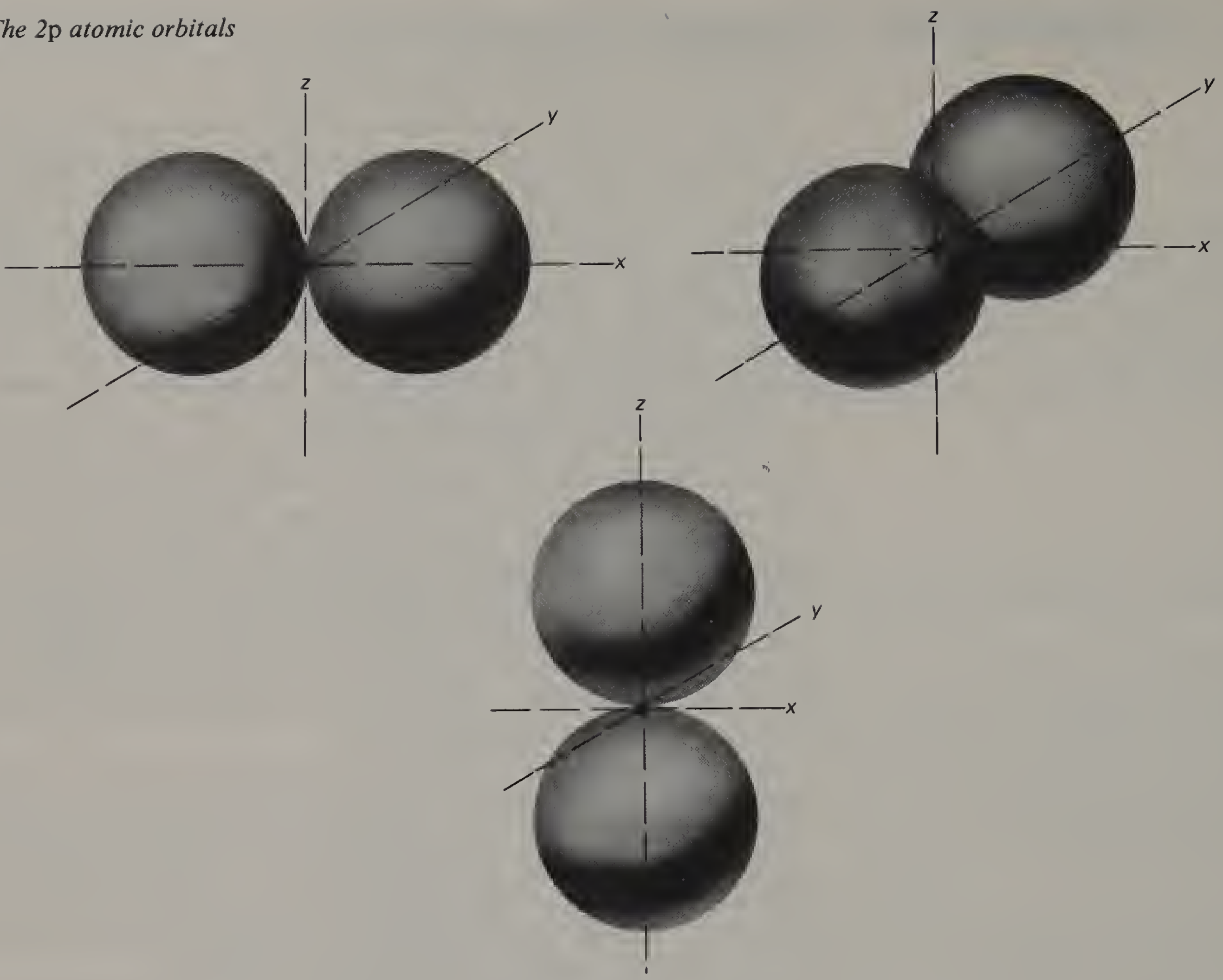


FIG. 4.3. *The* 2p *atomic orbitals*



elements, the three $2p$ orbitals are completed by the introduction of one more electron into each, then the $3s$ orbital is occupied, after which three $3p$ orbitals and the $3d$ orbitals (of different symmetry from the s and p orbitals) are available.

The electronic configuration of an atom is conveniently described as in Table 4.1; the superscript ^{2} indicates that there are two electrons in the orbital concerned, and where there is no superscript the number is one.

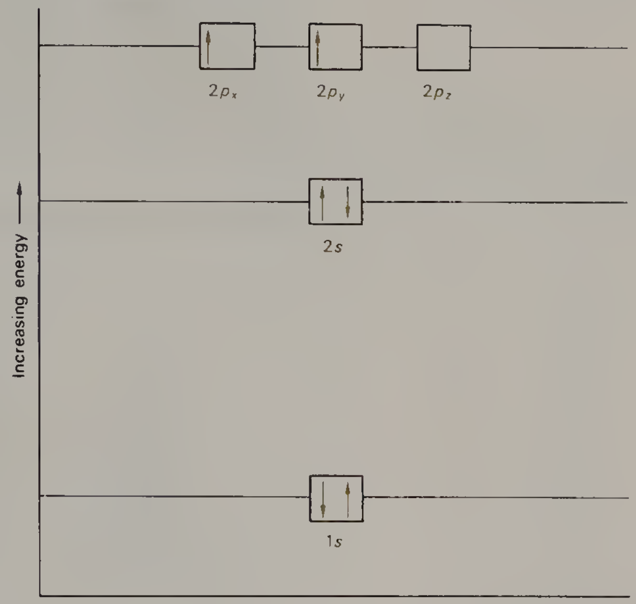
Table 4.1. Electronic configurations

ELEMENT	ATOMIC NUMBER Z	ELECTRONIC CONFIGURATION
Hydrogen	1	$1s$
Helium	2	$1s^2$
Lithium	3	$1s^2, 2s$
Beryllium	4	$1s^2, 2s^2$
Boron	5	$1s^2, 2s^2, 2p_x$
Carbon	6	$1s^2, 2s^2, 2p_x, 2p_y$
Nitrogen	7	$1s^2, 2s^2, 2p_x, 2p_y, 2p_z$
Oxygen	8	$1s^2, 2s^2, 2p_x{}^2, 2p_y, 2p_z$
Fluorine	9	$1s^2, 2s^2, 2p_x{}^2, 2p_y{}^2, 2p_z$
Neon	10	$1s^2, 2s^2, 2p_x{}^2, 2p_y{}^2, 2p_z{}^2$

4.3
Chemical bonding

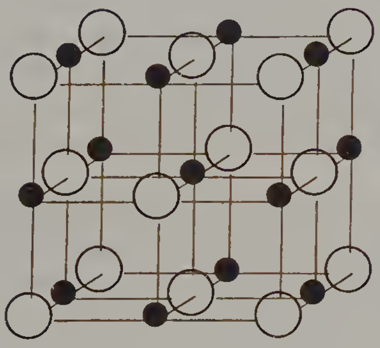
Atoms tend to adopt an electronic configuration in which each orbital has its full complement of two electrons. Two atoms form a bond by the transfer of an electron from one to the other or by sharing two electrons, one from each atom, so that singly occupied orbitals become filled.

FIG. 4.4. *The electronic configuration of carbon*



An **electrovalent (ionic) bond** is formed when one atom donates one or more electrons to an atom of a different element, forming charged particles known as ions. This happens, for example, with lithium and fluorine: the lithium atom donates its one $2s$ electron to the fluorine atom, each ion then having an electronic configuration of filled orbitals. The ions, being oppositely charged, are held together by electrostatic forces. These forces act equally in all directions, so that the electrovalent bond is **non-directional**; for example, in the crystal of lithium fluoride, each lithium ion (Li^+) is equidistant from six fluoride ions (F^-), and *vice-versa* (Fig. 4.5).

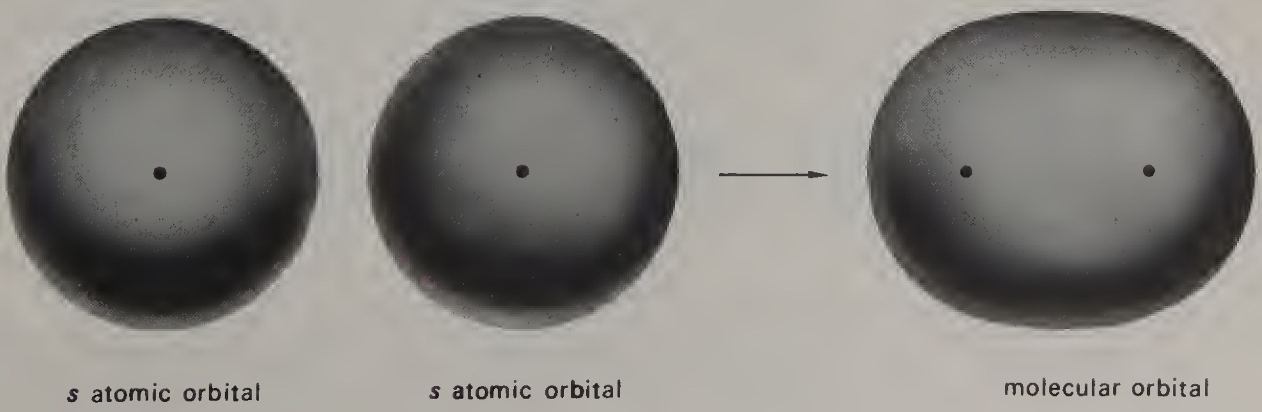
FIG. 4.5. *The lithium fluoride lattice*



A **covalent bond** is formed by the sharing of two electrons, one being contributed by each atom.

Suppose that two hydrogen atoms approach each other. The $1s$ atomic orbitals of each atom can overlap, with the result that two molecular orbitals are formed; these are similar to atomic orbitals except that they are associated with two nuclei instead of one. One of the molecular orbitals is of lower energy than the atomic orbitals and is described as a **bonding molecular orbital**; the other, of higher energy, is an **antibonding molecular orbital**. The two $1s$ electrons from the hydrogen atoms occupy the lower energy, bonding orbital, with their spins paired, and the antibonding orbital remains empty. Consequently, the energy of the system is lower than that of the separate atoms, and the molecule is more stable than the two atoms.

FIG. 4.6. *The formation of the* s-s *molecular orbital from two* s *atomic orbitals*



Note that the two hydrogen nuclei remain separated in the molecule. This is because, as the nuclei approach each other, on the one hand, the degree of overlap between the atomic orbitals increases and so therefore does the effectiveness of the bonding, but on the other hand the repulsive force between the nuclei themselves increases. Consequently, there is an optimum distance of separation at which the total energy reaches a minimum; this is the most stable situation. Therefore, each covalent bond is characterised by a particular **bond length** and has a particular **bond energy**. Bond lengths can be measured by *X*-ray crystallography and by microwave spectroscopy; they are mostly 100–200 pm and some typical values are in Table 4.2. Bond energies can be measured by calorimetry and spectroscopic methods; typical values are in Table 4.3.

Table 4.2. Some bond lengths

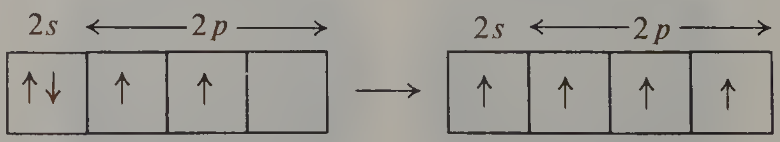
	pm
C—H	109
C—C	154
C=C	134
C≡C	119
C—O	143
C=O	122
C—N	147
C=N	130
C≡N	116
O—H	96

Table 4.3. Some bond energies

	kJ mol^{-1}		kJ mol^{-1}
C—C	345	C—F	450
C=C	610	C—Cl	339
C≡C	835	C—Br	284
C—H	413	C—I	213
C—N	304	N—H	391
C≡N	889	O—H	490
C—O	358	N—N	163
C=O	749	O—O	146

Consider next the approach of two helium atoms to each other. As with hydrogen atoms, the 1*s* orbitals of each overlap to form two molecular orbitals, one bonding and one antibonding. In this case, however, there are four 1*s* electrons—two from each atom—to occupy the molecular orbitals; consequently, each of these contains a pair of electrons, and the effectiveness of the pair in the bonding orbital in holding the atoms together is nullified by the effect of the pair in the antibonding orbital, so that no bond is formed between two helium atoms.

From this example, it can be appreciated that, for the overlap of two atomic orbitals to result in the formation of a bond, each should contain only one electron; then the bonding molecular orbital will be filled and the antibonding one empty. Therefore we can expect the number of bonds which an element forms to be equal to the number of unpaired electrons in its atomic structure. For example, the hydrogen atom has one unpaired electron and forms one bond, as in H_2; the nitrogen atom has three unpaired electrons and forms three bonds, as in NH_3. However, a problem is posed by the carbon atom, which has two unpaired electrons and yet forms four bonds. The explanation is that one of the 2*s* electrons in carbon is transferred to the 2*p* orbital, thereby yielding four unpaired electrons so that four bonds can be formed:

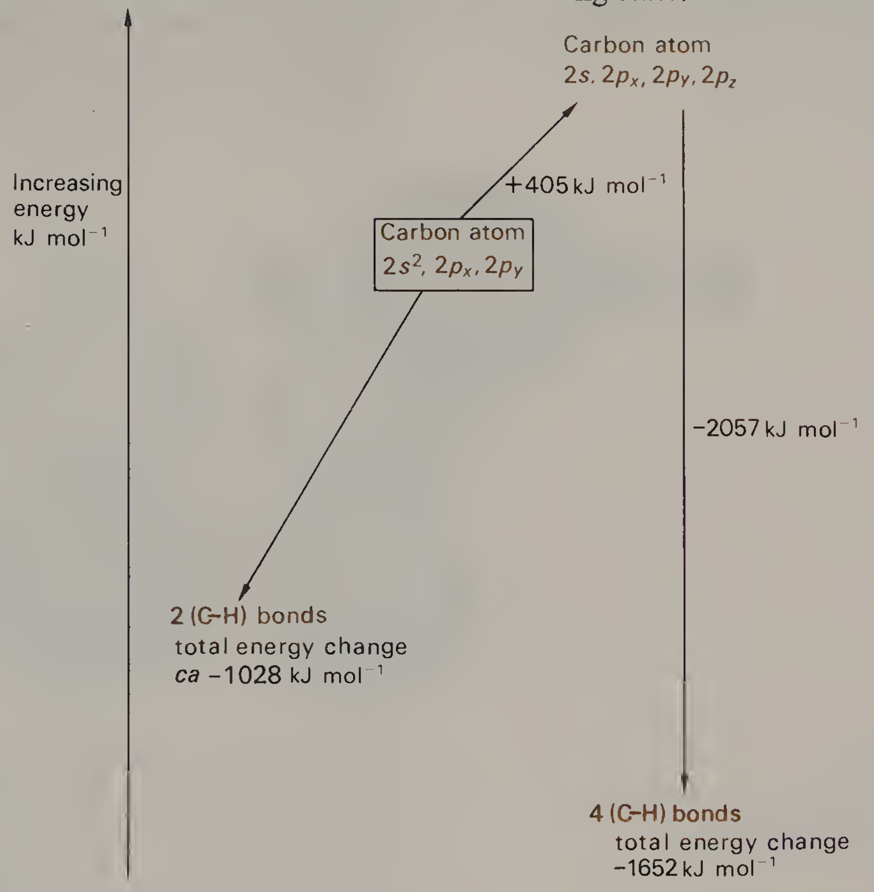


Carbon in its ground state

Carbon in its bonding state

Although the transfer of the electron from the 2*s* to the 2*p* orbital (known as **promotion**) requires energy, it is more than compensated by the release of energy which accompanies the formation of four bonds compared with two. This can be represented as in Fig. 4.7. Although the energy change in forming 2 C—H bonds from a carbon atom in the ground state is not known, it is not likely to be more than half the value for the formation of 4 C—H bonds from a carbon atom in its bonding state.

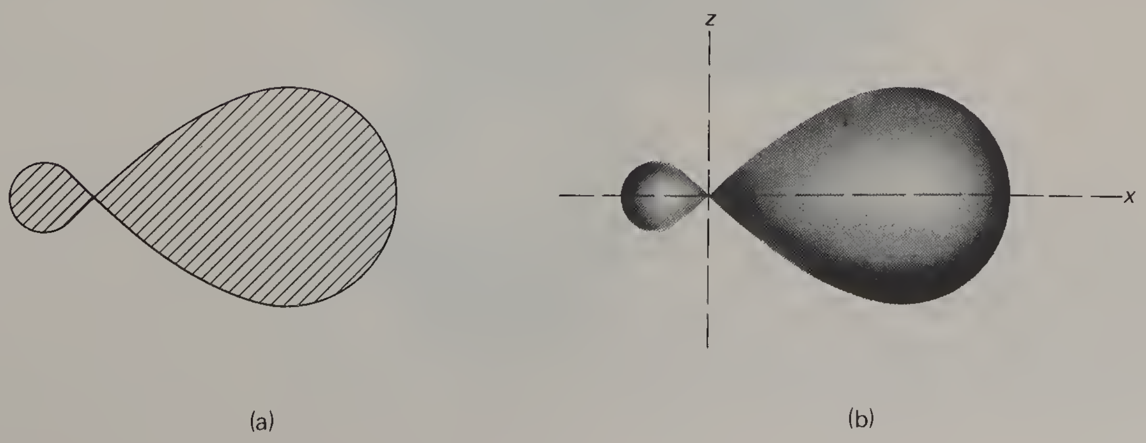
FIG. 4.7. *An energy diagram showing that carbon prefers to form four bonds*



4.4 Saturated carbon compounds

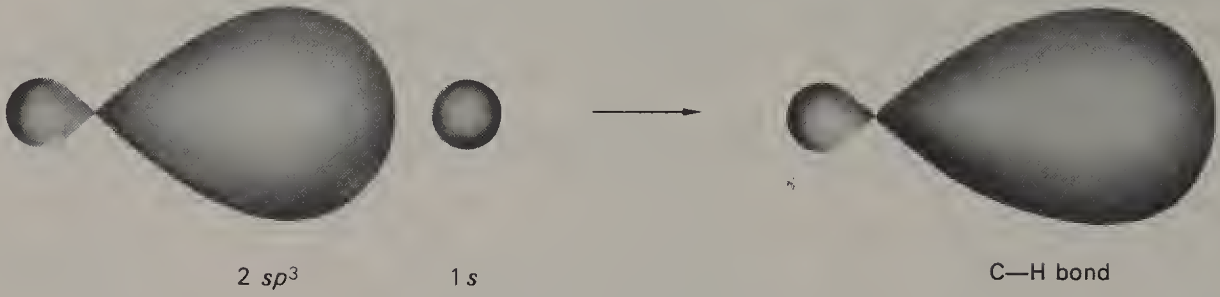
In a simple molecule like methane it would appear at first sight that there would be two types of bonds: one type would be formed by overlap of the singly occupied 2*s* orbital of carbon with the singly occupied 1*s* orbital of a hydrogen atom, and the other would be formed by overlap of each of the three singly occupied 2*p* orbitals of carbon with the 1*s* orbital of each of three hydrogen atoms. However, methane is known to be a symmetrical molecule, containing four C—H bonds of equal length and at equal angles to each other; if the carbon atom were placed at the centre of a regular tetrahedron, the four hydrogen atoms would be at the four corners. This can be understood by considering the four unfilled carbon orbitals to be

FIG. 4.8. *The* sp³ *hybridised atomic orbital.* (*a*) *Cross-section,* (*b*) *Shape*



'mixed' so that each has 1/4 s character and 3/4 p character; the process of mixing is described as **hybridisation** and the resulting orbitals as sp^3 orbitals. These orbitals have a different shape compared with both s and p orbitals. Like p orbitals, they are directional, but unlike p orbitals, one lobe is larger than the other (Fig. 4.8). It is the larger lobe which overlaps with another atomic orbital, such as the 1s orbital of a hydrogen atom, to form molecular orbitals. For example, the formation of one C—H bond in methane can be represented as in Fig. 4.9. The process of hybridisation occurs because the four directional orbitals which result allow greater overlap with the atomic orbitals of other atoms than if carbon formed its bonds with one 2s and three 2p atomic orbitals; in this way, the total bonding is increased and therefore the potential energy of the system is decreased.

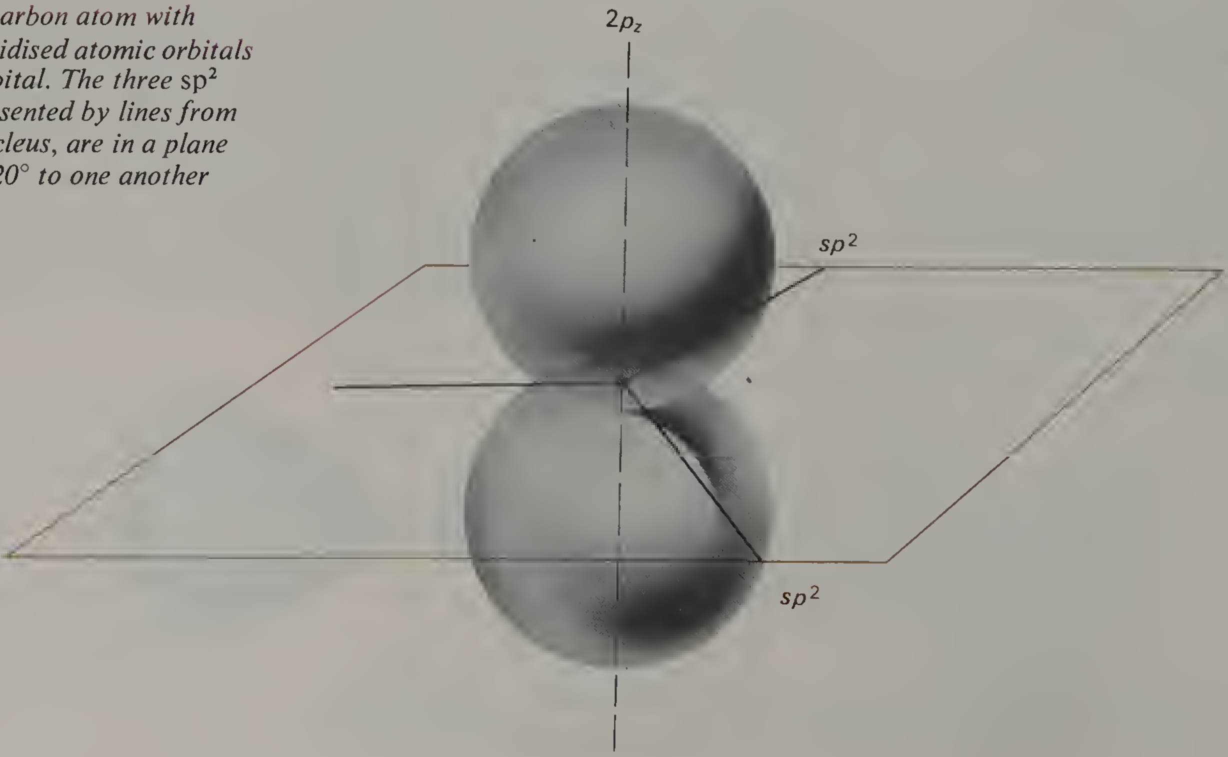
FIG. 4.9. *The formation of a C—H bond from an* s *atomic orbital (hydrogen) and an* sp³ *hybridised atomic orbital (carbon). Cross-section of the atomic and molecular orbitals*



4.5 Unsaturated carbon compounds

There are two other ways in which the atomic orbitals of carbon can be hybridised. First, the one singly occupied 2s orbital and two of the three singly occupied 2p orbitals can be hybridised to give three sp^2 orbitals, leaving the remaining 2p orbital intact. The three sp^2 orbitals are arranged symmetrically in a plane, making angles of 120° with each other; the unaltered 2p orbital is perpendicular to this plane (Fig. 4.10).

FIG. 4.10. *A carbon atom with three* sp² *hybridised atomic orbitals and one* p$_z$ *orbital. The three* sp² *orbitals, represented by lines from the carbon nucleus, are in a plane at angles of 120° to one another*



This is the state of hybridisation adopted by the carbon atoms in ethene, C_2H_4. Each carbon atom forms one bond with the other carbon atom and two to hydrogen atoms by means of its three sp^2 orbitals. This leaves a singly occupied p orbital on each carbon atom (Fig. 4.11), and these two p orbitals can overlap laterally with each other to form a bonding molecular orbital between the carbon atoms (Fig. 4.12).

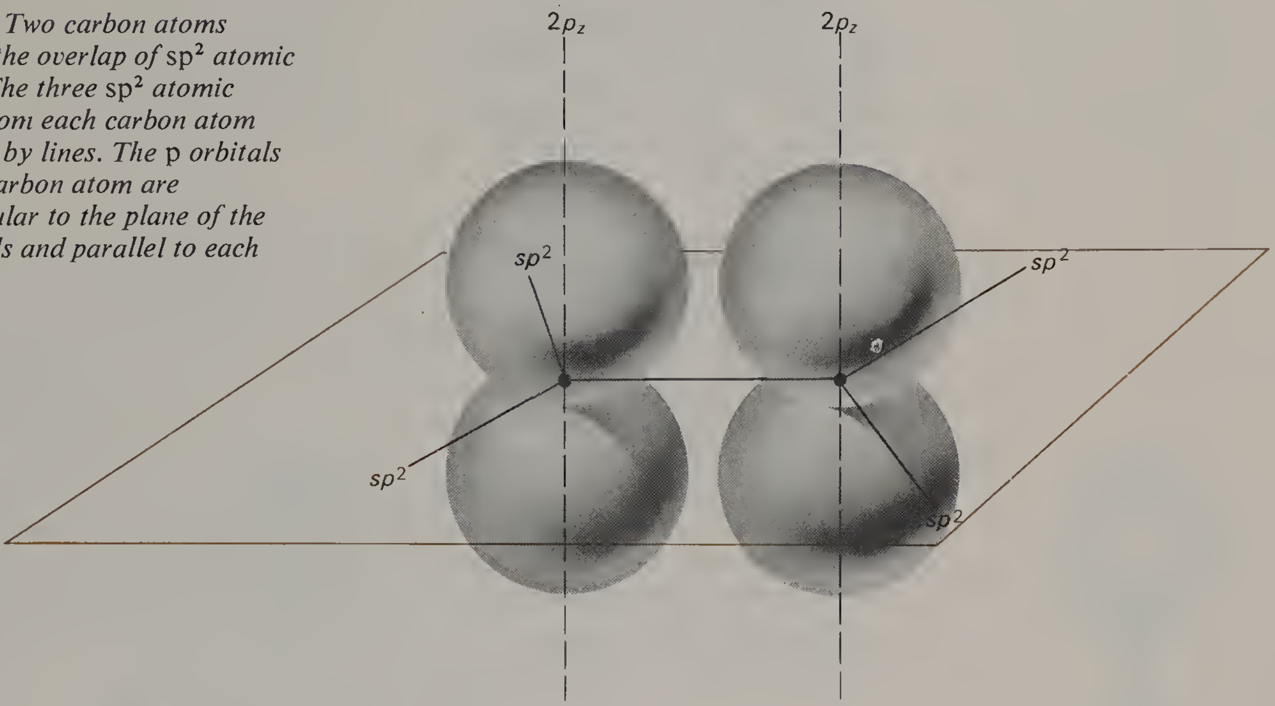


FIG. 4.11. *Two carbon atoms joined by the overlap of* sp^2 *atomic orbitals. The three* sp^2 *atomic orbitals from each carbon atom are shown by lines. The* p *orbitals for each carbon atom are perpendicular to the plane of the* sp^2 *orbitals and parallel to each other*

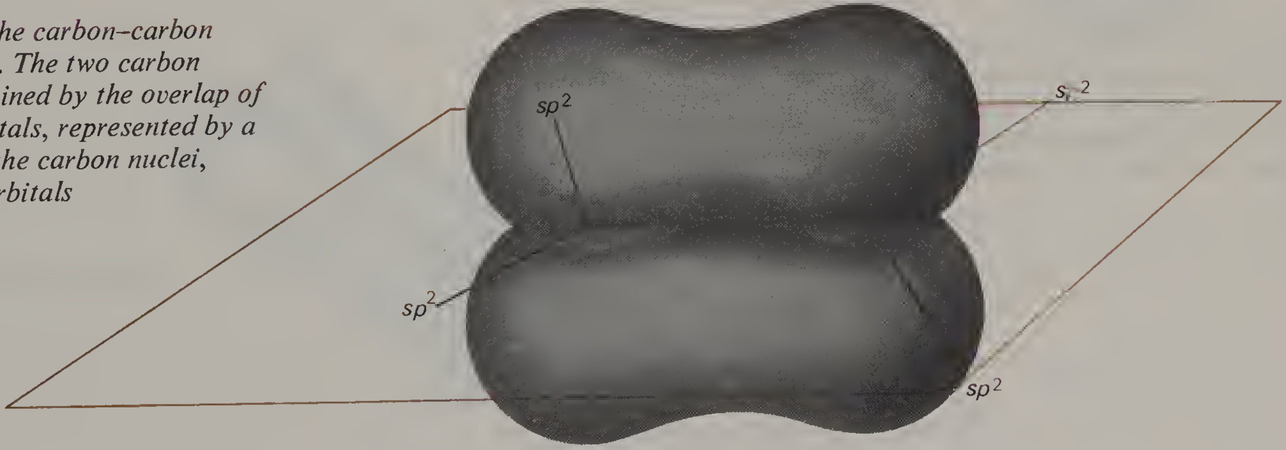
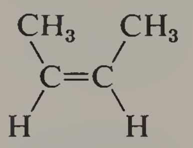
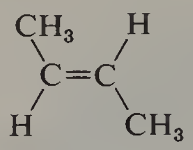


FIG. 4.12. *The carbon–carbon double bond. The two carbon atoms are joined by the overlap of two* sp^2 *orbitals, represented by a line joining the carbon nuclei, and two* p *orbitals*

Two properties of the carbon–carbon double bond in ethene and its derivatives can be understood immediately in the light of this description. First, the bond is shorter than a carbon–carbon single bond (Table 4.2). This is because relatively more bonding is gained by the overlap of *two* sets of orbitals as the nuclei approach each other in forming C=C than in the overlap of one set of orbitals in formation of C—C, while the repulsive forces between the nuclei are the same in each case. Secondly, the carbon–carbon double bond is resistant to rotation, because this reduces the extent of overlap of the *p* orbitals; if the bond was twisted by 90°, the *p*-orbital overlap would be reduced to zero and the bond energy would be that of a single bond, so that about 265 kJ mol^{-1} would be required. It is because of this that **geometrical isomerism** (15.4) occurs; for example, the compounds





do not interconvert because the process of interconversion would necessitate destruction of the bond formed by *p*-orbital overlap.

The final type of hybridisation for carbon involves the mixing of one 2*s* orbital with one 2*p* orbital; two *sp*-hybridised orbitals are formed, the larger lobes of which point in diametrically opposite directions from the nucleus. The remaining unpaired electrons are in the original 2*p* orbitals, which are perpendicular to each other and to the direction of the *sp* orbitals.

Ethyne, C_2H_2, is the simplest compound formed from *sp*-hybridised orbitals. Each carbon atom bonds with the other carbon atom and with one hydrogen atom by use of its *sp* orbitals, the two bonds being at an angle of 180°, and forms two further bonds with the other carbon atom by *p*-orbital overlap (Fig. 4.13). Just as the C═C bond is shorter than C—C, so C≡C is shorter than C═C (Table 4.2).

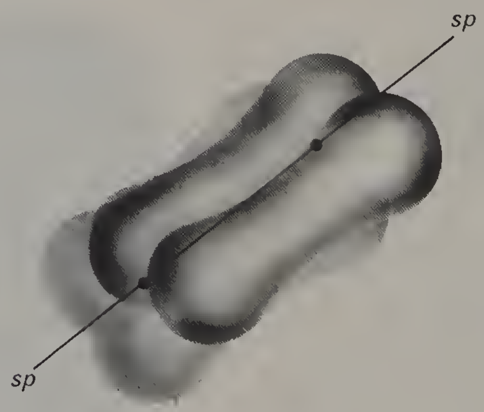
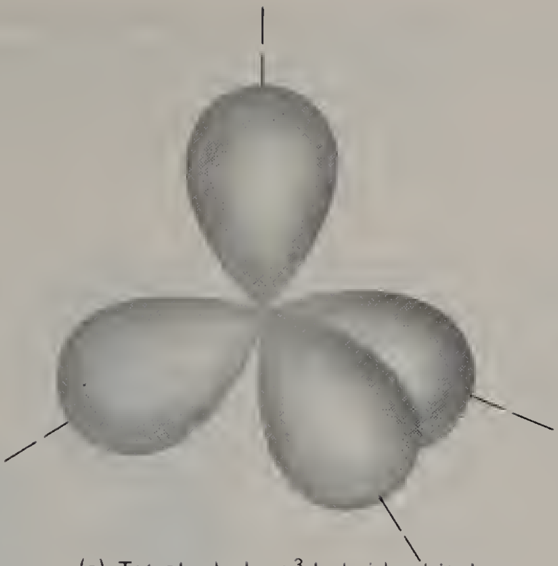


FIG. 4.13. *The carbon–carbon triple bond. The two carbon atoms are joined by the overlap of two* sp *orbitals, represented by a line joining the carbon nuclei, and four* p *orbitals, two from each carbon atom*

Bonds between two atoms which are symmetrical about the axis joining the nuclei of the atoms are described as **sigma bonds (σ-bonds)**; examples are the bonds formed by *s* atomic orbitals (e.g. in H_2) and by sp^3, sp^2 and *sp* hybridised orbitals (e.g. in methane, ethene and ethyne), summarised in Fig. 4.14. Bonds formed by lateral *p* orbital overlap are not symmetrical about the axis joining the nuclei; they are described as **pi-bonds (π-bonds)**.

FIG. 4.14. *The three types of hybridised orbitals for the carbon atom. (a) Tetrahedral* sp^3 *hybrid orbitals; (b) Coplanar* sp^2 *hybrid orbitals; (c) Collinear* sp *hybrid orbitals*



(a) Tetrahedral sp^3 hybrid orbitals

(b) Coplanar sp^2 hybrid orbitals

(c) Collinear sp hybrid orbitals

4.6 Delocalised bonds

So far, all the molecular orbitals we have described have been constituted from the overlap of two atomic orbitals and are centred around two nuclei. The bonds to which these molecular orbitals correspond are known as **localised** bonds.

There are also **delocalised** bonds, in which pairs of electrons are associated with bonding molecular orbitals which extend over three or more atoms. They occur less commonly than localised bonds, but they confer special properties on the compounds containing them.

Benzene, C_6H_6, contains delocalised bonds. The six carbon atoms are arranged in the form of a regular hexagon and each forms three localised bonds with sp^2-hybridised orbitals, two to other carbon atoms and one to a hydrogen atom. This leaves a singly occupied *p* orbital on each carbon atom, and each *p* orbital overlaps with the *p* orbital on either side of it (Fig. 4.15). The overlap of these six atomic *p* orbitals gives rise to six molecular π orbitals, of which three are of bonding and three are of antibonding type. The six electrons from the six atomic *p* orbitals then occupy the three bonding molecular π orbitals as three pairs; thus, there are three delocalised π bonds. The shape of one of these three molecular orbitals is shown in Fig. 4.15; the overall effect of filling each with a pair of electrons is to give the same distribution of electron density between each pair of carbon atoms.

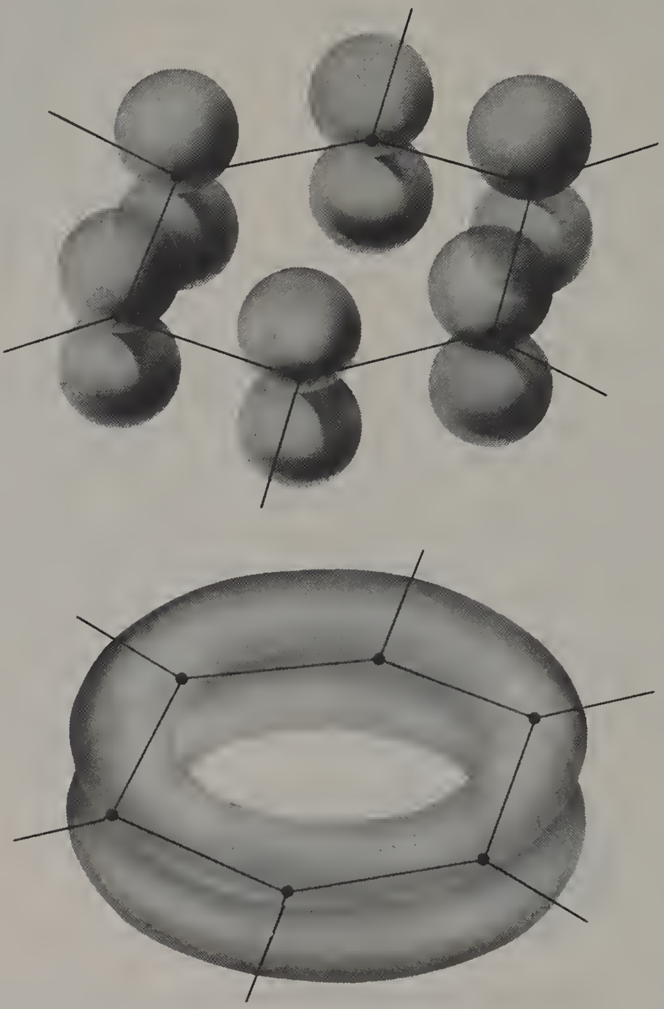
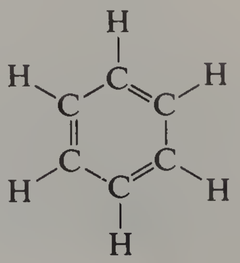


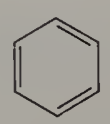
FIG. 4.15. *Structure of benzene. Each carbon atom forms three σ bonds, two to other carbon atoms and one to a hydrogen atom (represented by lines). In addition the six atomic* p *orbitals shown in the upper diagram overlap laterally to give delocalised π molecular orbitals, one of which is shown in the lower diagram*

Delocalised π orbitals are much larger than the localised π orbitals in, say, ethene. The electrons in them can be found in a greater volume than for localised orbitals; in a sense, they have a greater freedom of movement, and it is a general principle that, the greater the freedom of movement of an electron, the lower is its energy. Hence, a special property of compounds containing delocalised bonds is that they are more stable than similar compounds which only contain localised bonds. The experimental evidence that benzene is stabilised in this way, and fuller details of its structure, are discussed later (8.2).

There is an alternative method of representing delocalised bonds. Thus, if we were to represent benzene as



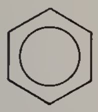
or



it would imply that three localised π-bonds are present. Instead, a widely used convention is to draw *two* structures:

The double-headed arrow ↔ is taken to mean that the actual structure lies between the two representations; in other words, each C—C bond is neither a simple single nor a simple double bond but is of intermediate type. This method is sometimes described as **mesomerism** ('in-betweenness'), and benzene is described as a **resonance hybrid** of the two structures. It is important to realise that benzene does not oscillate between these structures; it exists in only one form, in which the six C—C bonds are of identical type.

In this text, delocalisation is sometimes described in terms of molecular orbitals, but in other cases it is more convenient to represent the benzene ring as



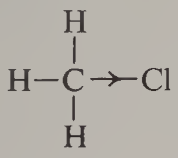
where the circle corresponds to the delocalised bonds.

4.7
The inductive effect

The two electrons in a bond between two atoms are attracted by the two nuclei. In a diatomic molecule in which the two atoms are the same, such as H_2 or Cl_2, attraction by one nucleus is as strong as attraction by the other and so it is as likely that the electrons will be found a particular distance from one nucleus as from the other; the bond is symmetrical in the sense that the centres of gravity of the negative and positive charges coincide. However, in a bond between unlike atoms, the nucleus of one atom exerts a stronger attractive force than that of the other; the electrons are more likely to be found nearer the former nucleus and the centres of gravity of the negative and positive charges do not coincide. For example, in hydrogen chloride the centre of gravity of the negative charges is nearer to chlorine than the centre of gravity of the positive charges, an effect which is represented as $\mathrm{H}{\rightarrowtail}\mathrm{Cl}$ where ${\rightarrowtail}$ represents the tendency of the electrons to lie nearer chlorine.

The magnitude of the opposite charges multiplied by the separation of their centres of gravity is defined as the **dipole moment** of the compound. This can be measured by finding how the compound affects the capacitance of a condenser; the greater the dipole moment, the more strongly the molecules tend to align themselves between the plates of the condenser (the positive end of the molecule being nearer to the negative plate, and *vice-versa*) and the lower is the capacitance.

The bonds in organic molecules are also polarised in this way by substituents such as the halogens. For example, chloromethane has a dipole moment of which the negative end is the chlorine atom:

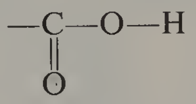


$$\mathrm{H}_3\mathrm{C}{\rightarrowtail}\mathrm{Cl}$$

It is useful to have a scale for describing the effects of different atoms to attract bonding electrons. For this purpose, hydrogen is chosen as a reference point; an atom or group which attracts the bonding electrons more strongly than hydrogen is described as having an electron-withdrawing **inductive effect**, symbolised as $-I$. For example, since the electrons in the C—Cl bond of CH_3—Cl lie relatively further from carbon than those in the C—H bond in CH_3—H, chlorine is a $-I$ substituent. On the other hand, alkyl groups are electron-releasing ($+I$) compared with hydrogen.

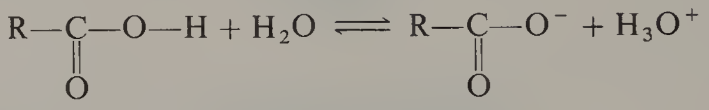
4.8 Organic acids and bases

Some types of organic grouping are acidic and others are basic. The commonest acid group is the carboxylic acid group:



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

Carboxylic acids, R—CO_2H, are weak acids compared with the mineral acids such as H_2SO_4; that is, the equilibrium



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\underset{\underset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

lies on the left-hand side.

The equilibrium constant, K, for this reaction is given by

$$K = \frac{[RCO_2{}^-][H_3O^+]}{[RCO_2H][H_2O]}$$

However, for dilute solutions of acids, $[H_2O]$ is essentially constant, and it is customary to define the acid dissociation constant, K_a, as:

$$K_a = \frac{[RCO_2{}^-][H^+]}{[RCO_2H]}$$

For example, for ethanoic acid, $K_a = 1{\cdot}7 \times 10^{-5}$ mol dm^{-3}.

There is some confusion about the use of units for equilibrium constants. As the equilibrium constant is described above, it has units of mol dm^{-3}. However, in more advanced textbooks, you will usually find the constant described as dimensionless. This is because relative activities of the ions and molecules, rather than concentrations, are used and these are themselves dimensionless.

Despite the small values of K_a for ethanoic and other carboxylic acids, they are still acidic enough to form salts with alkalis and turn blue litmus paper red. In contrast, alcohols, which also dissociate,

$$R-O-H + H_2O \rightleftharpoons R-O^- + H_3O^+$$

have such small dissociation constants (K_a is *ca.* 10^{-15}) that they exhibit few of the properties usually associated with acids; for example, although they form salts and liberate hydrogen when treated with sodium,

$$ROH + Na \rightarrow RO^-Na^+ + \tfrac{1}{2}H_2$$

they do not turn blue litmus paper red.

The reason for the greater acid strength of carboxylic acids than alcohols can be understood by considering the bonding in the corresponding anions, RCO_2^- and RO^-. In the former, the atomic *p* orbitals on the carbon and two oxygen atoms of the carboxylate group interact to give three delocalised π molecular orbitals; the four *p* electrons occupy the two lowest energy orbitals of these three, of which one is bonding and one is non-bonding. The shape of the bonding π molecular orbital is shown in Fig. 4.16.

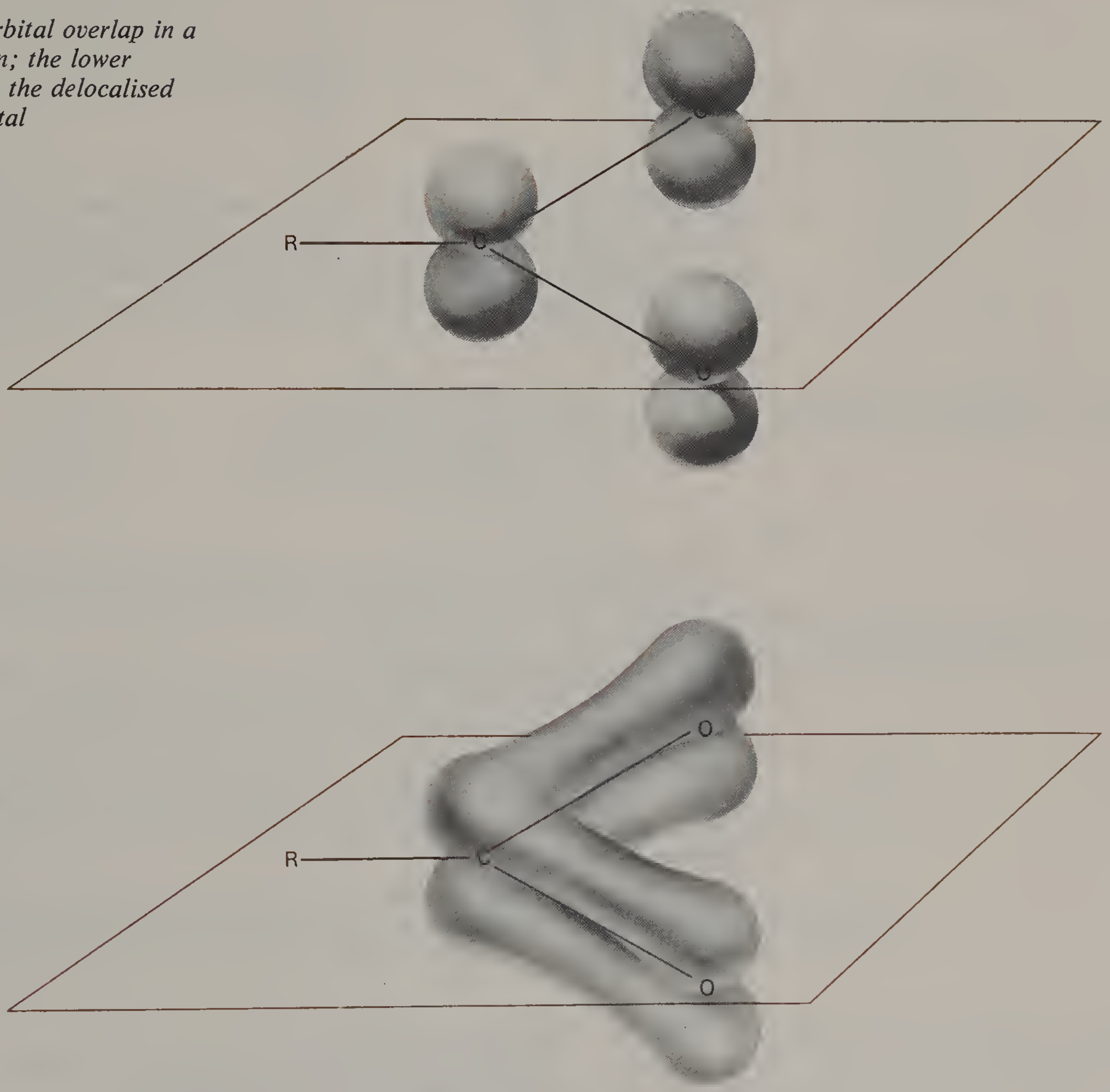
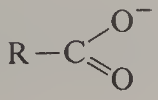
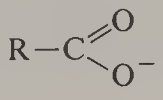


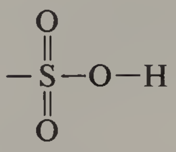
FIG. 4.16. p-*Orbital overlap in a carboxylate ion; the lower diagram shows the delocalised bonding π orbital*

The anion is thus symmetrical, with the negative charge shared equally by the two oxygen atoms. This can perhaps be seen more easily by representing the anion in terms of the theory of mesomerism; two structures can be drawn:

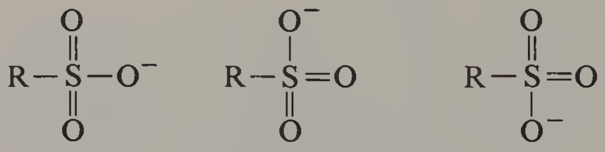
and the actual structure is intermediate between the two, with the equivalent of half a negative charge on each oxygen atom. For the ion RO^-, on the other hand, the charge is localised on one oxygen atom. Now, it is a general principle that the potential of a charged system decreases as the volume associated with the charge becomes larger (in electrostatics, the potential of a charged sphere is inversely proportional to the volume of the sphere). Therefore, the carboxylate ion, RCO_2^-, in which the charge is delocalised, is relatively more stable than the ion RO^- and is formed the more readily.

Another acid grouping is



$$-\mathrm{S}(=\mathrm{O})_2-\mathrm{O}-\mathrm{H}$$

in organic sulphonic acids, $R—SO_3H$. These acids are much stronger than the carboxylic acids and are as strong as mineral acids like H_2SO_4. This again can be understood in terms of charge delocalisation; in the sulphonate anion, *three* oxygen atoms share the negative charge, as represented by the three structures



$$\mathrm{R}-\mathrm{S}(=\mathrm{O})_2-\mathrm{O}^- \qquad \mathrm{R}-\mathrm{S}(-\mathrm{O}^-)(=\mathrm{O})=\mathrm{O} \qquad \mathrm{R}-\mathrm{S}(=\mathrm{O})(-\mathrm{O}^-)=\mathrm{O}$$

In addition to the effect of charge-sharing described above, the strengths of acids are dependent upon the presence of substituents in the rest of the molecule.

For example, chloroethanoic acid ($ClCH_2—CO_2H$) is a stronger acid than ethanoic acid (Table 4.4). This is because chlorine has a $-I$ effect; that is, the chlorine nucleus, by its strong attraction for the electrons in the C—Cl bond, enables the negative charge in the ion $Cl—CH_2—CO_2^-$ to be spread through the molecule more effectively than in the ethanoate ion. Two chlorine substituents are more effective than one, and three are more effective than two.

The fluorine atom, having a stronger attraction for electrons, causes fluoroethanoic acid to be a stronger acid than chloroethanoic acid. Bromoethanoic and iodoethanoic acids are, as expected, weaker acids (Table 4.4).

Table 4.4. Dissociation constants of some halogeno-substituted carboxylic acids

ACID	K_a AT 25°C
$CH_3—CO_2H$	$1{\cdot}7 \times 10^{-5}$
$ClCH_2—CO_2H$	$1{\cdot}4 \times 10^{-3}$
$Cl_2CH—CO_2H$	$5{\cdot}1 \times 10^{-2}$
$Cl_3C—CO_2H$	$2{\cdot}2 \times 10^{-1}$
$FCH_2—CO_2H$	$2{\cdot}2 \times 10^{-3}$
$ClCH_2—CO_2H$	$1{\cdot}4 \times 10^{-3}$
$BrCH_2—CO_2H$	$1{\cdot}3 \times 10^{-3}$
$ICH_2—CO_2H$	$6{\cdot}9 \times 10^{-4}$

From such evidence, it can be shown that the following groups exert a $-I$ effect with respect to hydrogen (in descending order of power):

$$NO_2,\quad CN,\quad F,\quad Cl,\quad Br,\quad I,\quad OH,\quad NH_2$$

Groups which are electron-releasing with respect to hydrogen ($+I$ groups) reduce acid dissociation constants (Table 4.5). For example, ethanoic acid is weaker than methanoic acid ($H—CO_2H$), and propanoic acid ($CH_3—CH_2—CO_2H$) is weaker still. Groups that exert a $+I$ effect are, in descending order of power:

Table 4.5. Dissociation constants of some carboxylic acids

ACID	K_a AT 25°C
$H—CO_2H$	$1{\cdot}7 \times 10^{-4}$
$CH_3—CO_2H$	$1{\cdot}7 \times 10^{-5}$
$CH_3CH_2—CO_2H$	$1{\cdot}3 \times 10^{-5}$
$C_6H_5—CO_2H$	$6{\cdot}3 \times 10^{-5}$
$C_6H_5CH_2—CO_2H$	$4{\cdot}9 \times 10^{-5}$

$$(CH_3)_3C,\quad (CH_3)_2CH,\quad C_2H_5,\quad CH_3$$

The amino group, $—NH_2$, is the most commonly found basic group in organic chemistry. It is basic because it can form a bond with a proton by means of the unshared pair of electrons on the nitrogen atom:

$$R—\ddot{N}H_2 + H_2O \rightleftharpoons R—\overset{+}{N}H_3 + OH^-$$

The equilibrium constant for this reaction is given by:

$$K = \frac{[R—\overset{+}{N}H_3][OH^-]}{[R—NH_2][H_2O]}$$

However, usually K is determined for a solution in water, which is in considerable excess over the other components, so that $[H_2O]$ is approximately constant. It is therefore customary to describe the base strength of an amine by K_b, given by:

$$K_b = \frac{[R—\overset{+}{N}H_3][OH^-]}{[R—NH_2]}$$

(the units are again omitted, p. 62).

Amines are weak bases; that is, K_b is small. For example, methylamine ($CH_3—NH_2$) has K_b (at 25°C) $= 4{\cdot}4 \times 10^{-4}$. Thus, they are far weaker bases than inorganic alkalis such as sodium hydroxide, although they are strong enough to form salts with acids.

4.9 Unstable intermediates in organic chemistry

As we have seen, the structures of organic compounds are characterised by the formation of four bonds by each carbon atom. However, there are also species in which the carbon atoms form fewer bonds, and although they are too unstable to exist as compounds which can be isolated, they are nevertheless important in occurring as short-lived intermediates in organic reactions. Two of the more important types with which this book will be concerned are **free radicals**, in which one of the carbon atoms has three bonds and one unpaired electron, and **carbonium ions**, in which one of the carbon atoms has three bonds and possesses a positive charge.

The simplest free radical is methyl, $\cdot CH_3$ (the dot signifies an unpaired electron). The radical has a planar structure in which the carbon atom forms three bonds to hydrogen atoms by sp^2-hybridised orbitals and possesses a p orbital with one electron in it (Fig. 4.17).

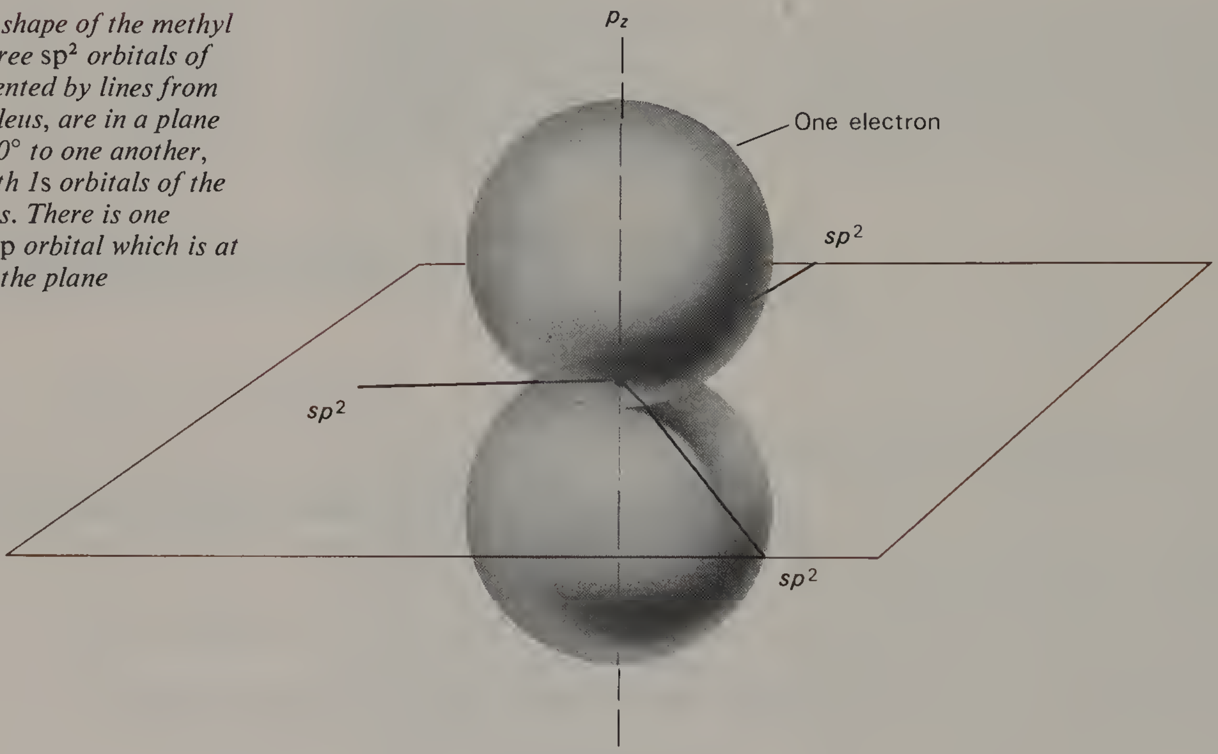


FIG. 4.17. *The shape of the methyl radical. The three* sp^2 *orbitals of carbon, represented by lines from the carbon nucleus, are in a plane at angles of 120° to one another, and overlap with 1s orbitals of the hydrogen atoms. There is one electron in the* p *orbital which is at right angles to the plane*

Free radicals are particularly important as intermediates in the reactions of alkanes. For example, in the chlorination of methane (5.4), the methyl radical is formed from methane and a chlorine atom:

$$CH_4 + Cl\cdot \rightarrow \cdot CH_3 + HCl$$

and then reacts with a molecule of chlorine:

$$\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

A carbonium ion has the same structure as a radical except that the p orbital is empty; thus, the carbon atom is associated with a positive charge. Carbonium ions are particularly important as intermediates in the reactions of alkenes, alkyl halides and alcohols. For example, in the addition of hydrogen chloride to ethene, a carbonium ion is formed first:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3{-}\overset{+}{C}H_2 + Cl^-$$

and then rapidly reacts with a chloride ion:

$$CH_3—\overset{+}{C}H_2 + Cl^- \rightarrow CH_3—CH_2Cl$$

The substituents in a compound are of importance in determining the ease of formation of a carbonium ion. For example, of the two carbonium ions

$$CH_3—\overset{+}{C}H—CH_3 \qquad\qquad CH_3—CH_2—\overset{+}{C}H_2$$

the former is attached to two alkyl substituents which are electron-releasing relative to hydrogen and the latter to only one. Consequently, the concentration of the positive charge is reduced to a greater extent in the former case and the former ion is therefore the more stable. This is important in governing the direction of addition of a proton to propene, $CH_3—CH{=}CH_2$ (6.4).

4.10
Practical work

Determination of dissociation constants of some carboxylic acids

Some of the evidence for the inductive effect of atoms and groups in organic molecules comes from a study of the dissociation constants of carboxylic acids. The dissociation constants can be readily obtained.

Experimental procedure

Prepare 50 cm^3 samples of several carboxylic acids of concentration 0·1 M (chosen from, for example, ethanoic, monochloroethanoic, dichloroethanoic, phenylethanoic acids), in 100 cm^3 beakers. Set up a pH meter and adjust the electrodes in the beaker so that they are well immersed in the solution but are not at the bottom of the beaker. Measure and record the pH of the solution.

Add 0·5 cm^3 of M sodium hydroxide solution from a burette, swirl the contents to ensure mixing, measure and record the pH of the solution again. Continue to do this until the end-point is nearly reached and then add the alkali drop by drop between each addition until after the end-point has been reached.

Calculation of the dissociation constant

For a weak acid, HX,

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Thus

$$\frac{1}{[H^+]} = \frac{1}{K_a} \times \frac{[X^-]}{[HX]}$$

or

$$pH = pK_a - \lg\frac{[X^-]}{[HX]}$$

When the solution was *half-neutralised*, $[X^-] = [HX]$ so that, at this point, the pH of the solution has the same value as the $pK_a(-\lg K_a)$ of the acid.

The pH of the half-neutralised solutions of carboxylic acids can be found from the titration curves obtained experimentally above.

4.11 Film

Chemical Bonding (F) (CHEM-study series). Guild Organisation Ltd.

4.12 Questions

1 Describe the bonding in methane and ethene in terms of orbitals.
Comment on the following boiling points:

$CH_3OC_2H_5$, 11°C; C_2H_5SH, 36°C; $(CH_3)_2CO$, 56°C;
$CH_3CH_2CH_2OH$, 97°C.

(C(T))

2 Discuss or explain the following.

(i) Ethanol (ethyl alcohol) boils at 78·3°C; dimethyl ether boils at $-24{\cdot}9$°C.
(ii) The pH of a solution containing ethanoic acid and sodium ethanoate is changed only slightly by the addition of a small amount of hydrochloric acid.
(iii) The effect of a magnetic field on the emissions from radio-active nuclei.
(iv) The H—C—H angle in methane is 109°28′, whilst the H—C—H angle in ethene is 120°.

(C(N and T))

3 Explain the following.

(i) The carbon–carbon bond lengths in benzene are all identical.
(ii) The carbon–oxygen bond length in dimethyl ether (1·43 Å) is longer than in propanone (1·24 Å).
(iii) Fluoroethanoic acid is a stronger acid than ethanoic acid.

4 Explain what you understand by the following terms; bond energy, hybridisation, mesomerism, delocalised bonds.

5 What do you understand by the term heat of hydrogenation?
The heats of hydrogenation of ethene and benzene are -120 and -210 kJ per mol, respectively. Comment.

Chapter 5

Alkanes

General formula

$$C_nH_{2n+2}$$

5.1 Nomenclature

The first four members of the series retain their original names. Alkanes with a straight chain containing five or more carbon atoms are named by combining a prefix derived from the Greek for the length of the chain with the suffix **-ane**.

Table 5.1. Physical properties of some alkanes

NAME	FORMULA	B.P./°C	M.P./°C	DENSITY/ g cm^{-3} (20°C)
Methane	CH_4	−162	−183	gas
Ethane	C_2H_6	−89	−172	gas
Propane	C_3H_8	−42	−188	gas
Butane	C_4H_{10}	−0·5	−135	gas
Pentane	C_5H_{12}	36	−130	0·626
Hexane	C_6H_{14}	69	−95	0·659
Heptane	C_7H_{16}	98	−91	0·684
Octane	C_8H_{18}	126	−57	0·703
Nonane	C_9H_{20}	151	−54	0·718
Decane	$C_{10}H_{22}$	174	−30	0·730
Undecane	$C_{11}H_{24}$	196	−26	0·740
Dodecane	$C_{12}H_{26}$	216	−10	0·749
Triacontane	$C_{30}H_{62}$	343	37	solid

5.2 Physical properties of alkanes

One of the characteristics of a homologous series is that successive members show a gradation of physical properties. This is illustrated for the alkanes in Table 5.1. As the series is ascended, the boiling point and density increase.

The boiling point depends on the attractive forces between the molecules of the liquid; the stronger these are, the more energy is needed to separate the molecules in order to convert the liquid into the vapour, and so the higher is the boiling point. The forces increase with the formula weight of the compound, so that when a **methylene group** (CH_2) is introduced into the alkane chain, the boiling point rises. However, as the molecular weight becomes larger, its percentage increase on introduction of a methylene group becomes smaller, so that the difference in boiling points between consecutive members of the homologous series decreases as the series is ascended, giving the smooth curve in Fig. 5.1 when the boiling point is plotted against the number of carbon atoms in the molecule.

The melting points of the alkanes do not fall on a smooth curve. As Fig. 5.2 shows, two curves can be drawn, one for the alkanes with an even number of carbon atoms and a lower one for those with an odd number. This is because, in the crystalline state, the molecules adopt a highly ordered arrangement in which the carbon chains form a zig-zag pattern. For the even

FIG. 5.1. *Plot of boiling point against the number of carbon atoms in straight-chain alkanes*

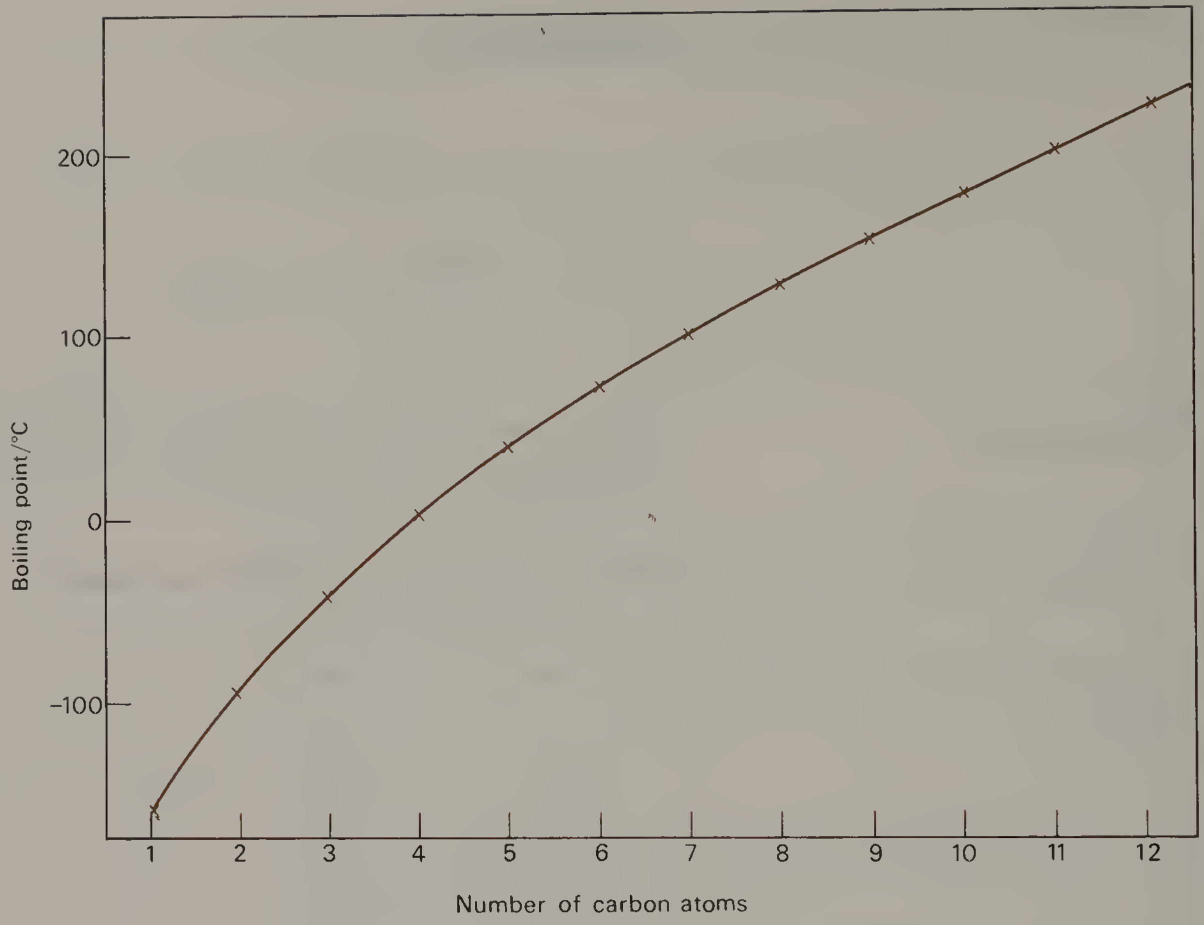
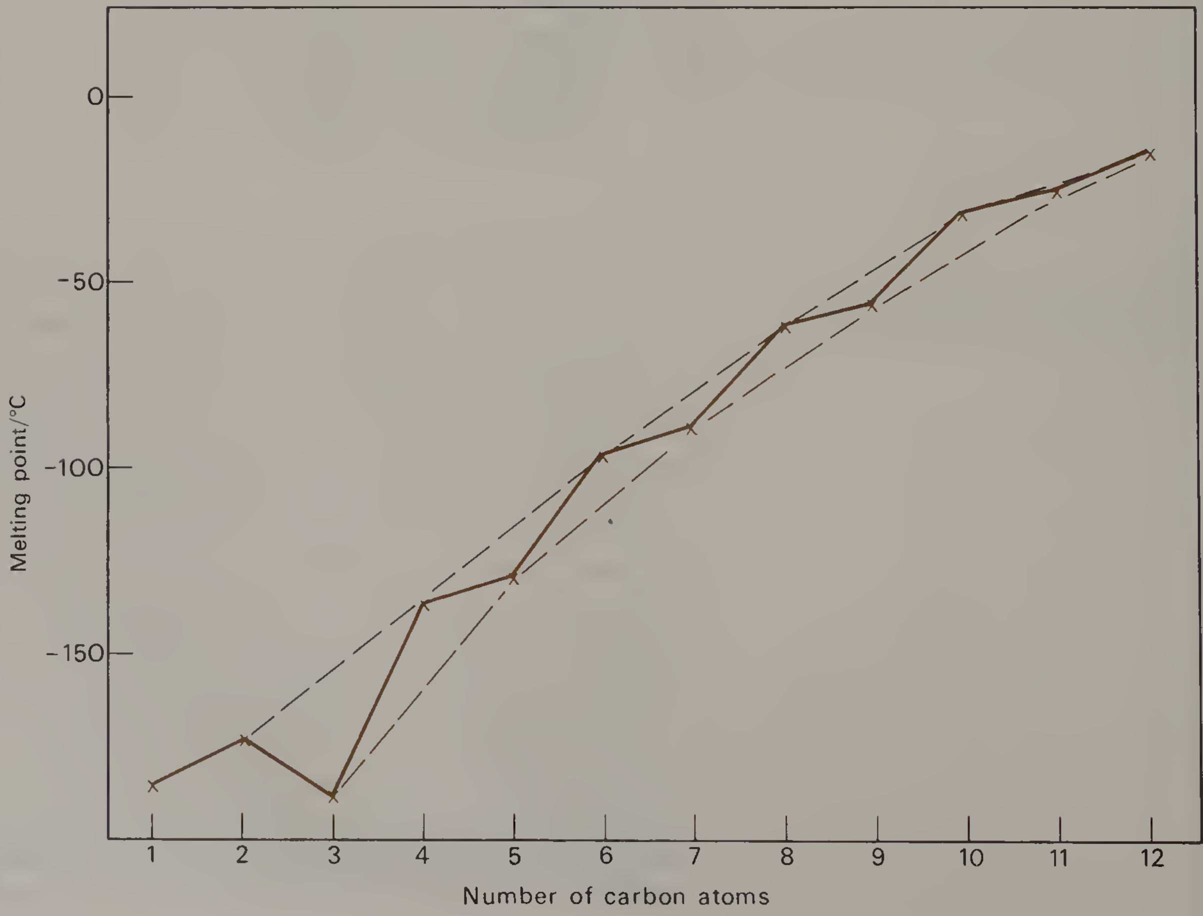


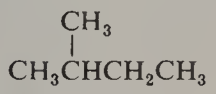
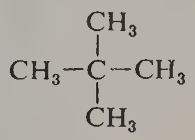
FIG. 5.2. *Plot of melting point against the number of carbon atoms in straight-chain alkanes*



members, different chains pack closer together than for the odd-numbered members, so that the attractive forces are larger for the members of the former group than for members of the latter group of similar size. It follows, in turn, that relatively more energy must be applied to separate the molecules with even numbers of carbon atoms and enable them to adopt the more random arrangement of the liquid state than to separate the molecules with odd numbers of carbon atoms.

Branched-chain alkanes have lower boiling points than their straight-chain isomers, and as branching increases the boiling point decreases still further. The examples in Table 5.2 illustrate the trend.

Table 5.2. Boiling points of the isomeric pentanes

NAME	FORMULA	B.P./°C
Pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-Methylbutane	 $CH_3\overset{\overset{\displaystyle CH_3}{\vert}}{C}HCH_2CH_3$	28
2,2-Dimethylpropane	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{C}}-CH_3$	10

The explanation is that increased branching gives the molecule a more nearly spherical shape and reduces the extent of contact between neighbouring molecules; consequently, the attractive forces are reduced and the boiling point decreases.

There is no regularity in the change of melting point with increasing branching in an alkane. This is because, whereas the linear alkanes all adopt a simple, close-packed structure in a crystal, the type of packing of branched members (and hence the attractive forces between the molecules) is not a simple function of structure.

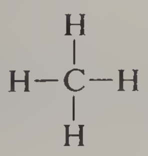
5.3
Occurrence of alkanes

The principal sources of alkanes are **natural gas** and **petroleum**. Natural gas contains mainly methane, with smaller amounts of the other gaseous alkanes such as ethane, propane and butane. Petroleum contains a wide range of alkanes, from the low molecular weight gases to the high molecular weight solids.

The uses of petroleum, both as a fuel and as a source of chemicals, are of outstanding importance. They are mentioned throughout this book, and are brought together in Chapter 20. The formation of deposits of natural gas and petroleum is discussed in Chapter 19.

5.4
Methane

Structural formula



$$H-\underset{\underset{\displaystyle H}{\vert}}{\overset{\overset{\displaystyle H}{\vert}}{C}}-H$$

Plate 5.1. An aerial view of the production platform 'Cormorant' in the North Sea. The platform is also used for pumping and storage of oil from other oil fields in the North Sea. It is linked by pipeline to the oil terminal at Sullom Voe in the Shetlands. The dish aerials and high mast on the right are part of the telephone communication system to other platforms in the North Sea and to Scotland. An idea of scale can be gained by comparing the size of the helicopter to that of the platform. (Esso Petroleum Co. Ltd.)

Occurrence

Natural gas is by far the most important source of methane (19.2). The gas is brought to Britain both by direct pipe-lines from the deposits below the North Sea and by specially constructed tankers which contain gas from the Libyan deposits which has been liquefied.

Chemical properties

1. Like the other alkanes of low formula weight, methane does not react with acids, alkalis or oxidising agents in solution. The lack of reactivity of alkanes towards inorganic reagents led to their being termed originally paraffins (Latin: *parum affinis*, little affinity).

2. Methane burns in air, with a hot, non-luminous flame, to carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Under carefully controlled conditions, methane is oxidised to other organic compounds. When a mixture of oxygen is compressed to a high pressure and passed through copper tubes at 200°C, methanol is formed:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH$$

Methane is now the most important source of ethyne. With a specially designed burner, it can be partially oxidised:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2$$

The heat liberated in this reaction is used to raise the temperature of a further amount of methane, which is heated for a very short time at 1500°C:

$$2CH_4 \rightarrow CH{\equiv}CH + 3H_2$$

Methane is also oxidised when it is mixed with steam and passed over nickel, and this reaction is used as a method for the manufacture of carbon monoxide and hydrogen ('synthesis gas', p. 321):

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

3. When methane and chlorine are mixed together *in the dark*, no reaction occurs. However, if the mixture is either heated or exposed to ultraviolet light (from a mercury lamp), a mixture of products is formed:

$$CH_4 + Cl_2 \rightarrow \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \rightarrow \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

With an excess of methane, chloromethane predominates, whereas with an excess of chlorine, tetrachloromethane is the main product.

These are examples of **substitution reactions**: substitution is defined as the replacement of one atom (or group of atoms) in a molecule by another atom (or group). When the reaction is brought about by ultraviolet light, it is described as a **photochemical reaction**.

A detailed examination of the relatively simple reaction between methane and chlorine to form chloromethane and hydrogen chloride:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \qquad \Delta H = -100 \text{ kJ mol}^{-1}$$

illustrates many interesting principles. First, although the reaction is exothermic, energy (in the form of either heat or light) must be supplied to the mixture for reaction to begin. Methane is transparent to ultraviolet light of

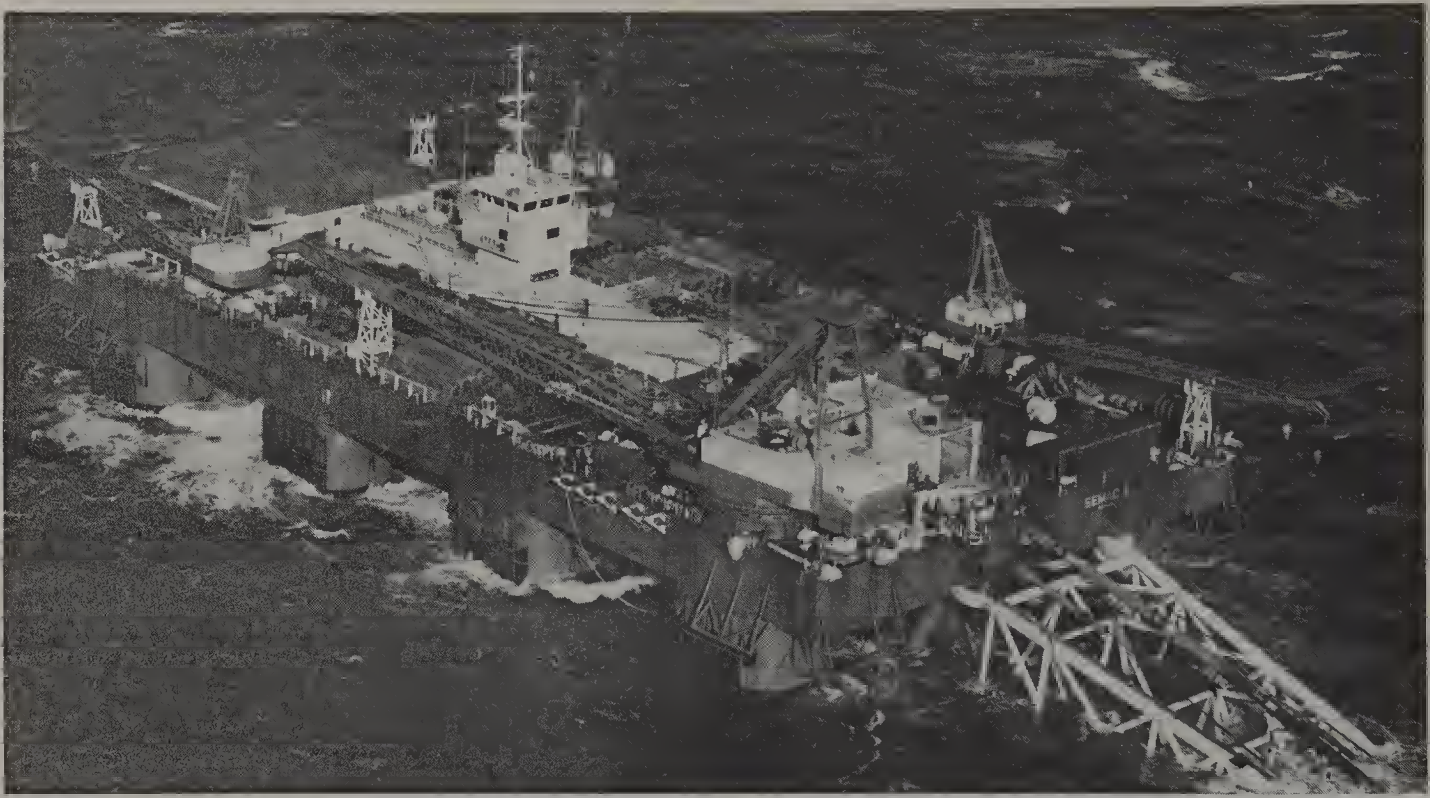


Plate 5.2. An undersea pipeline for gas being laid by a semi-submersible barge (above). The pipeline (1 m in diameter) coming ashore from the North Sea on to a beach near Aberdeen, Scotland. (Shell Photo Service).

the wavelength used, about 300 nm, but chlorine is not. Chlorine absorbs the light, the energy of which is equivalent to about 400 kJ mol^{-1}; this is considerably greater than the bond strength of the chlorine molecule (242 kJ mol^{-1}) which consequently splits into chlorine atoms:

$$\text{Cl—Cl} \rightarrow \text{Cl}\cdot + \cdot\text{Cl} \qquad (1)$$

Each atom retains one electron of the pair which formed the covalent bond. An atom or group of atoms which possesses an unpaired electron is called a **free radical** (p. 66). The energy supplied to the chlorine molecule is not enough to produce ions, Cl^+ and Cl^- (1130 kJ mol^{-1}).

Each chlorine atom then reacts with a molecule of methane by abstracting a hydrogen atom to form hydrogen chloride and a methyl radical:

$$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot\text{CH}_3 \qquad (2)$$

The methyl radical reacts with a molecule of chlorine to form chloromethane and a chlorine atom:

$$\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot \qquad (3)$$

The chlorine atom produced by reaction (3) can then react with another molecule of methane according to reaction (2); thus reactions (2) and (3) can occur successively once an initial supply of chlorine atoms has been provided.

However, there are other reactions which can intervene to stop the successive occurrence of reactions (2) and (3); these are processes in which two free radicals combine with each other:

$$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2 \qquad (4)$$

$$\text{Cl}\cdot + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{Cl} \qquad (5)$$

$$\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \qquad (6)$$

Now, at any instant, the concentrations of chlorine atoms and methyl radicals are very small compared with the concentration of methane and chlorine. Therefore, the chances of a collision between two atoms, an atom and a radical, or two radicals, are small compared with the chances of a collision between a chlorine atom and a molecule of methane or between a methyl radical and a molecule of chlorine. As a result, many thousands of molecules of chloromethane are formed by reactions (2) and (3) for each molecule of chlorine which is decomposed by reaction (1).

The characteristics described above are typical of a **chain reaction**. There is an **initiating step**—reaction (1); **propagating steps**, which keep the chain reaction in operation—reactions (2) and (3); and **terminating steps**, which bring the chain to an end—reactions (4), (5) and (6).

It is often difficult to test for whether a reaction occurs *via* free radicals. Two methods in this case involve adding another substance. For example, if tetraethyllead vapour is added, the reaction rate is increased considerably. This is because the lead compound decomposes to supply more free radicals:

$$(\text{C}_2\text{H}_5)_4\text{Pb} \rightarrow 4\cdot\text{C}_2\text{H}_5 + \text{Pb}$$

some of which react with chlorine to form chlorine atoms:

$$\cdot\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}\cdot$$

On the other hand, if oxygen is added, the rate is reduced, probably because oxygen reacts with methyl radicals and so prevents them taking any further part in the chain reaction.

In reactions (1), (2) and (3) covalent bonds are broken so that one electron of the pair in each bond becomes associated with each of the atoms or groups. These are examples of **homolysis** or **homolytic fission** (Greek: *lysis*, splitting). A second way in which a bond can undergo fission is for both electrons of the bond to become associated with one of the two atoms or groups:

$$A—B \rightarrow A^+ + B^-$$

Examples of this process, **heterolysis** or **heterolytic fission**, are described in the next chapter.

Uses

The uses of methane are discussed above and in Section 20.3.

5.5
Other alkanes

Ethane, propane and butane are obtained in two ways: from 'wet' natural gas (available in large quantities, for example, in the United States) (19.2) and from the gas above, and dissolved under pressure in, oil deposits (for example, in the North Sea, off the coast of the United Kingdom) (19.3).

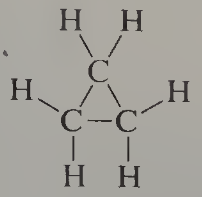
The alkanes are heated to high temperature in absence of air, a process known as **cracking**, to yield ethene and propene (20.4). In turn, these two alkenes are the major starting materials for a wide variety of polymers (21.2) and other important chemicals (20.4).

The other properties of ethane and propane are similar to those of methane. They do not react with acids, alkalis or oxidising agents in solution; they burn in air; and they are readily chlorinated. A large number of chloroalkanes can be made; for example, ethane gives chloroethane (C_2H_5Cl), two dichloroethanes ($ClCH_2—CH_2Cl$ and $CH_3—CHCl_2$), two trichloroethanes ($ClCH_2—CHCl_2$ and $CH_3—CCl_3$), two tetrachloroethanes ($ClCH_2—CCl_3$ and $Cl_2CH—CHCl_2$), pentachloroethane ($Cl_2CH—CCl_3$) and hexachloroethane ($Cl_3C—CCl_3$).

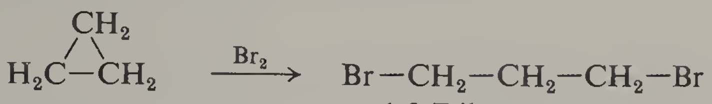
The uses of ethane and higher alkanes are described in Section 20.3.

5.6
Cycloalkanes

Cycloalkanes are classified as **alicyclic** compounds. The simplest is cyclopropane:

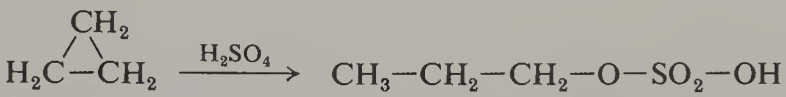


The angles between the atoms in the ring are 60°, whereas sp^3 orbitals are at angles of 109° 28′. Consequently, the overlap between the pairs of orbitals is not as complete as in the non-cyclic alkanes, and so the C—C bond strengths are less; the ring is said to be **strained**. This in turn makes cyclopropane more reactive than, for example, propane towards reagents which break C—C bonds. Thus, cyclopropane reacts readily with bromine in the absence of light:



1,3-Dibromopropane

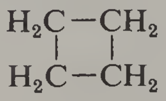
and with sulphuric acid:



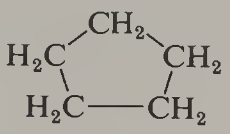
Propyl hydrogensulphate

In these respects it resembles an alkene such as propene (6.4).

In cyclobutane, the angles between the carbon atoms are 90°. Thus, the ring is strained, although not so much as in cyclopropane. As would be expected, cyclobutane undergoes the same reactions as cyclopropane but less readily.



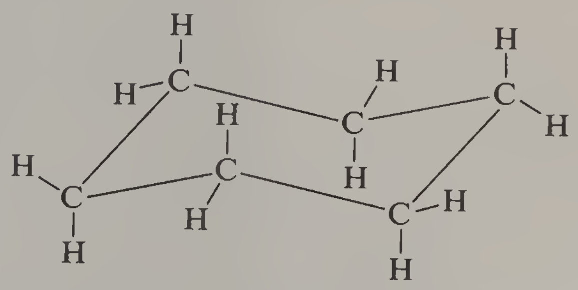
Cyclobutane



Cyclopentane

Cyclopentane has bond angles of 108°, so close to the tetrahedral value that the ring can be regarded as strainless. As expected, it resembles the non-cyclic alkanes and does not undergo the ring-opening reactions of cyclopropane and cyclobutane.

The structure of cyclohexane is of particular note. Were the carbon atoms in a plane, the bond angles would be 120° and would therefore be strained, though in the opposite sense compared with those in cyclopropane. However, the preferred angle of 109° 28′ can be obtained by 'buckling' of the ring, and this is indeed the structure of cyclohexane; a two-dimensional representation is



and is sometimes referred to as the **chair** structure. All the cycloalkanes with seven or more members in the ring have strainless or nearly strainless structures, although the exact shapes of the larger ones are not known. They all resemble the non-cyclic alkanes in their properties.

5.7 Practical work

Carry out the following reactions with a liquid alkane (e.g. pentane or hexane) and a liquid cycloalkane (e.g. cyclohexane).

1. Place a few drops of the liquid on a watch-glass or an evaporating basin and apply a lighted splint. Note the colour of the flame.

2. To a few drops of the liquids in separate test-tubes, add:
   (a) 5 drops of an alkaline potassium manganate(VII) solution (made by dissolving about 0·1 g of sodium carbonate in 1 cm^3 of a 1 per cent solution of potassium manganate(VII)), shake the mixture and see whether the liquid is oxidised;
   (b) 5 drops of a solution of bromine in tetrachloromethane, shake the mixture and see whether the bromine is decolorised.

3. Cracking of paraffin oil. See p. 311.

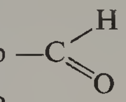
5.8 Resource materials

Lists of films, videotapes and further reading on prospecting for petroleum and natural gas, and the subsequent manufacture of chemicals, are given on pages 313 and 324–5.

5.9 Questions

1 Outline **two** laboratory methods for the preparation of methane. Give **two** instances of the natural occurrence of methane.

From the properties of methane deduce the characteristic chemical behaviour of the carbon–hydrogen linkage in organic chemistry. How is the behaviour of this linkage modified when it occurs

(a) in the group  $-C(H)=O$ (as in ethanal),

(b) in benzene?

To 30 cm^3 of a mixture of methane and carbon monoxide are added 50 cm^3 of oxygen, and the mixture is exploded. After shaking with potassium hydroxide solution, 20 cm^3 of gas are left. Calculate the composition by volume of the original mixture. (All volumes are measured at room temperature and pressure.) (JMB)

2 Give equations for four methods of preparing ethane, naming the reagents and stating the conditions required.

Indicate briefly how and under what conditions methane reacts with chlorine.

Give the molecular formula for the hydrocarbon of molecular weight 56, and write down structural formulae for the isomers.

3 Give two methods for preparing ethane in the laboratory.

A mixture of 10 cm^3 of a gaseous hydrocarbon and 100 cm^3 of oxygen (excess) was exploded. The volume after explosion was 75 cm^3, and this was reduced to 35 cm^3 on treatment with potassium hydroxide solution. Deduce the molecular formula of the hydrocarbon and give its possible structural formulae. (All measurements were made at the same temperature and atmospheric pressure.)

4 Give equations, and conditions, for the reactions (if any) between methane and (a) chlorine, (b) bromine in the absence of light, (c) sulphuric acid.

How would you expect cyclobutane to react with these reagents?

5 An equimolar mixture of methane and chlorine is made up.
   (i) What, if anything, happens if the mixture is stored in the dark?
   (ii) What would you expect to happen if the mixture were exposed to sunlight?
   (iii) What is the importance of the sunlight in the above reaction?
   (iv) What mechanism would you propose for the reaction in (ii)?
   (v) Name the reactive species in this mechanism.

Chapter 6

Alkenes

General formula

$$C_nH_{2n}$$

6.1 Nomenclature

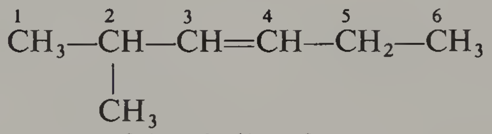
The compounds are named as for the alkanes, but with the suffix **-ene** instead of -ane and the inclusion before the suffix of a number to describe the position of the double bond in the chain where more than one is possible. For this purpose, the chain is numbered from the end nearer to the double bond and the lower number of the two which describe the positions of the carbon atoms in the double bond is employed. For example:

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

But-1-ene

$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

Pent-2-ene



$$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{CH}}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

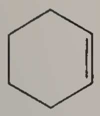
2-Methylhex-3-ene

The two lowest members of the series are sometimes described by their original names: ethene ($CH_2=CH_2$) is known as ethylene, and propene ($CH_3-CH=CH_2$) as propylene. 2-Methylpropene, $(CH_3)_2C=CH_2$, is sometimes referred to as isobutylene or isobutene.

6.2 Physical properties of alkenes

The melting points and boiling points of the alkenes are very close to those of the alkanes with the same number of carbon atoms. Ethene, propene and the butenes are gases at room temperature, and the higher members are liquids (Table 6.1).

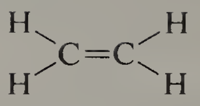
Table 6.1. Some alkenes

NAME	FORMULA	B.P./°C
Ethene	$CH_2=CH_2$	−102
Propene	$CH_3-CH=CH_2$	−48
But-1-ene	$C_2H_5-CH=CH_2$	−6·5
trans-But-2-ene*	$CH_3-CH=CH-CH_3$	1
cis-But-2-ene*	$CH_3-CH=CH-CH_3$	4
2-Methylpropene	$(CH_3)_2C=CH_2$	−6·5
Pent-1-ene	$C_3H_7-CH=CH_2$	30
Hex-1-ene	$C_4H_9-CH=CH_2$	63
Cyclohexene		83
Phenylethene	$C_6H_5-CH=CH_2$	145

* These are geometrical isomers, which are discussed in Section 15.4.

6.3 Ethene

Structural formula



Manufacture

The naphtha fraction from the distillation of petroleum, which contains alkanes with 4–10 carbon atoms, is passed with steam through pipes heated at 700–900°C. The ethene formed is purified by fractional distillation (20.4).

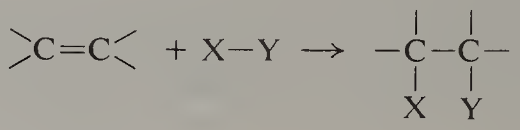
Smaller alkanes, such as ethane and propane, which are available (depending on geographic location) either in 'wet' natural gas or in the gas above and dissolved in oil deposits (5.5), are cracked with steam in a similar way.

Both processes yield a variety of products, of which ethene and propene are the most important. They are separated and purified by distillation.

Chemical properties

(a) Addition reactions

Ethene, and all other alkenes, are characterised by their addition reactions in which the double bond is converted into a single bond and atoms or groups are added to each of the two carbon atoms. The general reaction is:



$$>C{=}C< \; + \; X{-}Y \;\rightarrow\; -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{Y}{\overset{|}{\underset{|}{C}}}-$$

The following are examples:

1. When ethene is mixed with hydrogen and passed over nickel at 150°C, ethane is formed:

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Ni as cat.}} CH_3{-}CH_3$$

The reaction takes place on the surface of the metal, which acts as a catalyst. Finely divided platinum or palladium are more active catalysts, and reaction takes place at room temperature.

2. Ethene reacts with chlorine to form 1,2-dichloroethane:

$$CH_2{=}CH_2 + Cl_2 \rightarrow \underset{\text{1,2-Dichloroethane}}{ClCH_2{-}CH_2Cl}$$

Similarly, with bromine, it forms 1,2-dibromoethane:

$$CH_2{=}CH_2 + Br_2 \rightarrow \underset{\text{1,2-Dibromoethane}}{BrCH_2{-}CH_2Br}$$

There is considerable evidence that these are *ionic* reactions (compare the *free-radical* reaction by which methane and chlorine give chloromethane, p. 75). Important information about the mechanism is provided by the observation that, if bromine is added to a solution of ethene in which sodium chloride is also present, 1-bromo-2-chloroethane is formed in addition to 1,2-dibromoethane. This points to the mediation of an organic cation which can react with either bromide ion or chloride ion:

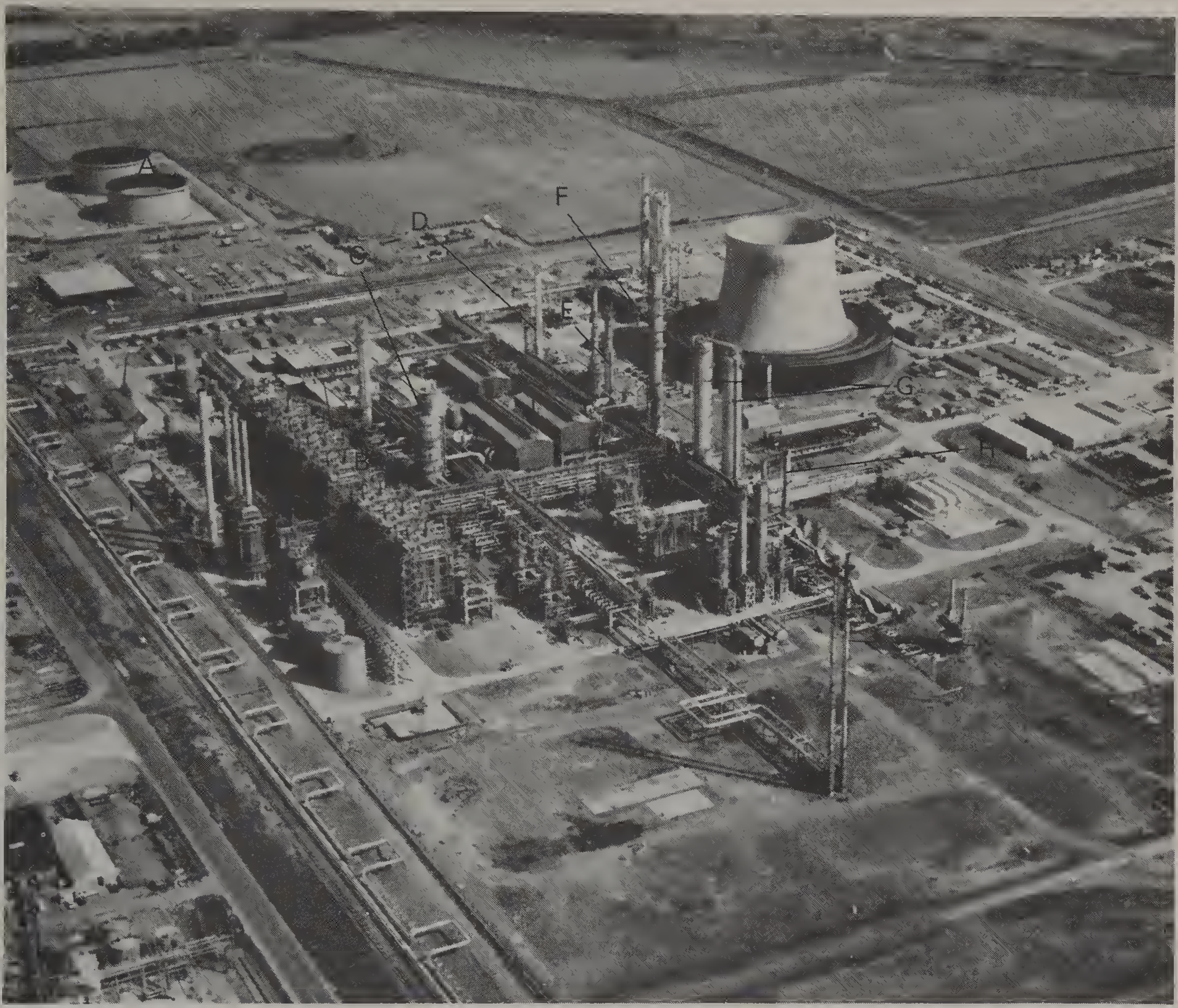
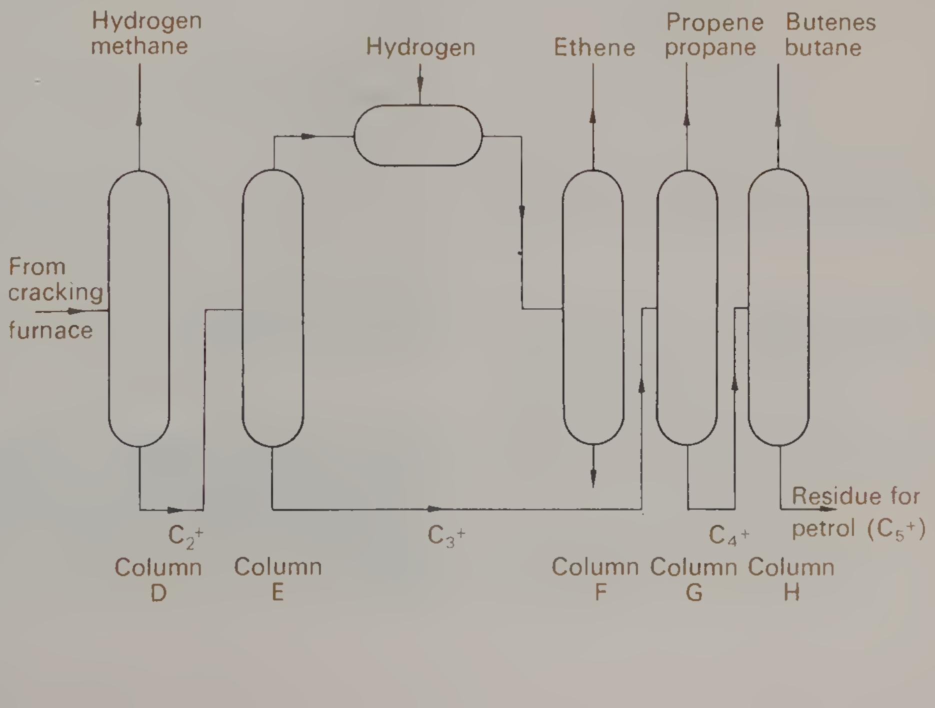
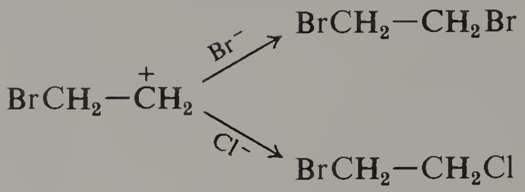


Plate 6.1. Steam cracking of naphtha to form alkenes (principally ethene and propene). This photograph shows one of the largest plants of its kind in Europe. A—Naphtha storage, B—Furnaces to crack naphtha, C—Primary fractionating column. Other fractionating columns are shown which remove D—methane, E—ethene and ethane, F—ethene from ethane, G—propene and propane, H—butenes and butane. Other parts of the site include I—steam boilers, J—compressors, K—flame stacks. (Imperial Chemical Industries PLC). See also Fig. 20.1.



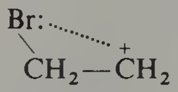
$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2{-}\overset{+}{C}H_2 + Br^-$$



$$BrCH_2{-}\overset{+}{C}H_2 \xrightarrow{Br^-} BrCH_2{-}CH_2Br$$
$$BrCH_2{-}\overset{+}{C}H_2 \xrightarrow{Cl^-} BrCH_2{-}CH_2Cl$$

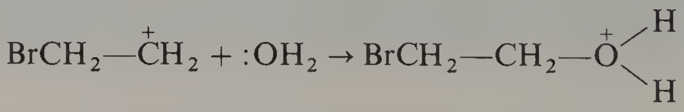
The cation $BrCH_2{-}\overset{+}{C}H_2$, and other cations in which a carbon atom bears the positive charge, are given the general name **carbonium ions**. In the first step the two electrons which form the new bond are both provided by the alkene; thus, the reagent (bromine or chlorine) is described as **electrophilic** (i.e. 'electron-seeking').

There is evidence that the cation $BrCH_2{-}\overset{+}{C}H_2$ should be more properly represented as



in which there is an (electrostatic) interaction between an unshared pair of electrons on bromine and the positively charged carbon atom. However, this idea does not affect the main conclusions here.

When the reaction with bromine is carried out in water, the main product is 2-bromoethanol. The first step of the reaction is the same as above, but the carbonium ion is a very reactive species which reacts with a molecule of water almost as readily as with a bromide ion; since there is much more water than bromide ion in the solution, the reaction with water predominates. The reaction occurs by the donation of an unshared pair of electrons on the oxygen atom of water to the electron-deficient carbon atom in the carbonium ion, followed by the loss of a proton:



$$BrCH_2{-}\overset{+}{C}H_2 + {:}OH_2 \rightarrow BrCH_2{-}CH_2{-}\overset{+}{O}H_2$$

$$\rightarrow BrCH_2{-}CH_2OH + H^+$$

2-Bromoethanol

A similar reaction occurs between ethene and chlorine water, 2-chloroethanol being formed.

3. Ethene reacts with hydrogen chloride to give chloroethane:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3{-}CH_2Cl$$

This is also an ionic reaction. The first step is the formation of two ions, the ethyl cation and the chloride anion:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3{-}\overset{+}{C}H_2 + Cl^-$$

The two ions then rapidly combine to form the product. In this reaction, hydrogen chloride is the electrophilic reagent.

Hydrogen bromide reacts more readily than hydrogen chloride, giving bromoethane, and hydrogen iodide reacts more readily still to give iodoethane.

4. When ethene is passed through concentrated sulphuric acid. ethyl hydrogensulphate is formed:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow \underset{\text{Ethyl hydrogensulphate}}{CH_3{-}CH_2{-}O{-}SO_2{-}OH}$$

Once again a carbonium ion is formed first, by reaction with the electrophilic sulphuric acid:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3{-}\overset{+}{C}H_2 + {}^{-}O{-}SO_2{-}OH$$

This ion then combines with a hydrogensulphate ion:

$$CH_3{-}\overset{+}{C}H_2 + {}^{-}O{-}SO_2{-}OH \rightarrow CH_3{-}CH_2{-}O{-}SO_2{-}OH$$

When the mixture is diluted and warmed, ethanol is produced:

$$CH_3CH_2{-}O{-}SO_2{-}OH + H_2O \rightarrow CH_3CH_2{-}OH + H_2SO_4$$

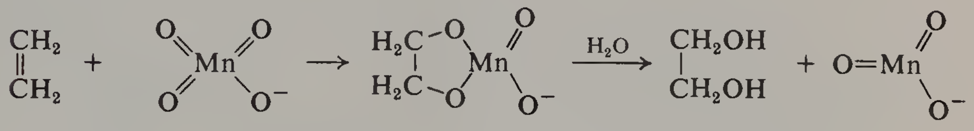
This is the basis of a method for manufacturing ethanol from ethene, but it is now being superseded by direct hydration with a solid catalyst (phosphoric acid on silica) at 300°C:

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_3PO_4/SiO_2\text{ as cat.}} CH_3CH_2OH$$

5. When ethene is passed through a dilute, alkaline solution of potassium manganate(VII), ethane-1,2-diol (ethylene glycol) is formed:

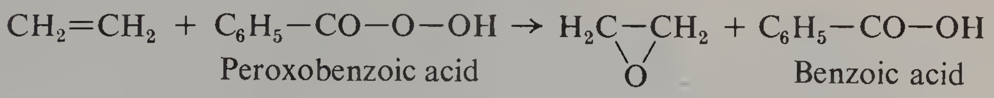
$$CH_2{=}CH_2 + H_2O + \text{‘O’} \rightarrow \underset{\text{Ethane-1,2-diol}}{HO{-}CH_2{-}CH_2{-}OH}$$

The manganate(VII) is the source of the necessary oxygen atom denoted ‘O’. The oxygen atom is never free but is thought to be transferred from the manganate(VII) ion to the alkene *via* a cyclic intermediate which is too unstable towards water to be isolated:



(Two MnO_3^- ions disproportionate to one $MnO_4{}^{2-}$ ion and MnO_2.)

6. When ethene is treated with a **peroxoacid** (a compound containing the group—CO—O—OH), epoxyethane is formed; for example, peroxobenzoic acid can be used:



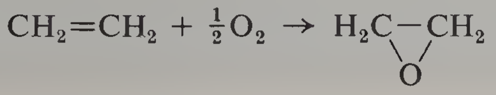
$$CH_2{=}CH_2 + \underset{\text{Peroxobenzoic acid}}{C_6H_5{-}CO{-}O{-}OH} \rightarrow \underset{\text{Epoxyethane}}{H_2C{-}CH_2\ (\text{O bridge})} + \underset{\text{Benzoic acid}}{C_6H_5{-}CO{-}OH}$$

Peroxobenzoic acid

Epoxyethane

Benzoic acid

Industrially, epoxyethane is made by passing a mixture of ethene and oxygen over a silver catalyst at 250°C:



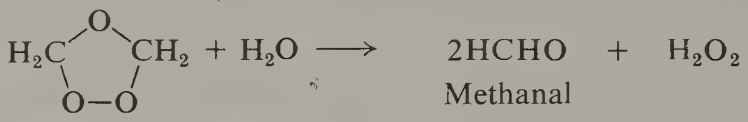
$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow H_2C{-}CH_2$$

(b) Other reactions

1. When trioxygen is passed through a solution of ethene in trichloromethane, ethene ozonide is formed:

Ethene ozonide

It is an unstable, explosive product, which is readily hydrolysed with water to a mixture of methanal and hydrogen peroxide; half the methanal is then oxidised to methanoic acid by the hydrogen peroxide.



$$HCHO + H_2O_2 \longrightarrow \underset{\text{Methanoic acid}}{HCO_2H} + H_2O$$

2. When subjected to very high pressures at 120°C in the presence of oxygen as a catalyst, ethene undergoes **polymerisation** to give the polymer, poly(ethene) (also known as polythene) (p. 328). Polymerisation is also catalysed by a mixture of triethylaluminium and titanium(IV) chloride, and this gives a type of poly(ethene) with more useful properties (p. 328).

Plate 6.2. Hortonspheres used to store liquefied gases (for example, ethene, propane and butanes, chloroethene) (Esso Petroleum Co. Ltd.)

Uses

Ethene is one of the most important raw materials for the chemical industry, particularly in making plastics (p. 328). One of these, poly(ethene), is made directly from ethene (21.2). A second, poly(chloroethene), is made from ethene *via* chloroethene. Ethene is chlorinated to form 1,2-dichloroethane, which is then vapourised and heated at 500°C to form chloroethene:

$$CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2{-}CH_2Cl$$

$$ClCH_2{-}CH_2Cl \rightarrow \underset{\text{Chloroethene}}{CH_2{=}CHCl} + HCl$$

Hydrogen chloride is separated and then passed with more ethene and oxygen over copper(II) chloride at 250°C. This is called an oxychlorination process:

$$CH_2{=}CH_2 + HCl + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CHCl + H_2O$$

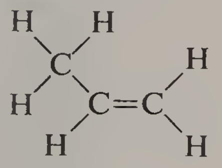
In this way, no chlorine is wasted. Each mole of chlorine yields two moles of chloroethene.

Ethene is also made into ethanol (used as a solvent and as a starting material for other products), epoxyethane (used in the manufacture of detergents and of ethane-1,2-diol), ethanal and higher straight-chain alkenes, used to make detergents.

The uses of ethene are further discussed in Section 20.4.

6.4
Propene

Structural formula



Manufacture

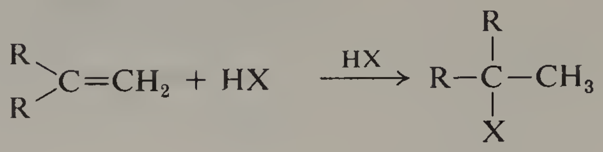
Propene is obtained with ethene from the cracking of alkanes. The processes are outlined on p. 80.

Chemical properties

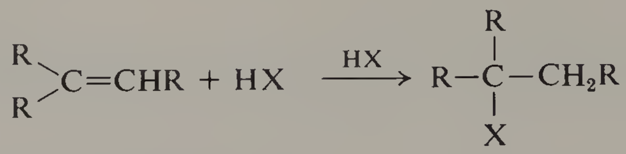
The chemistry of propene is similar to that of ethene. It burns in air, can be reduced with hydrogen over metal catalysts, is polymerised to poly(propene) (p. 328) and undergoes addition reactions with the halogen acids, the halogens, sulphuric acid, potassium manganate(VII) and peroxoacids. However, there is a feature in its reactions with acidic reagents which does not apply to ethene; thus, reaction with an acid of general formula HX could give either of two products:

$$CH_3{-}CH{=}CH_2 + HX \rightarrow CH_3{-}CH_2{-}CH_2X \text{ or } CH_3{-}CHX{-}CH_3$$

In practice, the second of these products is the major one. With more highly substituted alkenes, the major products are as follows:



$$R_2C{=}CH_2 + HX \xrightarrow{HX} R\text{—}\underset{X}{\overset{R}{C}}\text{—}CH_3$$



$$R_2C{=}CHR + HX \xrightarrow{HX} R\text{—}\underset{X}{\overset{R}{C}}\text{—}CH_2R$$

These observations were first made by Markownikoff and can be summarised as an empirical rule known as **Markownikoff's rule**: when an acid HX adds to the double bond of an alkene, the hydrogen atom becomes attached to the carbon atom which has the larger number of hydrogen atoms.

The principle which underlies this empirical rule is as follows. The proportion of each of the two products from an alkene is determined by the relative rates of the addition of the proton to each carbon atom, for once this step has occurred the uptake of an anion X^- follows immediately. Now, of the two possible carbonium ions which can be formed during the first step of the reaction of propene,

$$CH_3\text{—}CH_2\text{—}\overset{+}{C}H_2 \qquad\qquad CH_3\text{—}\overset{+}{C}H\text{—}CH_3$$

the first is a primary carbonium ion, with only one alkyl group attached to the positively charged carbon atom, whereas the second is a secondary carbonium ion, with two alkyl groups attached to the positively charged carbon atom. Since an alkyl group is electron-releasing relative to a hydrogen atom (4.8), it reduces the density of positive charge on the neighbouring carbon atom, and this makes the ion more stable. Two alkyl groups are more effective than one, so that the secondary carbonium ion is more stable than the primary carbonium ion. Consequently, the secondary ion is formed the more rapidly, and the major product from propene is of the type $CH_3\text{—}CHX\text{—}CH_3$.

When three alkyl groups are attached to a positively charged carbon atom, the stabilising effect is increased further; i.e. the order of stability of carbonium ions is tertiary > secondary > primary. Thus,

$$R_2C{=}CH_2 \text{ forms } \underset{\text{tertiary}}{R_2\overset{+}{C}\text{—}CH_3} \text{ faster than } \underset{\text{primary}}{R_2CH\text{—}\overset{+}{C}H_2}$$

$$R_2C{=}CHR \text{ forms } \underset{\text{tertiary}}{R_2\overset{+}{C}\text{—}CH_2R} \text{ faster than } \underset{\text{secondary}}{R_2CH\text{—}\overset{+}{C}HR}$$

Free-radical addition to propene

When propene reacts with hydrogen bromide in the presence of an organic peroxide, the product is mainly 1-bromopropane:

$$CH_3\text{—}CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3\text{—}CH_2\text{—}CH_2\text{—}Br$$

whereas in the absence of a peroxide the main product is 2-bromopropane.

This is because, in the presence of a peroxide, a radical chain reaction occurs which is more rapid than the electrophilic addition which gives 2-bromopropane. The peroxide, containing the relatively weak O—O bond (p. 54), breaks down to give two radicals:

$$R—O—O—R \rightarrow 2R—O\cdot$$

These radicals react with hydrogen bromide to give a bromine atom:

$$R—O\cdot + H—Br \rightarrow R—O—H + Br\cdot$$

The bromine atom adds to the alkene mainly at the unsubstituted carbon atom, giving the radical $CH_3—\dot{C}H—CH_2—Br$ (which is more stable than the alternative radical, $CH_3—CHBr—\dot{C}H_2$):

$$CH_3—CH{=}CH_2 + Br\cdot \rightarrow CH_3—\dot{C}H—CH_2—Br$$

and this radical abstracts a hydrogen atom from another molecule of hydrogen bromide:

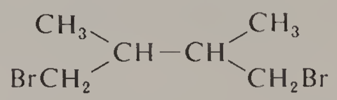
$$CH_3—\dot{C}H—CH_2—Br + H—Br \rightarrow CH_3—CH_2—CH_2—Br + Br\cdot$$

The bromine atom formed can add to another molecule of propene, so that a chain reaction is propagated; the chain ends when two radicals meet and combine. In summary:

$$\text{Initiation} \begin{cases} RO—OR \rightarrow 2RO\cdot \\ RO\cdot + HBr \rightarrow ROH + Br\cdot \end{cases}$$

$$\text{Propagation} \begin{cases} Br\cdot + CH_3—CH{=}CH_2 \rightarrow CH_3—\dot{C}H—CH_2Br \\ CH_3—\dot{C}H—CH_2Br + HBr \rightarrow CH_3—CH_2—CH_2Br + Br\cdot \end{cases}$$

$$\text{Termination} \begin{cases} 2Br\cdot \longrightarrow Br_2 \\ Br\cdot + CH_3-\dot{C}H-CH_2Br \longrightarrow CH_3-CHBr-CH_2Br \\ 2CH_3-\dot{C}H-CH_2Br \longrightarrow \end{cases}$$



Hydrogen chloride and hydrogen iodide do not react in this way. This is because, although halogen atoms are generated in the initiation step in each case, one or other of the propagating steps is so slow that the overall rate of the chain reaction is less than that of the electrophilic addition. With hydrogen chloride, the slow step is

$$CH_3—\dot{C}H—CH_2Cl + HCl \rightarrow CH_3—CH_2—CH_2Cl + Cl\cdot$$

and with hydrogen iodide it is

$$I\cdot + CH_3—CH{=}CH_2 \rightarrow CH_3—\dot{C}H—CH_2I$$

Since alkenes form peroxides slowly when exposed to air, it is not always necessary to add a peroxide in order to bring about the chain reaction with hydrogen bromide. Indeed, if the product of the electrophilic addition is required, it is necessary for the alkene to be a freshly prepared (or freshly distilled) sample.

Uses

As with ethene, the principal use of propene is as a raw material to make plastics, the most important being poly(propene), poly(propenenitrile) (*via* propenenitrile), perspex (*via* propanone) and the glyptal resins (*via* propane-1,2,3-triol). These are discussed in more detail in Chapter 21.

The single most important chemical made from propene is propanone (12.3). The uses of propene are summarised in Section 20.4.

6.5 Practical work

Small-scale preparation of cyclohexene

To 10 cm^3 of cyclohexanol in a flask, add, with a dropping pipette, 4 cm^3 of concentrated phosphoric acid, shaking the flask.

Assemble the apparatus (Fig. 6.1), and heat the flask gently, distilling over the liquid.

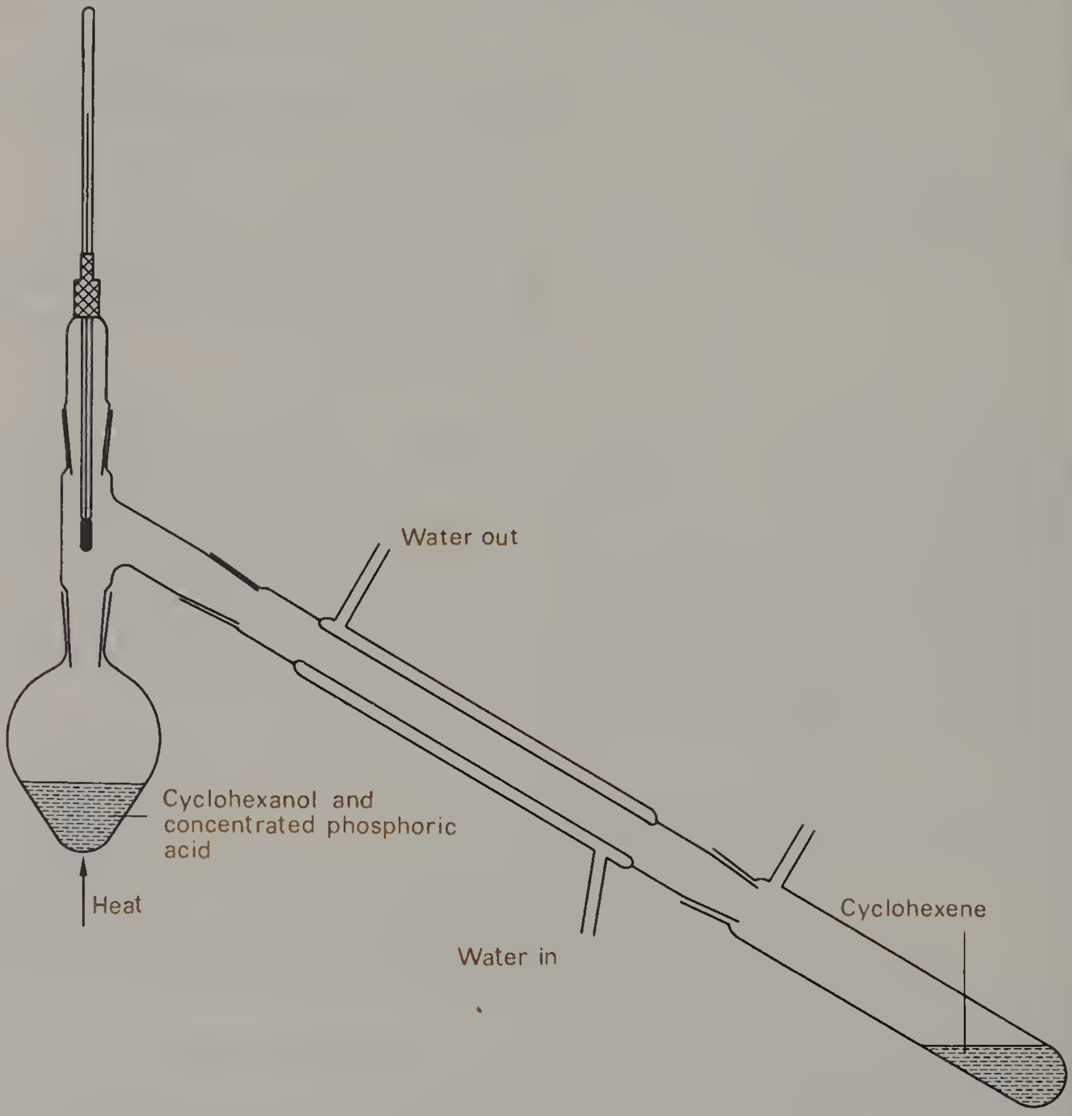


FIG. 6.1. *Preparation of cyclohexene*

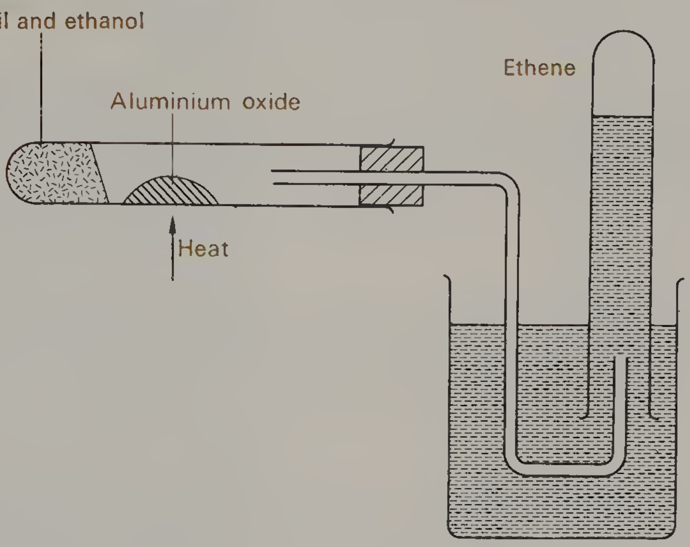
Pour the distillate into a separating funnel and add 2 cm^3 of a saturated solution of sodium chloride. Shake the mixture and allow the two layers to separate. Run off the lower layer and then run the top layer, containing cyclohexene, into a small flask. Add 2 or 3 pieces of anhydrous calcium chloride, stopper the flask and shake until the liquid is clear.

Decant the liquid into a clean distillation flask and distil it, collecting the liquid boiling at 81–85°C.

Test-tube preparation of ethene

Place ethanol in a test-tube, to a depth of 2·5 cm. Add Rocksil until the ethanol has been soaked up. Place about 1 g of aluminium oxide half-way along the tube (Fig. 6.2). Fit a cork and delivery tube to the test-tube and heat the aluminium oxide with a gentle flame. Collect 4 or 5 test-tubes of ethene by displacement of water, placing corks in the test-tubes when they have been filled.

FIG. 6.2. *Test-tube preparation of ethene*



Cracking of oil to form alkenes

For details, see Section 19.10.

Reactions of alkenes

Carry out the following reactions with a gaseous alkene (*e.g. ethene*) *and a liquid alkene* (*e.g. cyclohexene*), *comparing the results of experiments* 1–3 *with those obtained with an alkane* (5.7).

1. (a) Ignite the ethene by applying a lighted splint to the mouth of the test-tube.
(b) Place a few drops of cyclohexene on a watch-glass and ignite.
Note the colour of the flame.

2. (a) Add a few drops of a solution of bromine in tetrachloromethane to a test-tube of ethene and shake the mixture.
(b) To a few drops of cyclohexene in a test-tube add a few drops of bromine in tetrachloromethane and shake the mixture.

3. (a) Add 3–4 drops of an alkaline solution of potassium manganate(VII) (made by dissolving about 0·1 g of anhydrous sodium carbonate in 1 cm^3 of a 1 per cent solution of potassium manganate(VII)) to a test-tube of ethene and shake the mixture.
Note the colour of the solution and whether any precipitate is formed.
(b) Repeat this experiment using 2 or 3 drops of cyclohexene instead of ethene.

4. *Polymerisation of alkenes.* The polymerisation of an aromatic alkene, phenylethene, $C_6H_5—CH=CH_2$, is described on p. 341.

5. *Mechanism of the addition of bromine to an alkene.*

Take especial care during this experiment. Bromine liquid and vapour are harmful to the skin and to breathe. You are advised to wear protective gloves as well as eye-protection and, if possible, to keep the experiment in a fume-cupboard.

(a) Make up a solution of 5 cm³ of cyclohexene in 10 cm³ of ethanol in a 100 cm³ conical flask. Add 2 cm³ of a saturated solution of sodium nitrate in water. Some of this salt recrystallises out of solution. Add water dropwise, with shaking, until the sodium nitrate redissolves.

Shake the solution vigorously, so that the two layers are thoroughly mixed, and add bromine, from a 10 cm³ burette at a rate not greater than one drop a second until a faint yellow colour persists. Note the burette reading before and after the addition of bromine.

Transfer the mixture to a separating funnel and collect the lower layer in a dry test-tube. Add some anhydrous magnesium (or sodium) sulphate, cork the tube and shake for a few minutes. Filter off the drying agent and collect the dry product in a dry test-tube.

Carry out the Lassaigne sodium fusion test for nitrogen on some of the product (p. 46).

(b) Make up a solution of 5 cm³ of cyclohexene in 10 cm³ of ethanol in a 100 cm³ conical flask. Shake vigorously and add bromine with care from a 10 cm³ burette until the mixture is pale yellow. Note the burette reading before and after the addition of bromine.

Shaking the mixture well, add 2 cm³ of a saturated solution of sodium nitrate in water and add water until the salt just redissolves.

Transfer the mixture to a separating funnel and collect a dry sample of the lower layer, as described in (a). Perform the Lassaigne sodium fusion test for nitrogen on some of the product (p. 46).

(c) Answer the following questions:

- (i) Did you find any significant difference in the volume of bromine used in experiments (a) and (b)? Explain this result.
- (ii) The densities of cyclohexene and bromine are 0·81 and 2·93 g cm^{-3} at 20°C. Calculate the number of moles of cyclohexene that react with one mole of bromine.

From the results of the Lassaigne tests, do you find that nitrogen is present in the products formed in experiments (a) or (b)? If so, what deductions can you make about the mechanism of the reaction between cyclohexene and bromine?

6. *Mechanism of the addition of bromine to an alkene: an alternative experiment.*

A saturated aqueous solution of bromine containing chloride ions is prepared by adding bromine to a saturated solution of sodium chloride and shaking or stirring the solution until no more bromine will dissolve.

Add the solution of bromine, a few drops at a time, to 5 cm³ of cyclohexene in a stoppered flask and shake until the bromine colour just persists. Transfer the mixture to a separating funnel containing 50 cm³ of 10% sodium thiosulphate solution, and rinse the reaction vessel with 20 cm³ of diethyl ether, adding this to the separating funnel. After shaking well, allow the layers to separate and run off and discard the aqueous layer. The ethereal solution is then run into another, stoppered, flask, and dried for a few minutes over anhydrous magnesium sulphate.

The products in the solution can be separated by thin-layer chromatography using either plates prepared as on p. 30 or specially-prepared commercial papers. 60–80 petroleum spirit is a good solvent. The solvent should not be allowed to rise higher than three-quarters of the way up the slide. After drying the slide, place it in a covered beaker containing a crystal of iodine. Brown stains will develop indicating the positions of the components.

The product from the bromine/chloride solution may yield 3 or more spots, showing that several products are formed. These may be identified by comparison with authentic samples of the possible products. If authentic samples are not available, most of them can be prepared readily by 'test-tube' techniques.

6.6 Resource materials

Lists of films, videotapes and further reading concerned with the manufacture of chemicals from petroleum sources are given on pages 324–5.

6.7 Questions

1 Describe in detail two test-tube reactions to show whether a given compound contains an unsaturated carbon–carbon link.

To 30 cm³ of a gaseous mixture of butadiene $CH_2{=}CH{-}CH{=}CH_2$ and but-1-ene $C_2H_5CH{=}CH_2$, 100 cm³ of hydrogen were added and the mixture was passed repeatedly over a hydrogenation catalyst in a closed system until no further reduction in volume occurred. The total volume was then 90 cm³. What was the composition by volume of the original mixture? (All volumes were measured at the same temperature and pressure.)

Give two sets of reactions by which chloroethene may be prepared.

Indicate the structure of poly(chloroethene). Give one industrial application of this material and mention the properties upon which this use depends. (JMB)

2 Describe how you would prepare a pure specimen of ethene from ethanol. By what reactions can the following be obtained from ethene: (a) ethanol, (b) ethyne, (c) ethane-1,2-diol.

3 Write an account of the laboratory preparation and of the properties of ethene, indicating how this substance may be distinguished from methane and from benzene.

4 (a) Name the organic products of the reaction of but-2-ene, $CH_3CH{=}CHCH_3$, with each of the following reagents and write a balanced equation for each reaction:

(i) hydrogen bromide,
(ii) bromine dissolved in trichloromethane,
(iii) a dilute alkaline solution of potassium permanganate.

(b) When a hydrocarbon C_xH_y is completely oxidised in oxygen the reaction which occurs can be represented by the following equation:

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$$

20·0 cm³ of a gaseous, unsaturated hydrocarbon *A* were exploded with 200 cm³ of oxygen and, after cooling to the original room temperature, 140 cm³ of gas remained. This volume was reduced to 20·0 cm³ on shaking the gas with potassium hydroxide solution. Deduce the molecular formula of *A*.

When the gas undergoes oxidation at the double bond, one mole of *A* gives one mole each of *B* and *C*, both of which have the molecular formula C_3H_6O. Both *B* and *C* give an orange precipitate with 2,4-dinitrophenylhydrazine and *B* reduces Fehling's solution while *C* does not.

Write structural formulae for *A*, *B* and *C* and explain the reactions involved. (L(X))

5 Draw a labelled diagram of an apparatus suitable for the preparation of a sample of trioxygen. Describe a method for determining the percentage by volume of trioxygen in the sample.

Write structural formulae (excluding cyclic structures) for the different isomers corresponding to the molecular formula C_4H_8 and explain how trioxygen may be used to distinguish between the isomers. (W)

6 Reaction of compound *A* (C_9H_{18}) with trioxygen and then water gave neutral compounds *B* (C_3H_6O) and *C* ($C_6H_{12}O$). *B* did not reduce Fehling's solution, but *C* did. Reduction of *C* with hydrogen and a catalyst gave *D* ($C_6H_{14}O$), which, when heated with concentrated hydrobromic acid, gave *E* ($C_6H_{13}Br$). *E* was heated with a concentrated solution of potassium hydroxide in ethanol, and gave *F* (C_6H_{12}). After being heated with alkaline potassium permanganate, *F* gave on acidification an acid *G* ($C_5H_{10}O_2$); treatment of *G* with *d*-morphine gave two products, separated by fractional crystallisation.

Identify the compounds *A–G*, explaining your reasoning. (C(N, S))

7 Reaction of compound *A* ($C_{11}H_{14}$) with trioxygen and then water gave *B* (C_8H_8O) and *C* (C_3H_6O) in equimolar amounts. *C* was unaffected by ammoniacal silver nitrate, but *B* reacted with this reagent to give *D* ($C_8H_8O_2$). When *D* was treated successively with sulphur dichloride oxide (or phosphorus trichloride) and ammonia, *E* (C_8H_9NO) was formed. *E* reacted with bromine and sodium hydroxide to give *F*(C_7H_9N), a much weaker base than methylamine.

Identify the compounds *A–F* so far as is possible and comment on the reactions. Suggest further experiments (a) to confirm the identification of *C*, and (*b*) to be carried out on compound *D* to complete the identification of compounds *D–F*. (C(T, S))

8 Describe in outline the preparation of propene starting from propanone.

Write down the structural formulae of the compounds obtained when propene is treated with the following reagents.

(a) Concentrated sulphuric acid.
(b) Bromine.
(c) Cold potassium permanganate solution.
(d) Trioxygen followed by water. (O and C)

9 When 25 cm^3 of the gaseous hydrocarbon, *A*, were exploded with 200 cm^3 of oxygen, the residual gases occupied 150 cm^3. After shaking the residual gases with excess aqueous sodium hydroxide, the final volume was 50 cm^3.
(All volumes were measured at room temperature and pressure.)

(a) Why was there a decrease in volume when the residual gases were shaken with aqueous sodium hydroxide? Give an equation.
(b) Calculate the molecular formula of *A*. Explain your working.
(c) Write the structural formulae of SIX possible compounds (cyclic and non-cyclic) which *A* could be and give the systematic names for each of the six formulae.
(d) Which of the six structural formulae show compounds which are
  (i) structural isomers;
  (ii) stereoisomers;
  (iii) optical isomers? (SUJB)

10 Reaction of a hydrocarbon, *A*, of molecular formula, $C_{10}H_{20}$, with trioxygen and then water gives two isomeric products, *B* and *C*, $C_5H_{10}O$.

Oxidation of *B* leads to an optically active acid, *D*, $C_5H_{10}O_2$, whereas oxidation of *C* leads to an acid *E*, $C_4H_8O_2$, which cannot be resolved into optically active forms.

Reduction of *C* gives *F*, $C_5H_{12}O$, dehydration of which, followed by reaction with trioxygen and then water, gives propanone as one of the products.

Deduce the structure of *A* and elucidate the reaction sequence.

11 A compound *A* reacts with bromine giving *B* ($C_5H_{10}Br_2$). Oxidation of *A* leads to two compounds *C* ($C_2H_4O_2$) and *D* (C_3H_6O). The silver salt of *C* contains 64·6 per cent Ag while *D* with 2,4-dinitrophenylhydrazine forms a derivative having the composition $C_9H_{10}N_4O_4$. *D* also reacts with iodine and sodium hydroxide forming tri-iodomethane. Deduce a structure for *A*.

12 (a) State two properties of carbonium ions.

(b) What is the formula of the carbonium ion formed when propene reacts with hydrogen bromide to form 2-bromopropane?

(c) State whether this carbonium ion is a primary, secondary or tertiary species.

(d) How does carbonium ion theory explain the fact that the principal product of the reaction between propene and hydrogen bromide is 2-bromopropane rather than 1-bromopropane?

(e) What reagents and conditions would be used to prepare propan-2-ol from 2-bromopropane?

(f) In what way would you alter the conditions in (e) in order to prepare propene rather than propan-2-ol from 2-bromopropane?

(JMB)

13 (a) State the Markownikoff rule for predicting the direction of electrophilic addition of hydrogen bromide to alkenes. Explain in detail the rule in terms of the relative stabilities of primary, secondary and tertiary carbonium ions.

(b) Propene reacts with hydrogen bromide to give a substance **A**, C_3H_7Br. Substance **A**, when heated with aqueous potassium hydroxide, gives an alcohol **B**.

(i) Derive structures for **A** and **B**.

(ii) Explain and illustrate the meanings of the terms base, nucleophile, and inductive effect by referring to the reactions of substance **A** with potassium hydroxide under various conditions.

(JMB)

14 Devise experiments to determine:

(a) the structure of the product(s) obtained by addition of hydrogen bromide to propene, $CH_3-CH=CH_2$;

(b) the structure of the product(s) obtained by elimination of hydrogen bromide from 2-bromobutane, $CH_3-CHBr-CH_2-CH_3$.

(O Schol.)

Chapter 7

Alkynes

General formula

$$C_nH_{2n-2}$$

7.1 Nomenclature

The compounds are named as for the alkenes but with the suffix **-yne**. For example:

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{C}\equiv\overset{1}{C}-H$$

is but-1-yne. However, the first member, ethyne ($CH\equiv CH$) is often described by its original name, acetylene, and its simple derivatives are sometimes described as substituted acetylenes: e.g. propyne ($CH_3-C\equiv CH$) is methylacetylene.

7.2 Physical properties of alkynes

The melting points and boiling points of the alkynes are similar to those of the alkanes with the same number of carbon atoms (cf. Table 5.1).

Table 7.1. Some alkynes

NAME	FORMULA	B.P./°C
Ethyne	$CH\equiv CH$	−83
Propyne	$CH_3-C\equiv C-H$	−23
But-1-yne	$C_2H_5-C\equiv C-H$	9
But-2-yne	$CH_3-C\equiv C-CH_3$	27
Pent-1-yne	$C_3H_7-C\equiv C-H$	40
Phenylethyne	$C_6H_5-C\equiv C-H$	143

7.3 Ethyne

Structural formula

$$H-C\equiv C-H$$

Manufacture

1. Calcium dicarbide is obtained by heating coke with calcium oxide in an electric furnace above 2000°C:

$$CaO + 3C \rightarrow CaC_2 + CO$$

Ethyne is produced by the treatment of calcium dicarbide with water:

$$CaC_2 + 2H_2O \rightarrow CH\equiv CH + Ca(OH)_2$$

2. Ethyne is now being increasingly made by the pyrolysis of methane at 1500°C (5.4).

Chemical properties

(a) Electrophilic addition reactions

Ethyne resembles ethene in undergoing addition reactions with electrophilic reagents. Examples are:

1. It reacts readily with the halogens. Chlorine reacts explosively:

$$CH{\equiv}CH + Cl_2 \rightarrow 2C + 2HCl$$

To prevent explosions, ethyne and chlorine are generally mixed in retorts filled with Kieselguhr and iron filings to absorb the heat of the reaction. Addition compounds are then formed:

$$CH{\equiv}CH \xrightarrow{Cl_2} \underset{\substack{\text{1,2-Dichloro-}\\\text{ethene}}}{ClCH{=}CHCl} \xrightarrow{Cl_2} \underset{\substack{\text{1,1,2,2-Tetra-}\\\text{chloroethane}}}{Cl_2CH{-}CHCl_2}$$

Bromine reacts less violently, giving 1,2-dibromoethene and, with an excess of bromine, 1,1,2,2-tetrabromoethane.

2. It reacts with the halogen acids, for example:

$$CH{\equiv}CH \xrightarrow{HCl} \underset{\text{Chloroethene}}{CH_2{=}CHCl} \xrightarrow{HCl} \underset{\substack{\text{1,1-Dichloro-}\\\text{ethane}}}{CH_3{-}CHCl_2}$$

(b) Other reactions

1. Ethyne resembles ethene in being reduced by hydrogen on certain metal surfaces (e.g. nickel at 150°C or platinum or palladium at room temperature). First ethene and then ethane are formed:

$$CH{\equiv}CH \xrightarrow{H_2} CH_2{=}CH_2 \xrightarrow{H_2} CH_3{-}CH_3$$

2. Ethyne differs from ethene in reacting with water in the presence of dilute sulphuric acid and mercury(II) sulphate ($HgSO_4$) at 60°C:

$$CH{\equiv}CH + H_2O \rightarrow \underset{\text{Ethanal}}{CH_3CHO}$$

This is the basis of a method for manufacturing ethanal, but it is now being superseded by one which starts with ethene, a cheaper raw material than ethyne (12.3).

3. Ethyne also differs from ethene in forming salts with several metals; for example, if ethyne is passed through an ammoniacal solution of copper(I) chloride, a red precipitate of copper(I) dicarbide is formed:

$$CH{\equiv}CH + Cu_2Cl_2 + 2NH_3 \rightarrow \underset{\substack{\text{Copper(I)}\\\text{dicarbide}}}{Cu_2C_2} + 2NH_4Cl$$

Similarly, if ethyne is passed through an ammoniacal solution of silver nitrate, a white precipitate of silver dicarbide, Ag_2C_2, is produced.

Uses

Many of the industrial uses of ethyne are now losing importance as methods for making the same compounds from ethene have been developed. The increase in energy prices in the 1970s accelerated the trend as ethene is cheaper to produce than ethyne; examples are the production of ethanal mentioned above and the formation of chloroethene by addition of hydrogen chloride to ethyne (p. 95), which is being superseded by the chlorination of ethene (6.3.)

One small-scale use is in oxyacetylene welding, which is based on the very high temperatures (*ca.* 3000°C) attained when ethyne burns in oxygen:

$$2CH{\equiv}CH + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

7.4
Other alkynes

The properties of other alkynes resemble those of ethyne except that only those alkynes in which the triple bond is at the end of the chain form metallic compounds. For example, propyne forms a silver salt, $CH_3C{\equiv}CAg$, but but-2-yne ($CH_3{-}C{\equiv}C{-}CH_3$) does not. This provides a method of distinguishing ethyne and alkynes of the type $RC{\equiv}CH$, which are acidic and form metal salts, from other alkynes and also from alkenes.

7.5
Practical work

Small-scale preparation of ethyne

Place 2 or 3 small pieces of calcium dicarbide in a test-tube and arrange the apparatus for collection of ethyne (Fig. 7.1). Add water dropwise and collect 4 or 5 test-tubes of gas, putting a cork in the test-tube when it is full of gas.

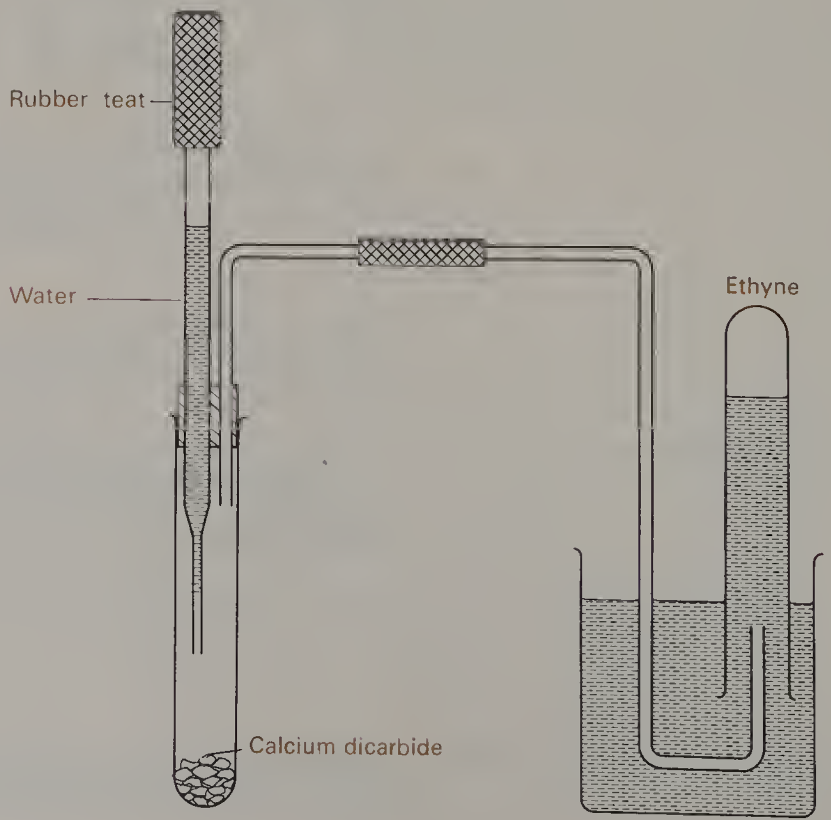


FIG. 7.1. *Test-tube preparation of ethyne*

Reactions of alkynes

Carry out the following experiments with a gaseous alkyne (e.g. ethyne) and a liquid alkyne (e.g. phenylethyne). Compare the results of experiments 1–3 *with those obtained with an alkane* (5.7) *and an alkene* (6.5).

1. (a) Ignite the gas by applying a lighted splint to the mouth of the test-tube.

(b) Place a small sample (a few drops) of the liquid alkyne on a watch-glass and ignite it.

Note the colour of the flames.

2. (a) Add a few drops of a solution of bromine in tetrachloromethane to a test-tube of gas and shake the mixture.

(b) To a few drops of the liquid alkyne in a test-tube, add a few drops of bromine in tetrachloromethane and shake the mixture.

3. (a) Add 3–4 drops of an alkaline solution of potassium manganate(VII) (made by dissolving about 0·1 g of anhydrous sodium carbonate in 1 cm^3 of a 1 per cent solution of potassium manganate(VII)) to a test-tube of gas and shake the mixture. Note the colour of the solution and whether any precipitate is formed.

(b) Repeat the experiment with 2 or 3 drops of the liquid alkyne instead of the gas, warming the mixture gently.

4. (a) Prepare an ammoniacal solution of copper(I) chloride by dissolving about 0·1 g of copper(I) chloride in 1 cm^3 of a dilute solution of ammonia. Generate some ethyne, and pass the gas through the solution (Fig. 7.2).

(b) Will this reaction occur with (i) propyne ($CH_3—C\equiv C—H$), (ii) but-2-yne ($CH_3—C\equiv C—CH_3$)?

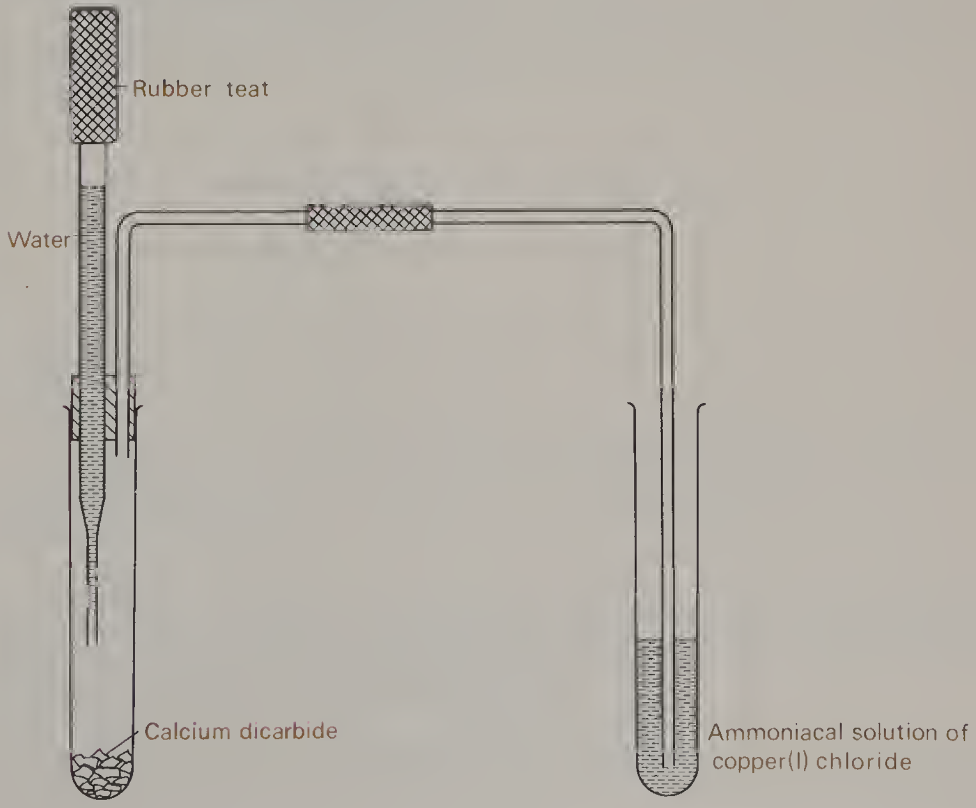


FIG. 7.2. *Reaction between ethyne and a copper(I) salt*

(c) Try the reaction with phenylethyne by shaking 2 or 3 drops of the liquid alkyne with 1 cm^3 of an ammoniacal solution of copper(I) chloride.

N.B. *If any solids are formed in* 4(*a*) *or* 4(*c*), *do not allow them to become dry. Wash them down the sink with plenty of water.*

7.6 Questions

1 With the aid of equations describe how and under what conditions ethyne (acetylene) reacts with (a) hydrogen, (b) chlorine, (c) hydrogen cyanide and (d) a solution of copper(I) chloride (cuprous chloride) in ammonia.

Explain briefly how you would demonstrate the presence of carbon and hydrogen in ethyne. Describe an experiment you would carry out to determine its formula. (AEB)

2 Discuss the meaning of the term *unsaturation*, illustrating your answer with reference to ethene and ethyne.

Outline the reactions by which ethyne may be converted to (a) ethanamide, (b) chloroethene, $CH_2{=}CHCl$, (c) ethane-1,2-diol, (d) benzene. (C(N))

3 Describe in outline **one** commercial preparation of ethyne.

State the reactions of ethyne with (a) chlorine and (b) aqueous mercury(II) sulphate (mercuric sulphate).

One mole of a hydrocarbon S (C_6H_{10}) gives 2 moles of ethanal with trioxygen. What are the possible structural formulae for S? (O and C)

4 (a) When 20 cm^3 of a gaseous hydrocarbon A was exploded with 150 cm^3 of oxygen, the residual gases occupied 110 cm^3. After shaking these gases with aqueous sodium hydroxide, the final volume was 30 cm^3 (all volumes at the same temperature and pressure). Calculate the molecular formula of A.

(b) Another hydrocarbon B, of molecular formula C_4H_6, formed a red precipitate with ammoniacal copper(I) chloride (cuprous chloride) and reacted with water in the presence of sulphuric acid and mercury(II) sulphate (mercuric sulphate) to give a compound C. C was unaffected by potassium permanganate but with iodine and warm aqueous sodium hydroxide gave a yellow crystalline precipitate with a characteristic odour. Deduce the structural formulae of B and C and explain the above reactions. (C(T))

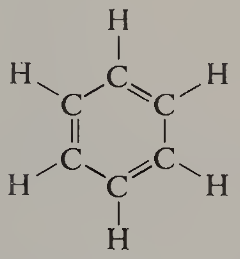
Aromatic compounds

8.1 Introduction

The term 'aromatic' was first used to describe a group of compounds which have a pleasant smell (aroma). These compounds include the cyclic compound, benzene, and its derivatives. The name aromatic has been retained since it is useful to classify these compounds separately; this is because their properties are so different from those of the aliphatic and alicyclic compounds.

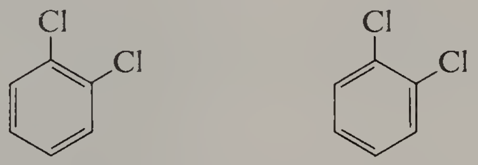
8.2 Structure of benzene

It has been known for over 100 years that benzene is a cyclic compound, with a six-membered ring of six carbon atoms and with one hydrogen atom attached to each carbon atom. Bearing in mind that carbon and hydrogen form four bonds and one bond respectively, it was natural to represent its structure as



in which single and double bonds alternate round the ring. However, the following evidence shows that this representation does not adequately describe the structure of benzene.

1. If the structure was correct, we should expect to be able to isolate two isomers of any disubstituted benzene in which the substituents were adjacent, for example:



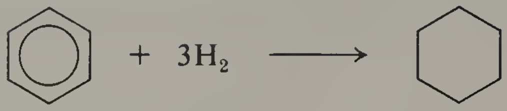
However, in no case has more than one isomer of any such compound been obtained.

2. As we shall see (8.3), benzene does not undergo the addition reactions which are characteristic of ethene (6.3) and other compounds which contain C=C bonds.

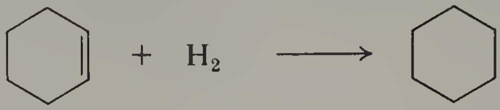
3. Whereas the length of a carbon–carbon single bond is 154 pm and that of a carbon–carbon double bond is 134 pm, the six carbon–carbon bonds in benzene are of equal length (139 pm), somewhat longer than double bonds but shorter than single bonds.

4. Benzene is a more stable compound than would be expected by comparison of its structure with that of an alkene, as shown by thermochemical

measurements. When benzene is reduced to cyclohexane:

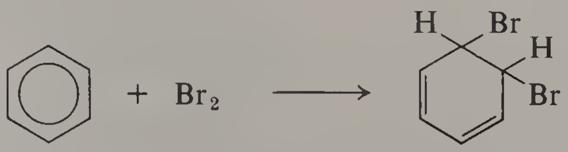


the heat evolved is 207 kJ mol^{-1}. When cyclohexene is reduced to cyclohexane:



the heat evolved is 119 kJ mol^{-1}. Now, the heat change in the latter reaction is associated with the conversion of a double bond into a single bond and the breaking of the H—H bond, each of which requires energy, and the formation of two C—H bonds, which releases energy. If benzene contained three alkene-like double bonds, we should expect that the heat evolved during its reduction would be three times that for cyclohexene, i.e. 357 kJ mol^{-1}, since the bond changes associated with the reduction of one molecule of cyclohexene take place three times over on the reduction of one molecule of benzene. The experimental value is $(357 - 207) = 150$ kJ mol^{-1} less than this, from which we infer that benzene is more stable by this amount of bonding energy than would be expected if it possessed alkene-like double bonds.

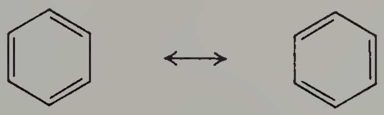
The differences described above between benzene and the alkenes can all be understood by consideration of the nature of the bonding in benzene. Each carbon atom is sp^2-hybridised, so that it forms three coplanar bonds, two with other carbon atoms and one with a hydrogen atom. These bonds are at an angle of 120° to each other, just as in an alkene, and this means that the six carbon atoms are in a plane and that there is no strain in the ring (compare cyclohexane, p. 77, where a planar structure would be strained because the normal bond angle for sp^3-hybridised carbon is 109°28′). The remaining electron is in a *p* orbital perpendicular to the plane of this ring, just as in ethene each of the carbon atoms has a *p* orbital perpendicular to the plane containing the atoms. Now, in benzene, each of these *p* orbitals can overlap with *both* the neighbouring *p* orbitals, Fig. 4.15 (p. 60). Since bond energies are determined by the extent of orbital-overlap (4.3), there is a greater degree of bonding in benzene than would be expected by comparison with ethene. This underlies the thermochemical stability of benzene and also its resistance to addition reactions, since a reaction such as:



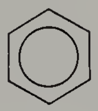
would result in the loss of the extensive *p*-orbital interactions. It also enables us to understand why the bond lengths in the ring are equal, because, as Fig. 4.15 shows, there is no difference in the type of bonding between one pair of adjacent carbon atoms and any other pair.

The bonds associated with the *p*-orbital interactions in benzene are termed **delocalised π-bonds**, in contrast to the **localised π-bond** in an alkene which is confined to only two atoms. The extra thermochemical stability of benzene as compared with what would be expected if it possessed alkene-like double bonds is termed its **delocalisation energy** or **stabilisation energy**.

As described in Chapter 4, there is an alternative way of representing the delocalised bonds in benzene, that is, by describing benzene as a resonance hybrid of two structures:



Although delocalisation in this book is often described in terms of molecular orbitals, it is sometimes easier to discuss the properties of aromatic compounds in terms of resonance hybrids. In equations, benzene is represented as:

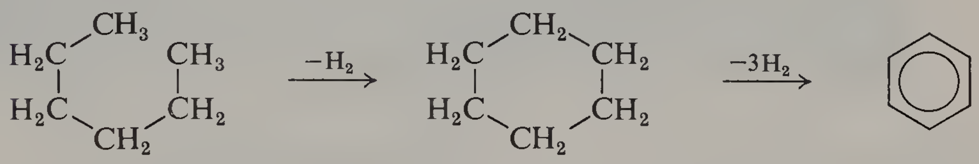


8.3 Benzene

Manufacture

1. *Based on petroleum*

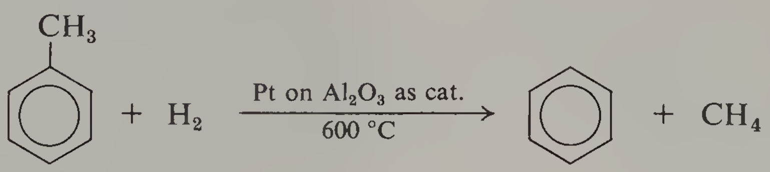
(a) If the gasoline and naphtha fractions from the distillation of petroleum (19.4) are passed over a catalyst (either platinum or molybdenum(VI) oxide, suspended on alumina) in presence of an excess of hydrogen, the straight-chain alkanes undergo cyclisation and dehydrogenation. For example, hexane is converted into benzene,



heptane into methylbenzene and octane into a mixture of ethylbenzene and dimethylbenzenes. The process is known as **reforming**. The separation of the mixture into pure aromatic hydrocarbons is described in Section 20.5.

(b) Benzene is one of the products when the light gas-oil fraction undergoes **catalytic cracking** (19.6).

(c) It is also formed from other aromatic hydrocarbons by **hydrodealkylation** (20.5), for example:



2. *Based on coal*

Benzene is obtained by the fractional distillation of coal tar, which is itself obtained by the destructive distillation of coal. This only becomes an important source of aromatic hydrocarbons when large quantities of coal are converted into coke, for steel-making, or coal-gas (where the country needs gas but does not have a ready source of natural gas).

Plate 8.1. A reforming unit. Naphtha is heated in a furnace (A), mixed with hydrogen, compressed to a high pressure (B) and passed over a heated platinum catalyst. The reactors are hidden in the photograph (C). Low boiling hydrocarbons are removed by fractional distillation, for example ethane, propane, butane (D). The residue, which is fractionated (E), contains principally the aromatic hydrocarbons, benzene, methylbenzene and dimethylbenzenes (Esso Petroleum Co. Ltd.)

Physical properties

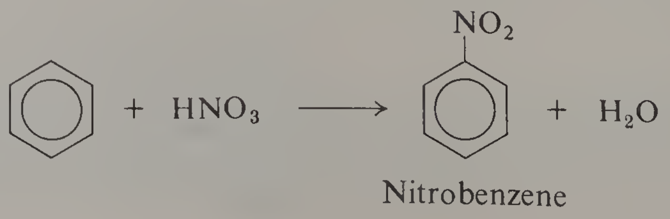
Benzene is a colourless liquid with a characteristic odour. It is insoluble in water but soluble in all organic solvents, and it is itself a very good solvent for organic compounds. It freezes at 5°C and boils at 80°C. Both the liquid and the vapour are highly poisonous, so that benzene must be used with care.

Chemical properties

(a) Substitution reactions

Benzene takes part in a variety of substitution reactions with electrophilic reagents.

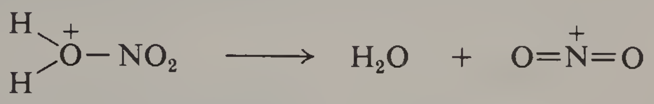
1. When treated with a mixture of concentrated nitric acid and concentrated sulphuric acid at room temperature, nitrobenzene is formed:



This reaction occurs in several stages. First, sulphuric acid is so strong an acid that it transfers a proton to nitric acid:

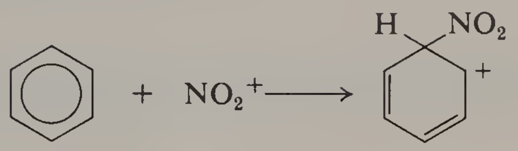
$$H_2SO_4 + H{-}O{-}NO_2 \rightleftharpoons HSO_4^- + H_2\overset{+}{O}{-}NO_2$$

The protonated nitric acid then undergoes a spontaneous heterolysis to form the **nitronium ion**, NO_2^+:

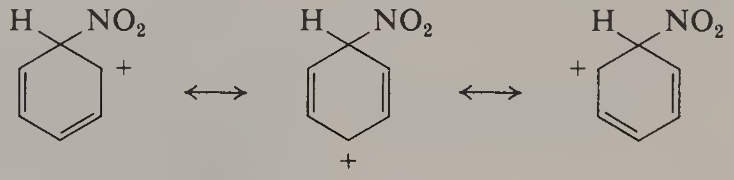


$$H_2\overset{+}{O}{-}NO_2 \longrightarrow H_2O + O{=}\overset{+}{N}{=}O$$

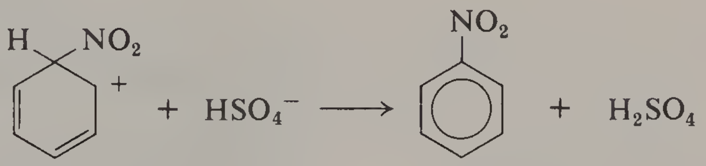
The nitronium ion is the electrophilic reagent with which benzene reacts. The first step is an addition:



The positive charge in this adduct is actually delocalised over three of the carbon atoms; the ion can be described as a resonance hybrid of three structures:



In the final step of the reaction, a proton is removed from the adduct by the hydrogensulphate anion:



There is strong evidence for the existence of the nitronium ion. For example, compounds such as nitronium perchlorate, NO_2ClO_4, have been prepared and shown, by X-ray analysis, to contain the ion NO_2^+. In addition, the depression of the freezing point of sulphuric acid by dissolved nitric acid is four times greater than expected; evidently each molecule of nitric acid provides four particles in the solution, consistent with the ionisation:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

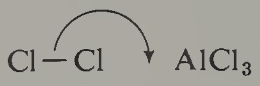
The mechanism described above is typical of the electrophilic substitution reactions of benzene, and the others will not be described in such detail.

2. If chlorine is passed through benzene *at room temperature* and in the presence of a catalyst, substitution takes place:

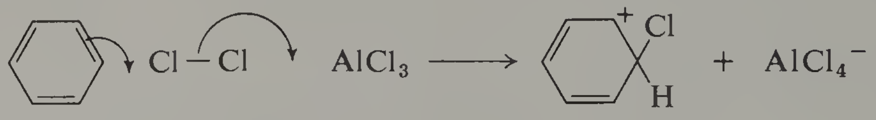
$$C_6H_6 + Cl_2 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5{-}Cl} + HCl$$

Suitable catalysts are iron filings and aluminium chloride; they are referred to as **halogen carriers**.

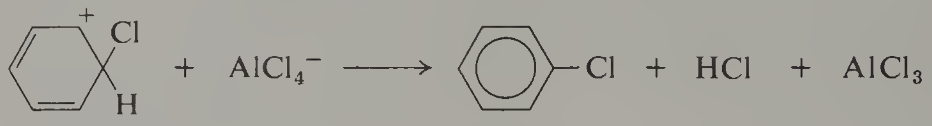
The function of the catalyst is to withdraw the electrons from the bond between the chlorine atoms, a process represented for aluminium chloride as:



where the curved arrow represents the tendency for two electrons to move into the vacant 3*p* orbital of the aluminium atom. As this happens, the benzene ring provides two electrons to make good the deficiency of electrons on one of the chlorine atoms, so that the whole process can be represented as:



The carbonium ion then reacts with the $AlCl_4^-$ ion:



so that the catalyst is regenerated.

When iron is used as the halogen carrier, it first reacts with chlorine to give iron(III) chloride which then catalyses the reaction in the same way as aluminium chloride.

In the presence of iron filings or aluminium bromide, benzene reacts with bromine to give bromobenzene:

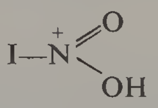
$$C_6H_6 + Br_2 \rightarrow \underset{\text{Bromobenzene}}{C_6H_5{-}Br} + HBr$$

The mechanism of the reaction is the same as that in chlorination.

The iodination of benzene is usually brought about by refluxing benzene, iodine and concentrated nitric acid:

$$C_6H_6 + I_2 \rightarrow C_6H_5I + HI$$

It was once thought that the function of the nitric acid was to oxidise the hydrogen iodide as it was formed and thereby prevent the reverse reaction. However, this cannot be the correct explanation, for hydrogen iodide does not react with iodobenzene to give benzene and iodine. It is now thought that the acid serves to provide the active iodinating species, possibly



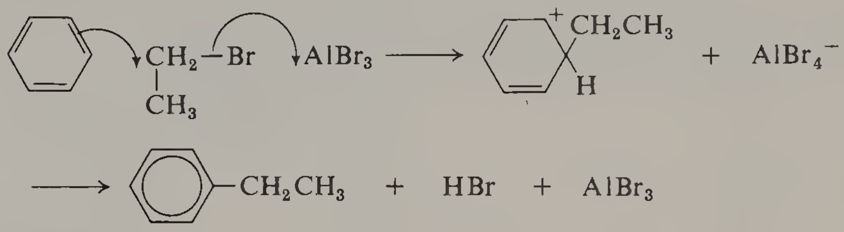
This is one example of the way in which our interpretations of the mechanisms of organic reactions change in the light of experimental evidence.

3. Benzene reacts with an alkyl halide in the presence of an aluminium halide to give an alkylbenzene, for example:

$$C_6H_6 + CH_3CH_2\text{—}Br \xrightarrow{AlBr_3 \text{ as cat.}} \underset{\text{Ethylbenzene}}{C_6H_5\text{—}C_2H_5} + HBr$$

The reaction, which is described as **alkylation**, occurs in a similar way to chlorination.

The catalyst withdraws the pair of electrons from the C—Br bond, the benzene ring provides a pair of electrons to form a bond to the alkyl group:



Methylbenzene is formed from benzene and iodomethane (the iodide being used as it is the only methyl halide which is a liquid at room temperature):

$$C_6H_6 + CH_3I \xrightarrow{AlCl_3 \text{ as cat.}} \underset{\text{Methylbenzene}}{C_6H_5\text{—}CH_3} + HI$$

A similar reaction takes place with acid halides to give ketones, for example:

$$C_6H_6 + CH_3\text{—}CO\text{—}Cl \xrightarrow{AlCl_3 \text{ as cat.}} \underset{\text{Phenylethanone}}{C_6H_5\text{—}CO\text{—}CH_3} + HCl$$

The process is known as **acylation.**

The reactions of aromatic compounds with alkyl halides and acid halides are known as **Friedel-Crafts reactions**, after the names of their two discoverers.

4. Benzene reacts with an alkene in the presence of an acid to give an alkylbenzene, for example:

$$C_6H_6 + CH_3\text{—}CH\text{=}CH_2 \xrightarrow{H^+ \text{ as cat.}} \underset{\text{(1-Methylethyl)benzene}}{C_6H_5\text{—}CH(CH_3)_2}$$

Reaction occurs by addition of a proton to the alkene to give a carbonium ion which then reacts with the aromatic compound:

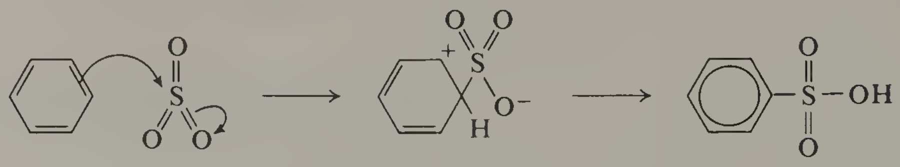
$$CH_3\text{—}CH\text{=}CH_2 + H^+ \rightarrow CH_3\text{—}\overset{+}{C}H\text{—}CH_3$$

$$C_6H_6 + CH_3\text{—}\overset{+}{C}H\text{—}CH_3 \rightarrow C_6H_5\text{—}CH(CH_3)_2 + H^+$$

5. If a mixture of benzene and concentrated sulphuric acid is heated for about 8 hours, benzenesulphonic acid is formed:

$$C_6H_6 + H_2SO_4 \rightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5\text{—}SO_2OH} + H_2O$$

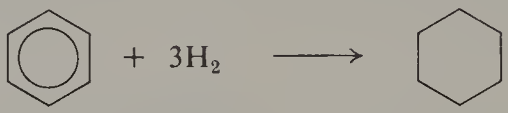
The reaction is another example of an electrophilic substitution. The reagent is sulphur trioxide, which is present in a solution of concentrated sulphuric acid and accepts a pair of electrons from benzene:



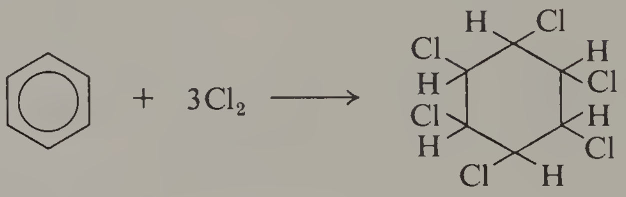
Note that in this organic sulphur compound, carbon is linked to sulphur, whereas in ethyl hydrogensulphate (p. 83) it is linked to oxygen ($CH_3—CH_2—O—SO_2—OH$).

(b) Other reactions

1. If a mixture of hydrogen and benzene vapour is passed over nickel at 150°C, cyclohexane is formed:



2. In the presence of ultraviolet light, benzene reacts with chlorine by addition:



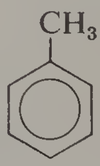
The resulting product, hexachlorocyclohexane, is a mixture of geometrical isomers, one of which is an important insecticide, sold as Gammexane.

Uses

The uses of benzene are discussed in Section 20.5.

8.4 Methylbenzene

Structural formula



Manufacture

Methylbenzene (toluene) is obtained both from coal and from petroleum in the same way as benzene.

Physical properties

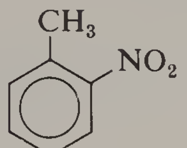
Like benzene, methylbenzene is a colourless liquid which is insoluble in water but soluble in organic solvents. It melts at −95°C and boils at 111°C. Note that the melting point is lower than that of benzene although methylbenzene has the higher formula weight. This is because the planar molecules of benzene can pack closely together in the crystal and the cohesive forces are strong, whereas the methyl group in methylbenzene prevents such close packing.

Chemical properties

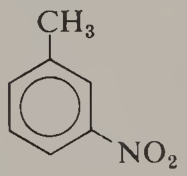
Methylbenzene undergoes three types of reactions: (a) electrophilic substitution in the ring, (b) addition to the ring and (c) substitution in the methyl group.

(a) Electrophilic substitution reactions

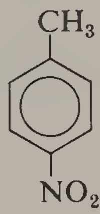
Methylbenzene reacts with all the electrophilic reagents which attack benzene, and in each reaction it is more reactive than benzene. There are three possible isomeric products in each case; for example, for nitration:



Methyl-2-nitrobenzene



Methyl-3-nitrobenzene

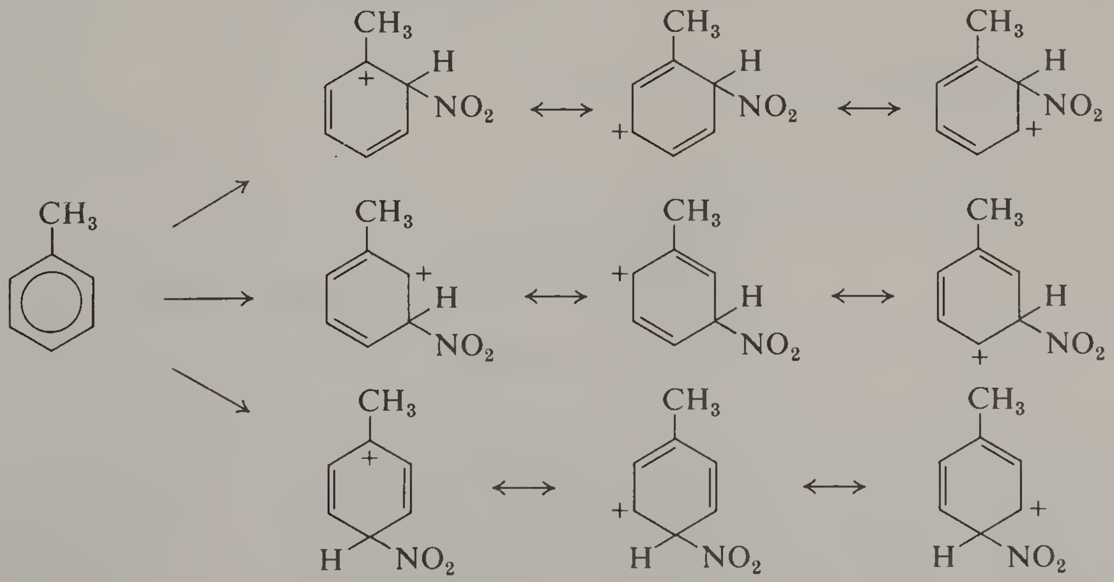


Methyl-4-nitrobenzene

The prefixes *ortho*, *meta* and *para*, usually abbreviated to *o*, *m* and *p*, are often used instead of the numbers 2, 3 and 4, respectively, for describing the relative positions of the substituents in a disubstituted benzene; for example, methyl-2-nitrobenzene can be called *o*-methylnitrobenzene.

Of these three products, the principal ones from methylbenzene are always the 2- and 4-isomers; for example, in nitration, with a mixture of concentrated nitric and sulphuric acids, the relative amounts of the three products, expressed as percentages, are 2-, 59; 3-, 4; 4-, 37. The methyl group in methylbenzene is described as **2-,4-directing** (*ortho*, *para*-directing).

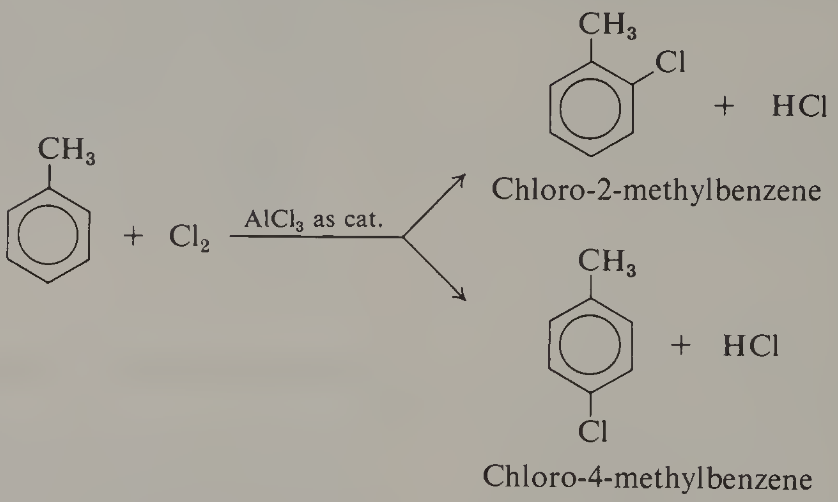
The reasons for both the greater reactivity of methylbenzene than benzene and the predominance of 2- and 4-substitution in methylbenzene can be understood by considering the first step in the reaction. Thus, in nitration:

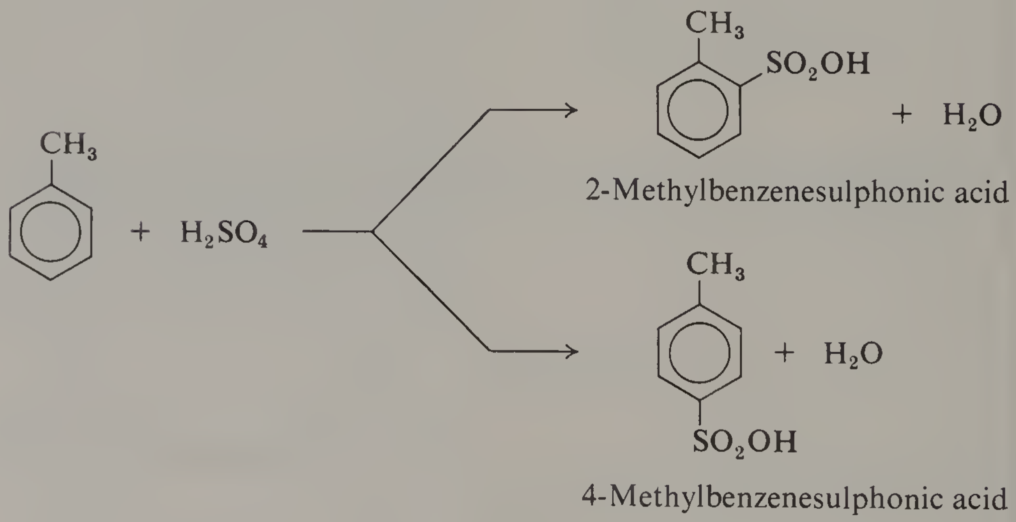


In each case a carbonium ion is formed which is a resonance hybrid of three structures; the positive charge is shared by three of the ring-carbon atoms.

Since the methyl group is electron-releasing ($+I$) and serves to stabilise a positive charge (4.9), each of the three adducts is more stable than that from benzene and is formed faster; thus, methylbenzene is more reactive than benzene. Of the three adducts, those formed by reaction at the 2- and 4-positions have positive charge adjacent to the methyl group, so that they are more stable than the adduct formed by reaction at the 3-position in which a carbon atom is interposed between the positive charge and the methyl group; consequently, reaction occurs faster at the 2- and 4-positions than at the 3-position, that is, methylbenzene is 2-,4-directing.

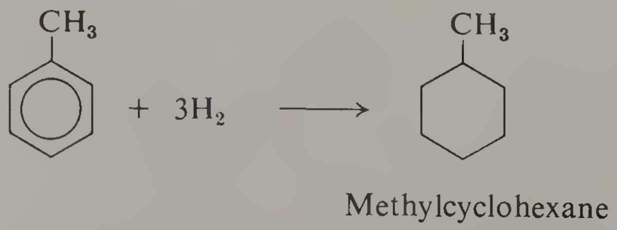
Other examples of electrophilic substitutions in methylbenzene are:





(b) Addition reactions

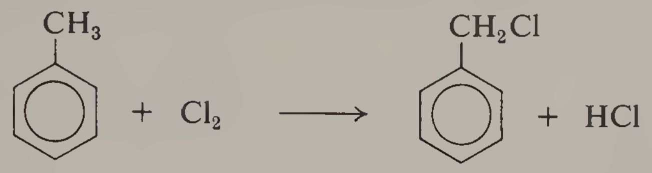
Methylbenzene resembles benzene in reacting with hydrogen on nickel at 150°C:



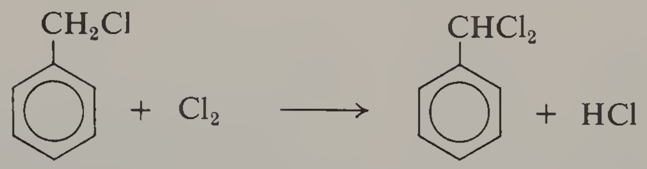
However, when treated with chlorine in the presence of ultraviolet light, it preferentially reacts in the methyl group (p. 109).

(c) Substitution in the methyl group

1. When chlorine is passed through boiling methylbenzene which is exposed to ultraviolet light, substitution of chlorine for hydrogen occurs:



(Chloromethyl)benzene



(Dichloromethyl)benzene

(Trichloromethyl)benzene

These reactions occur *via* free radicals, as in the chlorination of methane (p. 73). They are in contrast to the ionic reactions which occur when methylbenzene is treated with chlorine at room temperature in the presence of a halogen carrier, which give mainly 2- and 4-chloro-derivatives in the same way as benzene gives chlorobenzene (p. 104).

2. The methyl group in methylbenzene can be oxidised to the aldehyde group, —CH=O, or to the carboxylic acid group, $—CO_2H$, depending on the oxidising agent:

$$C_6H_5—CH_3 \xrightarrow{CrO_2Cl_2} \underset{\text{Benzaldehyde}}{C_6H_5—CHO}$$

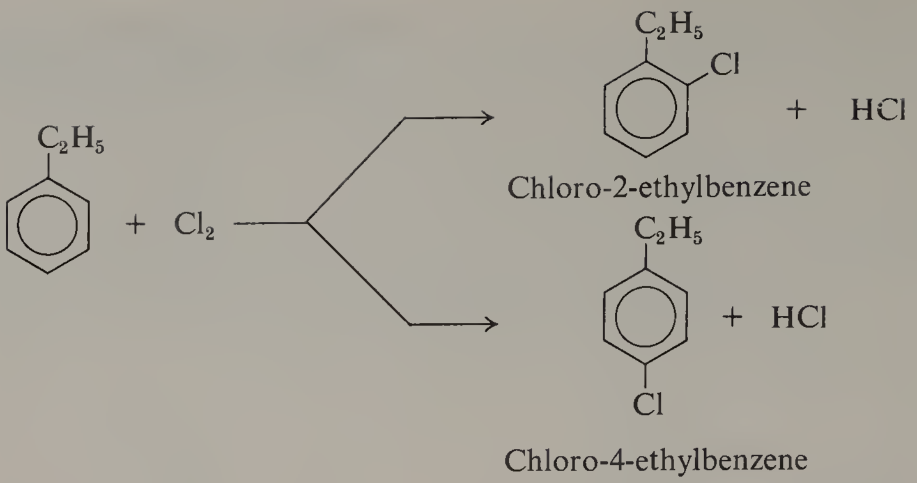
$$C_6H_5—CH_3 \xrightarrow[\text{alkaline}]{KMnO_4} \underset{\text{Benzoic acid}}{C_6H_5—CO_2H}$$

Uses

The uses of methylbenzene are discussed in Section 20.5.

8.5
Substitution in other aromatic compounds

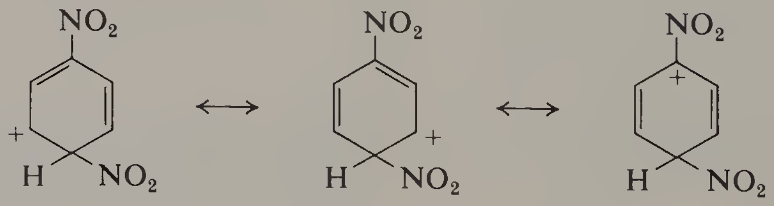
As we have seen, the methyl group in methylbenzene is 2-,4-directing in electrophilic substitutions because it is an electron-releasing group and preferentially stabilises the adducts formed by the reaction at the 2- and 4-positions. Other alkyl groups have the same effect; for example, chlorination of ethylbenzene in the presence of a halogen carrier gives mainly chloro-2- and chloro-4-ethylbenzene:



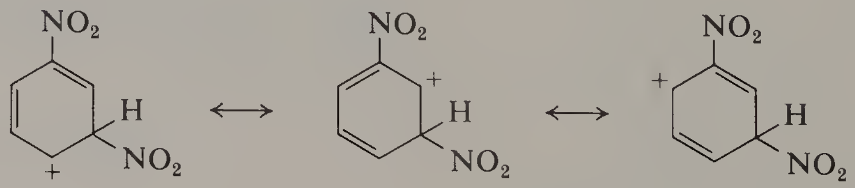
Chloro-2-ethylbenzene

Chloro-4-ethylbenzene

When an electron-attracting group such as —NO_2 or —CN (p. 65) is attached to the benzene ring, it reduces the stability of the intermediate cation in an electrophilic substitution reaction. Consequently, compounds such as nitrobenzene ($C_6H_5NO_2$) and benzonitrile (C_6H_5CN) react less rapidly than benzene. This destabilising effect is greatest for reaction at the 2- or 4-position, for the electron-attracting substituent is then adjacent to one of the carbon atoms which shares the positive charge, for example,



whereas for reaction at the 3-position an extra carbon atom is interposed between the substituent and the charge, for example:

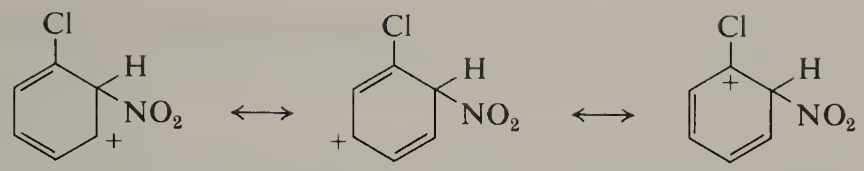


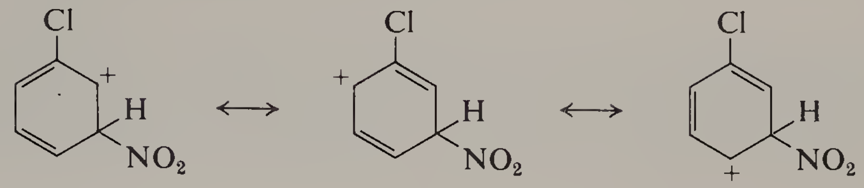
Hence these electron-attracting substituents are 3-directing.

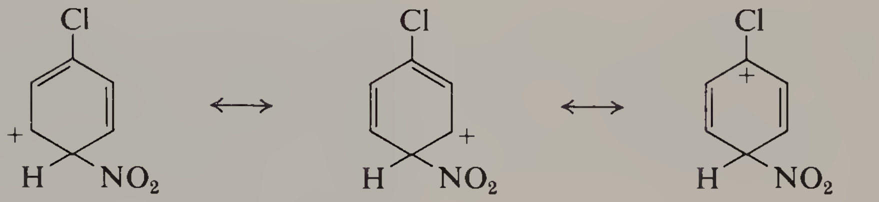
An illustration of the inhibiting effect which the nitro group has on electrophilic substitution, as well as its 3-directing capacity, is provided by the nitration of nitrobenzene: when benzene is treated with a mixture of concentrated nitric and concentrated sulphuric acids at room temperature, nitrobenzene is formed, but the temperature has to be raised to about 50°C for further reaction to occur to give 1,3-dinitrobenzene.

In contrast, those electron-attracting groups bonded to benzene which contain an atom with an unshared pair of electrons directly attached to the aromatic ring are 2-,4-directing in electrophilic substitution; examples are —Cl, —OH and —NH_2.

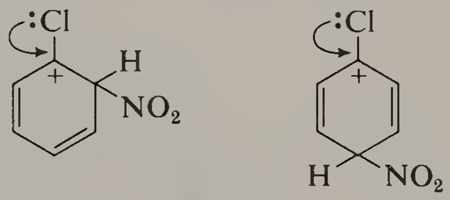
The reason is again apparent when the intermediate adducts in the substitution are considered. For example, when chlorobenzene is nitrated, the possible adducts are:



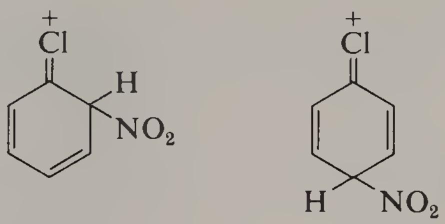




In the cases of the 2- and 4-adducts, the positive charges are delocalised not only on to three carbon atoms but also on to the chlorine atom; that is, a *p* orbital on chlorine can overlap with the adjacent carbon *p* orbital, the result being that the pair of electrons in the chlorine *p* orbital is partly donated to the carbon *p* orbital, so reducing the deficiency of electrons in the latter. This can be represented as follows:

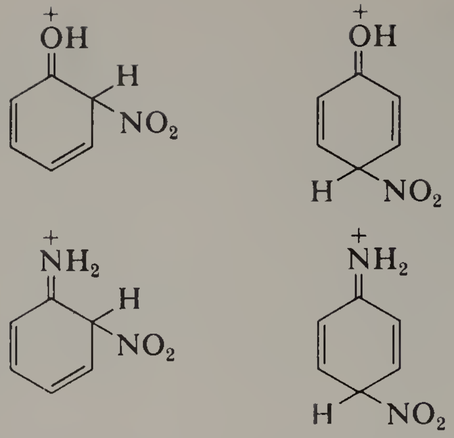


This corresponds to the sharing of the positive charge by the chlorine atom in addition to the carbon atoms, and could be represented alternatively by the structures:

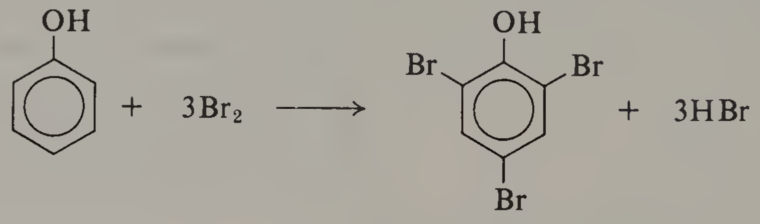


This extra delocalisation of the charge, which cannot occur when the reagent adds to the 3-position, makes the adducts formed by reaction at the 2- and 4-positions more stable than that formed by reaction at the 3-position; hence the chlorine substituent is 2-,4-directing.

The hydroxyl (—OH) and amino (—NH_2) substituents, each of which contains unshared pairs of electrons, act in the same way as the chlorine substituent; their ability to stabilise the 2- and 4-adducts formed during electrophilic substitution can be represented as follows:



Oxygen and nitrogen release *p* electrons in this way more readily than does chlorine, and as a result phenol (C_6H_5—OH) (p. 159) and phenylamine (C_6H_5—NH_2) (p. 256) are much more reactive than chlorobenzene or benzene. For instance, they are so reactive towards chlorine and bromine that it is impossible to stop the reaction before all the activated positions have been substituted, even in the absence of a halogen carrier, for example:



2,4,6-Tribromophenol

Summary of directing power of substituents

2-,4-DIRECTING (ORTHO,PARA-DIRECTING)		3-DIRECTING (META-DIRECTING)
Substituent is electron-releasing (+*I* effect)	Substituent is electron-attracting (−*I* effect) but possesses an unshared pair of electrons	Substituent is electron-attracting (−*I* effect)
—Alkyl, as in methylbenzene C_6H_5—CH_3	—Halogen (—F, —Cl, —Br, —I), as in chlorobenzene, C_6H_5—Cl —OH, as in phenol, C_6H_5—OH —NH_2, as in phenylamine, C_6H_5—NH_2	—NO_2, as in nitrobenzene C_6H_5—NO_2 —CHO, as in benzaldehyde, C_6H_5—CHO —COR, as in phenylethanone C_6H_5—$COCH_3$ —CO_2H, as in benzoic acid, C_6H_5—CO_2H —SO_2OH, as in benzenesulphonic acid, C_6H_5—SO_2OH

8.6 Practical work

Reactions of methylbenzene

Compare your results with those obtained with an alkane (p. 77) and an alkene (p. 89).

1. To 5 drops of methylbenzene in a test-tube, add 1 cm^3 of a solution of bromine in tetrachloromethane and shake.

2. Place 5 drops of methylbenzene in each of two test-tubes, and to one of them add a few iron filings. Add 3 drops of bromine to both test-tubes and note whether there is evolution of gas from either. It may take a few minutes to see whether a gas is evolved. Test the gas with moist blue litmus paper.

3. To 10 drops of *concentrated* nitric acid in a test-tube, carefully add 10 drops of *concentrated* sulphuric acid, shaking the mixture and cooling the test-tube under a stream of cold water. Add the mixture of acids to 5 drops of methylbenzene in another test-tube, and shake this mixture under a stream of cold water; then pour into a beaker containing about 10 cm^3 of cold water. Observe whether a new liquid is formed and note its smell.

4. To 4 drops of methylbenzene, add 10 drops of *concentrated* sulphuric acid in a test-tube. Warm until the methylbenzene has dissolved into the acid layer. Pour the mixture into 10 cm^3 of a cold saturated solution of sodium chloride. White crystals of a mixture of sodium methylbenzenesulphonates are formed.

5. Make up about 25 cm^3 of an alkaline solution of potassium manganate(VII) (add 0·1 g of sodium carbonate to a 10 per cent solution of potassium manganate(VII)).

To 10 drops of methylbenzene, add the alkaline solution of potassium manganate(VII) in a flask. Heat the mixture under reflux (Fig. 2.1) until the purple colour disappears.

Cool the mixture and add dilute sulphuric acid until the mixture is acid to litmus. Add solid sodium metabisulphite until the brown solid (manganese(IV) oxide) has dissolved. Filter the white crystals of benzoic acid and recrystallise them from hot water. Find the m.p. of benzoic acid.

8.7 Questions

1 Describe **two** reactions which show that ethene (an alkene) and benzene are different and **two** reactions which show them to be similar.

Show by diagrams how you consider benzene to be structurally related to ethene and then briefly explain why it differs in its behaviour. (JMB)

2 How, and under what conditions, does (i) chlorine, (ii) nitric acid, react with (a) benzene, (b) methylbenzene?

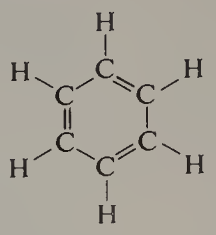
Outline how benzene may be converted into methylbenzene and vice versa. (C(N))

3 Distinguish between an aliphatic and an aromatic compound.

Give one reaction to illustrate the saturated nature and one reaction to illustrate the unsaturated nature of the benzene molecule.

Explain how you would convert benzene into (a) benzene carboxylic acid (benzoic acid), (b) methylbenzene (toluene), (c) hydroxybenzene (phenol), and also how each of these products may be reconverted into benzene. (AEB)

4 The average bond energies associated with the C—H bond, the C—C bond and the C=C bond are respectively 98·7, 82·6 and 146·0 kcal $mole^{-1}$. Use these values to calculate the theoretical enthalpy of formation of the molecule:



In practice, the enthalpy of formation of benzene from atoms is 1317 kcal mole^{-1}. How do you account for the difference in these quantities? Discuss the action of bromine on benzene in the light of your answer.

The normal length of a C—C bond is 1·54 Å, and for a C=C bond is 1·33 Å. Suggest values, which might be observed experimentally, for the lengths of the various bonds in

(a) benzene,
(b) graphite,
(c) diamond, and
(d) buta-1,3-diene ($CH_2{=}CH{-}CH{=}CH_2$).

Indicate briefly the reasons for your answers. (L(X))

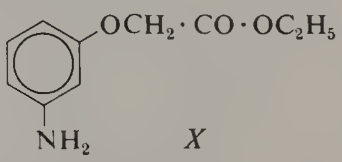
5 There are **three** typical ways in which methylbenzene might react with chlorine. State what these are and indicate the conditions necessary for two of them to take place.

How can methylbenzene or its chlorination products be converted into benzaldehyde?

6 (a) Write equations to show how, given supplies of benzene and methylbenzene, you would prepare the following compounds. (Full practical details are not required, but reagents and conditions should be indicated.)

(i) C_6H_5I, (ii) $C_6H_5NHCOCH_3$, (iii) C_6H_5CHO.

(b) A compound is believed to have structure *X*.



X

By what chemical reactions would you show the presence of:

(i) the benzene ring;
(ii) the amino group;
(iii) the ester group? (C(N, S))

7 How is methylbenzene obtained industrially and how may it be prepared from benzene? By what reactions may (a) benzaldehyde, (b) benzoic acid, (c) a chloromethylbenzene, and (d) benzene be obtained from methylbenzene?

8 Both ethene and benzene are unsaturated compounds. They both react with chlorine under different conditions and by different mechanisms.

(a) State what is meant by *unsaturated compounds*.
(b) Give the structures of ethene and benzene and discuss the similarities and differences between them.
(c) State how ethene and benzene react with chlorine, giving the conditions and the mechanisms of the reactions in each case. (AEB)

9 Give the name and formula of one example of an alkane, an alkyne and an aromatic hydrocarbon. Compare and contrast the reactions of the named compounds with (a) bromine, (b) potassium manganate(VII) (potassium permanganate), and (c) sulphuric acid.
Give a mechanism for (i) the reaction of the alkane with bromine, (ii) the reaction of the alkene with sulphuric acid, (iii) the reaction of the aromatic hydrocarbon with a nitrating mixture. (L)

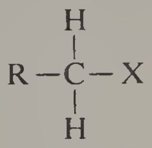
Chapter 9

Halogen compounds

9.1
Introduction

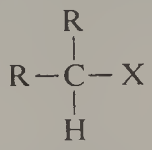
The four halogens (fluorine, chlorine, bromine and iodine) are contained in several types of organic compound:

Alkyl halides, in which the halogen atom is attached to a saturated carbon atom (e.g. bromoethane, $CH_3—CH_2—Br$). These can be subdivided into three classes, according to how many alkyl groups are attached to the carbon atom which is bonded to the halogen:



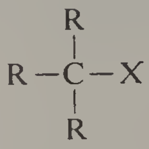
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-X$$

Primary



$$R-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-X$$

Secondary



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-X$$

Tertiary

These descriptions correspond to those of the related alcohols (10.2).

Unsaturated halides, in which the halogen atom is attached to a carbon atom which forms a double or triple bond (e.g. chloroethene, $CH_2{=}CH—Cl$).

Aryl halides, in which the halogen atom is attached to an aromatic ring (e.g. chlorobenzene, $C_6H_5—Cl$).

There are also **polyhalides**, which contain more than one halogen atom (e.g. 1,2-dichloroethane, $CH_2Cl—CH_2Cl$; trichloromethane, $CHCl_3$).

9.2
Nomenclature

Alkyl halides are named as derivatives of the corresponding alkane, a number being inserted to indicate the position of the halogen atom in the carbon chain where there would otherwise be ambiguity. The simpler ones can also be named by combining the names of the appropriate alkyl group and the halide; for example, CH_3Cl is chloromethane or methyl chloride. Unsaturated halides are generally named as derivatives of the corresponding alkene or alkyne. Examples are in Table 9.1. Aryl halides are described in Section 9.6.

This section considers chlorides, bromides and iodides. Fluorides are discussed separately (9.7).

9.3
Alkyl halides

Physical properties

Chloromethane, chloroethane and bromomethane are colourless gases at room temperature. The other lower members are colourless liquids with a sweet smell. Iodides have a higher boiling point than bromides, which, in turn, boil at higher temperatures than the chlorides (Table 9.1).

The alkyl halides are insoluble in water, but are soluble in organic solvents.

Alkyl chlorides are less dense than water, but the bromides and iodides are denser.

Table 9.1. Some aliphatic halides

NAME	FORMULA	B.P./°C
Chloromethane	CH_3Cl	–24
Bromomethane	CH_3Br	4
Iodomethane	CH_3I	42
Chloroethane	CH_3CH_2Cl	12
Bromoethane	CH_3CH_2Br	38
Iodoethane	CH_3CH_2I	72
1-Chloropropane	$CH_3CH_2CH_2Cl$	47
2-Chloropropane	$CH_3\overset{\overset{Cl}{\vert}}{C}HCH_3$	36
1-Chlorobutane	$CH_3CH_2CH_2CH_2Cl$	78
2-Chlorobutane	$CH_3CH_2\overset{\overset{Cl}{\vert}}{C}HCH_3$	68
2-Chloro-2-methylpropane	$(CH_3)_3CCl$	51
1-Bromobutane	$CH_3CH_2CH_2CH_2Br$	102
Dichloromethane	CH_2Cl_2	40
1,1-Dichloroethane	CH_3CHCl_2	57
1,2-Dichloroethane	$ClCH_2CH_2Cl$	84
1,2-Dibromoethane	$BrCH_2CH_2Br$	131
Trichloromethane	$CHCl_3$	61
Tri-iodomethane	CHI_3	m.p. 119
Tetrachloromethane	CCl_4	77
Chloroethene	$CH_2{=}CHCl$	–14

Laboratory preparations

1. From alcohols

(a) *Alkyl chlorides*

(i) By treating the alcohol with sulphur dichloride oxide (a liquid, b.p. 77°C). Sulphur dioxide and hydrogen chloride are evolved:

$$R{-}OH + SOCl_2 \rightarrow R{-}Cl + SO_2 + HCl$$

An organic base (for example, pyridine) is often added to neutralise the hydrogen chloride.

(ii) By treating the alcohol with hydrogen chloride:

$$R{-}OH + HCl \rightarrow R{-}Cl + H_2O$$

To obtain good yields from primary and secondary alcohols, anhydrous conditions are necessary and even then primary alcohols react slowly unless anhydrous zinc chloride is used as a catalyst with the hydrogen chloride. However, tertiary alcohols react readily even in the presence of water and concentrated hydrochloric acid can be used.

(b) *Alkyl bromides*

(i) By treating the alcohol with a mixture of red phosphorus and bromine:

$$2P + 3Br_2 \rightarrow 2PBr_3$$

$$3R{-}OH + PBr_3 \rightarrow 3R{-}Br + H_3PO_3$$

(ii) By treating the alcohol with hydrogen bromide. It is convenient to generate the hydrogen bromide *in situ* by the reaction of potassium bromide with concentrated sulphuric acid:

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$

$$R—OH + HBr \rightarrow R—Br + H_2O$$

(c) *Alkyl iodides*

(i) By treating the alcohol with a mixture of red phosphorus and iodine:

$$2P + 3I_2 \rightarrow 2PI_3$$

$$3R—OH + PI_3 \rightarrow 3R—I + H_3PO_3$$

(ii) By treating the alcohol with a concentrated solution of hydriodic acid:

$$R—OH + HI \rightarrow R—I + H_2O$$

The hydrogen iodide can be prepared *in situ* from potassium iodide and phosphoric acid:

$$3KI + H_3PO_4 \rightarrow 3HI + K_3PO_4$$

(Sulphuric acid is not used because it oxidises hydrogen iodide.)

2. From alkenes

Hydrogen halides react with alkenes to form alkyl halides. The orientation in the addition reaction is described by Markownikoff's rule (6.4), for example:

$$CH_3—CH{=}CH_2 + HCl \rightarrow \underset{\text{2-chloropropane}}{CH_3—CHCl—CH_3}$$

Manufacture of alkyl chlorides

1. By addition of hydrogen chloride to an alkene (6.3). For example, over 90% of chloroethane is made by this route, from ethene and hydrogen chloride.
2. By direct chlorination of alkanes (5.5).

Chemical properties

(a) Substitution reactions

The most important reactions of alkyl halides are those in which the halogen atom, X, is replaced by another group. They can be represented by the general equation:

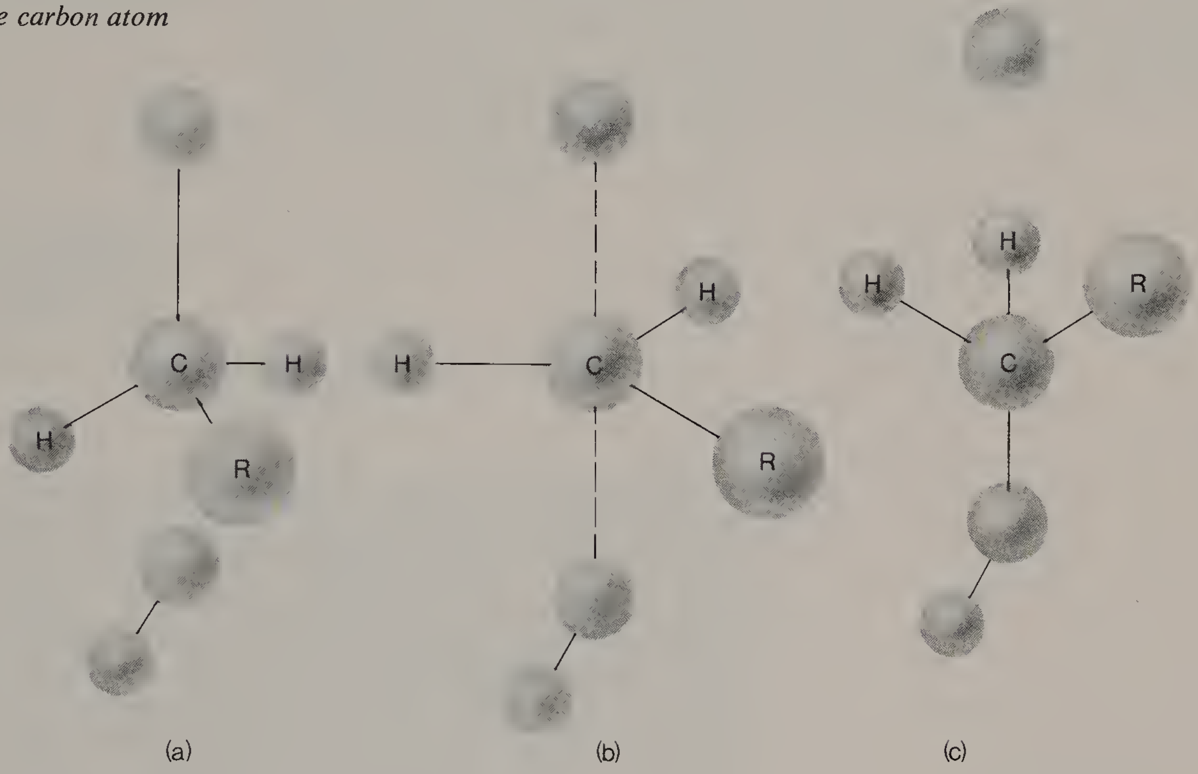
$$R—X + Y—Z \rightarrow R—Z + Y—X$$

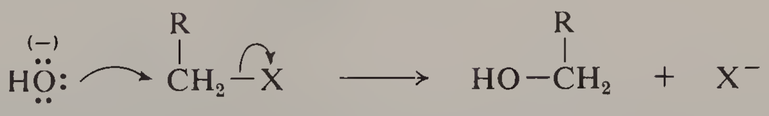
An example is the hydrolysis of an alkyl halide with sodium hydroxide:

$$R—X + NaOH \rightarrow R—OH + NaX$$

The mechanisms of these reactions have been studied in great detail and are well understood. There are two general mechanisms. The first applies to *primary* halides, RCH_2X. The reagent (e.g. hydroxide ion) approaches the carbon atom of the C—X bond in the halide from the side opposite to the halogen atom. As it does so, it begins to form a bond to the carbon atom, while the bond between the carbon atom and the halogen begins to break (Fig. 9.1). The pair of electrons which forms the new bond is supplied by the reagent, and the pair of electrons in the C—X bond is gradually acquired completely by the halogen atom. A convenient representation of these processes is:

FIG. 9.1. *The mechanism of an* S_N2 *reaction of an alkyl halide,* RCH_2X. *(a) The approach of a hydroxide ion; (b) The transition state, showing that the alkyl group,* RCH_2, *is planar; (c) The reaction product,* RCH_2OH, *is formed and the four bonds are tetrahedrally arranged around the carbon atom*



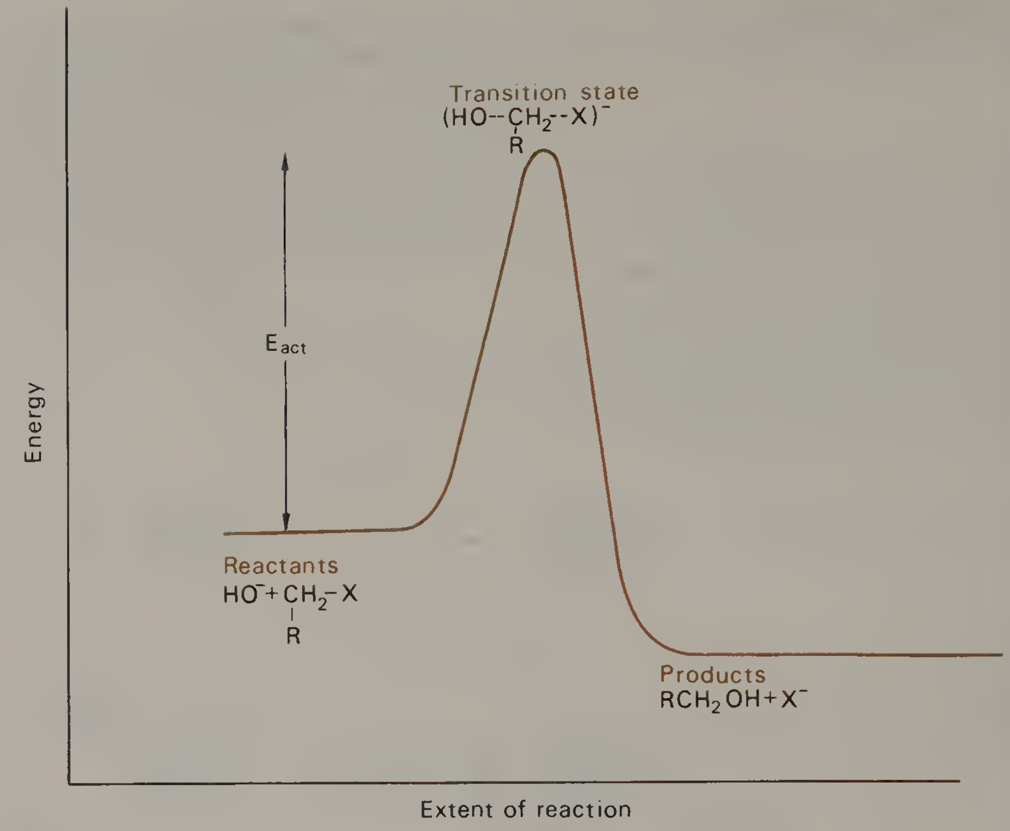


$$\overset{(-)}{\mathrm{H\ddot{\underset{..}{O}}}:} \curvearrowright \overset{\displaystyle R}{\overset{|}{\mathrm{CH_2}}}\overset{\curvearrowright}{-}\mathrm{X} \longrightarrow \mathrm{HO}-\overset{\displaystyle R}{\overset{|}{\mathrm{CH_2}}} + \mathrm{X}^-$$

where each curved arrow represents the movement of a pair of electrons. Eventually, the new bond is fully formed and the C—X bond is completely broken.

The energy change during the reaction is shown in Fig. 9.2. At first, more energy is needed to break the C—X bond than is supplied by the formation of the new C—O bond, and the energy of the system increases. A peak is reached, corresponding approximately to the situation in which the C—X bond is 'half-broken' and the C—O bond is 'half-formed'; the system is then described as being at its **transition state**. The energy then decreases, corresponding to the completion of the formation of the C—O bond. The difference in energy between the transition state and the reactants is the

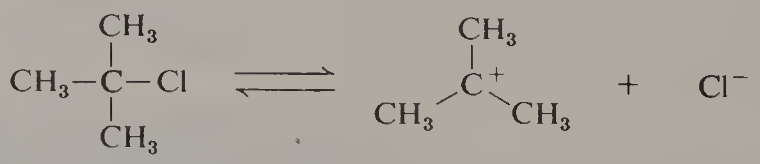
FIG. 9.2. *The variation in energy as the reactants* $RCH_2X + OH^-$ *are converted into the products* $RCH_2OH + X^-$



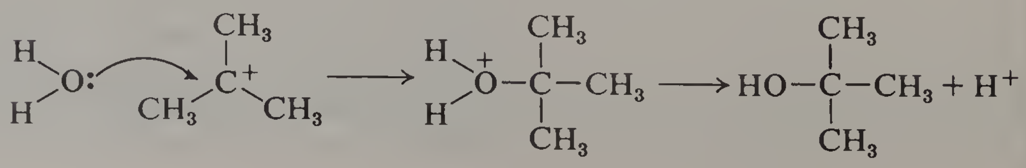
activation energy of the reaction. There is in effect a barrier to the reaction; a collision between the reactants can only lead to the formation of products when the reactant molecules possess between them enough excess of kinetic energy to surmount the barrier. In many cases, only a small proportion possesses sufficient energy, and reaction is slow. However, kinetic energy rises with temperature, and so the rate is increased by heating.

Other reagents which possess at least one unshared pair of electrons can replace the hydroxide ion in this reaction. Such reagents are described as **nucleophiles** ('nucleus-seeking') or **nucleophilic reagents**. Since two species —the reagent and the alkyl halide—are brought together in formation of the transition state, the reaction is **bimolecular**. The overall reaction is referred to as an S_N2 reaction (Substitution, nucleophilic, bimolecular).

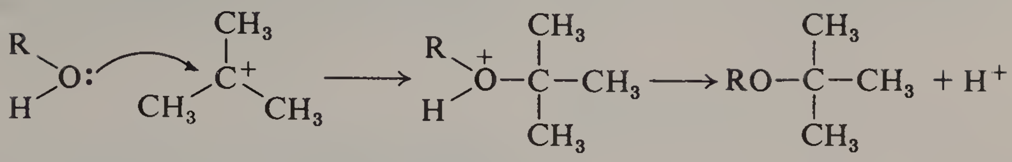
The second mechanism applies to *tertiary* halides. These ionise spontaneously in solution, forming a carbonium ion and a halide ion, for example:



The rate of ionisation is fairly small, and the equilibrium lies well to the left-hand side. However, the carbonium ion is very reactive and is attacked by other nucleophiles which may be present. For example, if water is the solvent, water itself acts as the nucleophile and an alcohol is formed:



If the solvent is an alcohol, an ether is formed:



$$\mathrm{ROH:} + (\mathrm{CH_3})_3\mathrm{C^+} \longrightarrow \mathrm{R(H)\overset{+}{O}{-}C(CH_3)_3} \longrightarrow \mathrm{RO{-}C(CH_3)_3} + \mathrm{H^+}$$

These reactions can be represented as in Fig. 9.3. The slow step is the breaking of the C—Cl bond to form the carbonium ion. This can then either revert to the reactants by recombining with chloride ion, or give products by reacting with water. Both these steps are fast, and although the recombination with chloride ion has the lower activation energy, most of the carbonium ions react with water because it is present in far higher concentration than chloride ion. The overall reaction is described as **unimolecular** because only one molecule is involved in the transition state of the slow step, and it is also described as an S_N1 reaction.

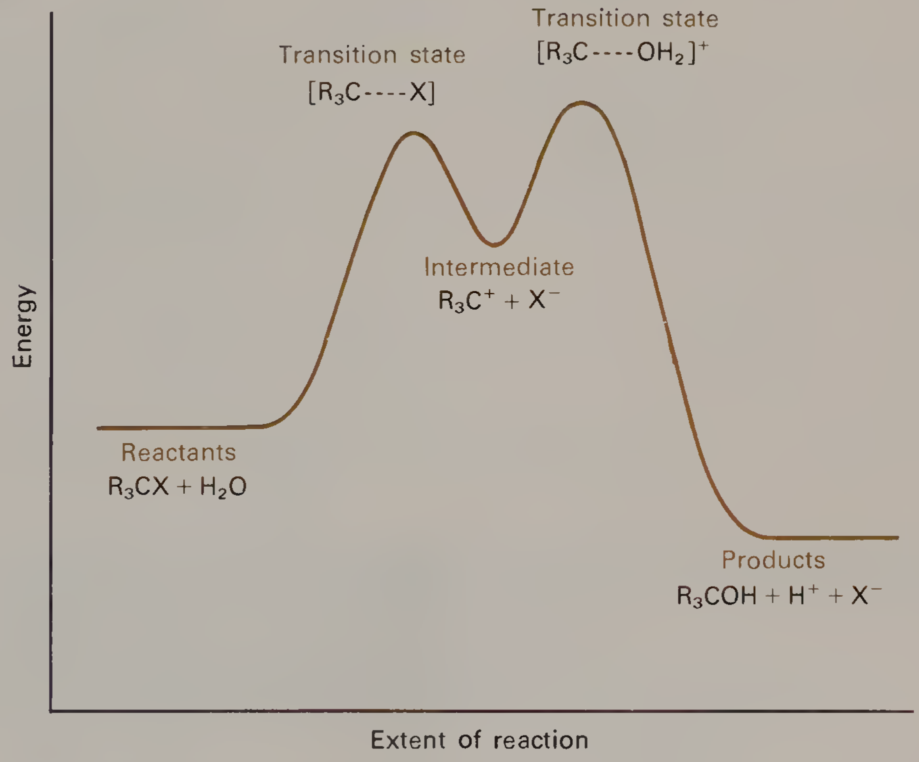


FIG. 9.3. *The variation in energy during the hydrolysis of a tertiary halogenoalkane by the* S_N1 *reaction*

The difference between tertiary and primary halides arises because a tertiary carbonium ion is a relatively more stable species than a primary carbonium ion (6.4) and is formed much faster. The activation energy for formation of a primary carbonium ion is so great that it is not formed at a significant rate under most conditions; instead, a nucleophilic reagent is needed to assist the breaking of the C—X bond.

Secondary alkyl halides (e.g. 2-chloropropane, $(\mathrm{CH_3})_2\mathrm{CH{-}Cl}$) are intermediate in behaviour between primary and tertiary halides; they react partly by the bimolecular S_N2 reaction and partly by the unimolecular S_N1 reaction.

The following are examples of these nucleophilic substitution reactions with **primary** alkyl halides.

(i) *Preparation of an alcohol.* By treatment of the halide with an aqueous solution of sodium hydroxide, for example:

$$C_2H_5-Br + NaOH \rightarrow C_2H_5-OH + NaBr$$

(ii) *Preparation of an ether.* By treatment of the halide with a solution of a sodium alkoxide in the corresponding alcohol, for example:

$$C_2H_5-Br + C_2H_5-O^-Na^+ \rightarrow \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + NaBr$$

The nucleophile is the alkoxide ion, $C_2H_5O^-$. However, with higher homologues, an alternative reaction—elimination of the hydrogen halide—is also important and is often the major reaction (p. 123).

(iii) *Preparation of amines.* By heating the halide with concentrated ammonia in a sealed tube. A mixture of amines is formed, for example:

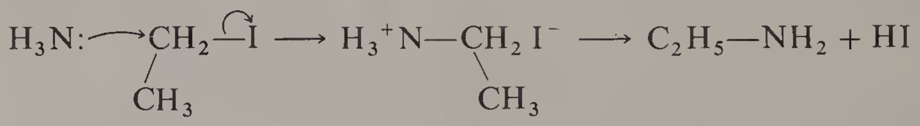
$$C_2H_5-I + NH_3 \rightarrow \underset{\text{Ethylamine}}{C_2H_5-NH_2} + HI$$

$$C_2H_5-I + C_2H_5-NH_2 \rightarrow \underset{\text{Diethylamine}}{(C_2H_5)_2NH} + HI$$

$$C_2H_5-I + (C_2H_5)_2NH \rightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + HI$$

$$C_2H_5-I + (C_2H_5)_3N \rightarrow \underset{\text{Tetraethylammonium iodide}}{(C_2H_5)_4N^+I^-}$$

Ammonia is a nucleophile:



$$H_3N\!:\longrightarrow \underset{CH_3}{CH_2}-I \longrightarrow H_3{}^{+}N-\underset{CH_3}{CH_2}\ I^- \longrightarrow C_2H_5-NH_2 + HI$$

Likewise, ethylamine, diethylamine and triethylamine are nucleophilic reagents.

In each of the first three equations, the first-formed product is therefore a substituted ammonium salt. However, this is in equilibrium with the amine, e.g.

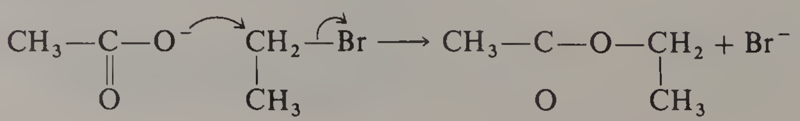
$$C_2H_5-\overset{+}{N}H_3\ I^- \rightleftharpoons C_2H_5-NH_2 + HI$$

and it is the amine which takes part in subsequent steps. Each amine is thereby removed from the equilibrium so that eventually, with a sufficient excess of the halide, the quaternary salt (tetraethylammonium iodide) is formed.

(iv) *Preparation of an ester.* By treatment of the halide with the silver salt of a carboxylic acid, for example:

$$C_2H_5-Br + \underset{\text{Silver ethanoate}}{CH_3-CO_2{}^-Ag^+} \rightarrow \underset{\text{Ethyl ethanoate}}{C_2H_5-O-CO-CH_3} + AgBr$$

The nucleophile is the ethanoate anion:



$$CH_3-\underset{\overset{\|}{O}}{C}-O^- \quad \underset{CH_3}{CH_2}-Br \longrightarrow CH_3-\underset{O}{C}-O-\underset{CH_3}{CH_2} + Br^-$$

(v) *Preparation of a nitrile.* By refluxing a solution of the halide and potassium cyanide in ethanol, for example:

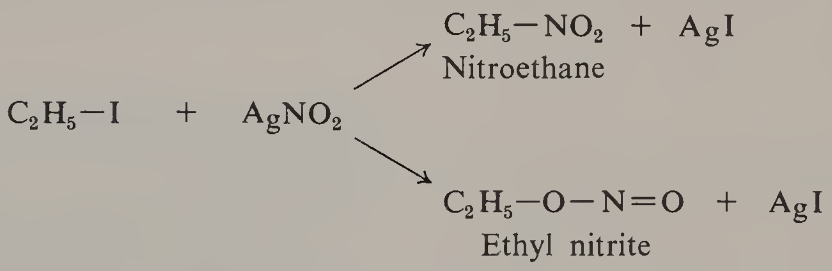
$$C_2H_5{-}Br + KCN \rightarrow \underset{\text{Propanenitrile}}{C_2H_5{-}CN} + KBr$$

The nucleophile is the cyanide anion, $N{\equiv}C^-$.

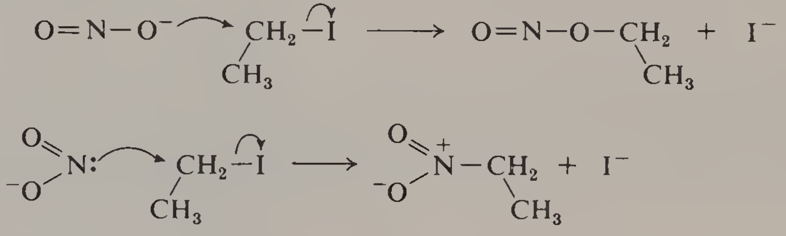
If silver cyanide is used, an *isocyano-compound* is formed:

$$C_2H_5{-}Br + AgCN \rightarrow \underset{\text{Isocyanoethane}}{C_2H_5{-}\overset{+}{N}{\equiv}\overset{-}{C}} + AgBr$$

(vi) *Preparation of a nitroalkane.* By refluxing a solution of the halide in ethanol with silver nitrite. A mixture of a nitroalkane and an alkyl nitrite is formed and can be separated by fractional distillation, for example:



The nucleophile is the nitrite ion, NO_2^-. It can react at either an oxygen atom or the nitrogen atom:



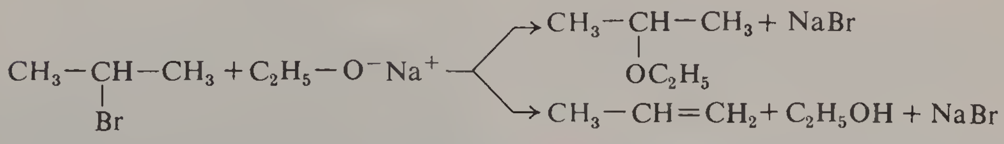
(vii) *Preparation of alkylaromatic compounds.* By reaction of the halide with the aromatic compound in the presence of an aluminium halide (Friedel-Crafts reaction, p. 105), for example:

$$C_6H_6 + C_2H_5{-}Br \xrightarrow{AlBr_3 \text{ as cat.}} \underset{\text{Ethylbenzene}}{C_6H_5{-}C_2H_5} + HBr$$

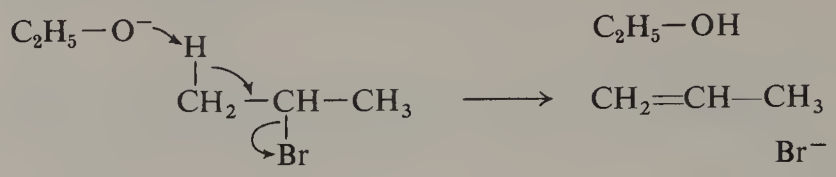
These reactions can be regarded either as electrophilic substitutions in the aromatic compound or nucleophilic substitutions by the aromatic compound on the alkyl halide (p. 105).

(b) Elimination reactions

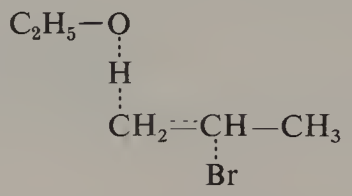
When 2-bromopropane is refluxed with a solution of sodium hydroxide in ethanol, both an ether and propene are formed:



The ether is formed by the S_N2 reaction and propene is formed by an elimination reaction: the base, ethoxide ion, abstracts a proton from the halide at the same time as the halide ion breaks away. The movements of electron-pairs are represented as follows:



At the transition state, the C—H and C—Br bonds are partially broken and the C═C and O—H bonds are partially formed:



Since two molecules are involved in the formation of the transition state, the reaction is bimolecular; it is described as an *E*2 reaction (*E*, elimination; 2, bimolecular).

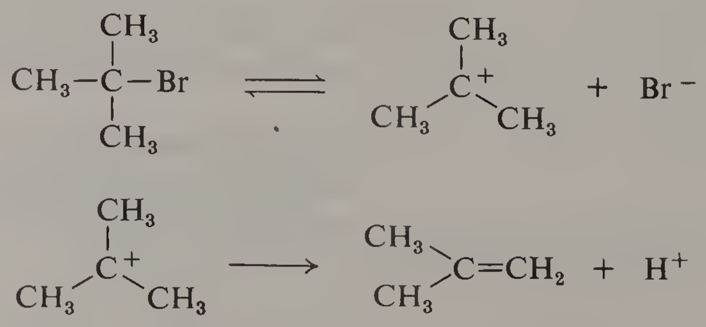
Competition between the S_N2 and *E*2 reactions occurs with other primary and secondary halides. The relative importance of each type of reaction depends on the solvent, the temperature and the structure of the halide; the ratio of elimination to substitution increases as:

(i) the solvent is changed from water (where the reagent is hydroxide ion) to an alcohol, ROH (where the reagent is the corresponding alkoxide ion, RO^-);

(ii) the temperature is increased;

(iii) the number of alkyl groups adjacent to the double bond in the resulting alkene is increased (for example, the reaction of bromoethane with a solution of sodium hydroxide in ethanol gives only 1 per cent of ethene, whereas 2-bromopropane, under the same conditions, gives 80 per cent of propene).

Tertiary alkyl halides, and to some extent secondary alkyl halides, undergo elimination by a different mechanism in which the first step is heterolysis of the carbon–halogen bond, for example:



This is described as an *E*1 reaction (*E*, elimination; 1, unimolecular). The intermediate carbonium ion is the same as is involved in substitution reactions, so that the *E*1 elimination competes with the S_N1 substitution. Under most conditions, the *E*1 reaction is the major process.

(c) Reactions with metals

Alkyl halides react with sodium to give alkanes, for example:

$$2C_2H_5{-}I + 2Na \rightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaI$$

This is the **Wurtz** reaction.

With magnesium, they form **Grignard reagents** (alkylmagnesium halides), for example:

$$C_2H_5{-}Br + Mg \rightarrow \underset{\substack{\text{Ethylmagnesium}\\ \text{bromide}}}{C_2H_5{-}MgBr}$$

These reagents are of especial value in synthesis (9.8).

Uses of alkyl halides

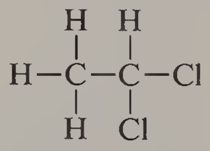
Alkyl halides are of great value in organic synthesis because of the variety of compounds which can be made from them by nucleophilic substitution and *via* Grignard reagents (9.8).

Tetraethyllead, which is the principal 'anti-knock' additive in petrol (19.4), is made by heating chloroethane with a lead–sodium alloy:

$$4C_2H_5{-}Cl + Pb + 4Na \rightarrow (C_2H_5)_4Pb + 4NaCl$$

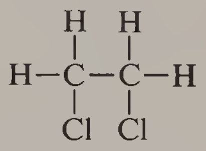
9.4
Polyhalides

Compounds in which two halogen atoms are attached to adjacent carbon atoms are known as *vic*-dihalides (*vicinal*, adjacent). Compounds in which two halogen atoms are attached to one carbon atom are known as *gem*-dihalides (*gemini*, twins). For example:



$$\begin{array}{ccccc} & & H & & H & \\ & & | & & | & \\ H & - & C & - & C & - Cl \\ & & | & & | & \\ & & H & & Cl & \end{array}$$

1,1-Dichloroethane
(a *gem*-dihalide)



$$\begin{array}{ccccc} & & H & & H & \\ & & | & & | & \\ H & - & C & - & C & - H \\ & & | & & | & \\ & & Cl & & Cl & \end{array}$$

1,2-Dichloroethane
(a *vic*-dihalide)

There are also compounds in which three or four halogen atoms are attached to one carbon atom [for example, trichloromethane ($CHCl_3$), tri-iodomethane (CHI_3), tetrachloromethane (CCl_4)].

vic-Dihalides are prepared by the addition of the halogen to an alkene, for example:

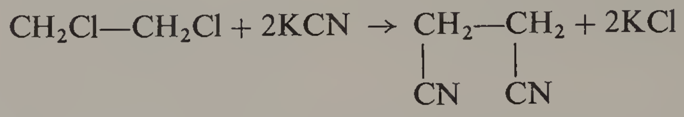
$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2Br{-}CH_2Br$$

The properties of *vic*-dihalides are very similar to those of alkyl halides. Thus, they undergo both substitution and elimination reactions, for example:

1. They undergo hydrolysis when heated with aqueous sodium hydroxide:

$$\underset{}{CH_2Cl{-}CH_2Cl} + 2NaOH \rightarrow \underset{\text{Ethane-1,2-diol}}{CH_2OH{-}CH_2OH} + 2NaCl$$

2. They react with a solution of potassium cyanide in ethanol to give dinitriles:



$$CH_2Cl{-}CH_2Cl + 2KCN \rightarrow \underset{\substack{|\\ CN}}{CH_2}{-}\underset{\substack{|\\ CN}}{CH_2} + 2KCl$$

3. They undergo elimination with a hot solution of sodium hydroxide in ethanol:

$$CH_2Cl{-}CH_2Cl + C_2H_5{-}O^- Na^+ \rightarrow CH_2{=}CHCl + C_2H_5OH + NaCl$$

$$CH_2{=}CHCl + C_2H_5{-}O^- Na^+ \rightarrow CH{\equiv}CH + C_2H_5OH + NaCl$$

gem-Dihalides are prepared from aldehydes or ketones with phosphorus pentahalides, for example:

$$CH_3{-}CH{=}O + PCl_5 \rightarrow CH_3{-}CHCl_2 + POCl_3$$

Hydrolysis regenerates the aldehyde or ketone, for example:

$$CH_3{-}CHCl_2 + 2NaOH \rightarrow CH_3{-}CHO + H_2O + 2NaCl$$

Hence, they can readily be distinguished from *vic*-dihalides, which give diols (dihydric alcohols) on hydrolysis.

Trichloromethane (chloroform) can be made in the laboratory by heating ethanol with bleaching powder. The bleaching powder provides chlorine, and reaction occurs in three stages, which can be represented by the following equations:

Oxidation:

$$CH_3{-}CH_2OH + Cl_2 \rightarrow CH_3{-}CHO + 2HCl$$

Chlorination:

$$CH_3{-}CHO + 3Cl_2 \rightarrow CCl_3{-}CHO + 3HCl$$

Hydrolysis:

$$2CCl_3{-}CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + \underset{\substack{\text{Calcium}\\ \text{methanoate}}}{(H{-}CO_2)_2Ca}$$

$$(Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O)$$

Trichloromethane is a colourless liquid with a characteristic sickly smell. It is almost insoluble in water but is soluble in most organic solvents. Its chemical properties are as follows:

1. It is oxidised in the presence of light and air to carbonyl chloride:

$$CHCl_3 + \tfrac{1}{2}O_2 \rightarrow \underset{\substack{\text{Carbonyl}\\ \text{chloride}}}{COCl_2} + HCl$$

Trichloromethane is stored in dark bottles to prevent the formation of carbonyl chloride, as it is intensely poisonous.

2. It is hydrolysed with alkali:

$$CHCl_3 + 4NaOH \rightarrow \underset{\text{Sodium methanoate}}{H{-}CO_2^-\,Na^+} + 3NaCl + 2H_2O$$

This reaction occurs by a different mechanism from those in the hydrolysis of other aliphatic halides. Trichloromethane is weakly acidic, and in basic solution ionises to a small extent to form a **carbanion**, CCl_3^-:

$$CHCl_3 + OH^- \rightleftharpoons \overset{-}{C}Cl_3 + H_2O$$

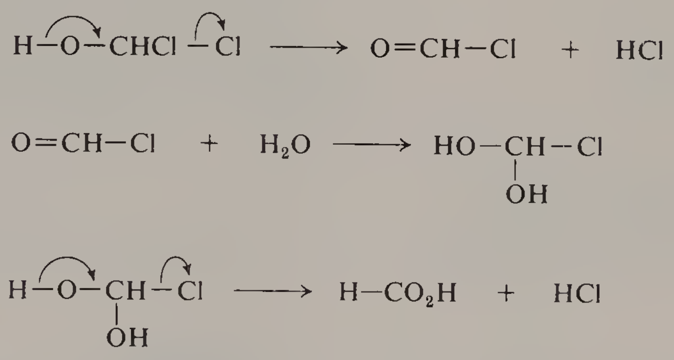
The carbanion eliminates a chloride ion to form a **carbene**:

$$\overset{-}{C}Cl_3 \rightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

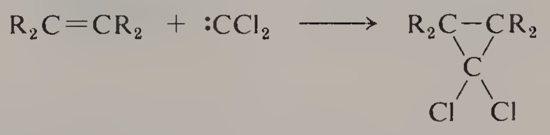
Dichlorocarbene has two electrons available for bonding and is therefore very reactive; thus, it is attacked by water:

$$:CCl_2 + H_2O \rightarrow HO{-}CHCl_2$$

The resulting unstable species reacts further:



The high reactivity of dichlorocarbene is also shown by its reaction with alkenes to give cyclopropane derivatives:



3. It reacts with a primary amine, in an ethanolic solution of potassium hydroxide, to form an isocyano-compound (**carbylamine reaction**):

$$CHCl_3 + 3KOH + R{-}NH_2 \rightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C} + 3H_2O + 3KCl$$

Isocyano-compounds have characteristic powerful and unpleasant smells, and their formation has sometimes been used as a test for primary amines.

This reaction also occurs *via* dichlorocarbene, which is formed in the basic solution:

$$CHCl_3 + OH^- \rightarrow \overset{-}{C}Cl_3 + H_2O$$

$$\overset{-}{C}Cl_3 \rightarrow :CCl_2 + Cl^-$$

$$R{-}NH_2 + :CCl_2 \rightarrow R{-}\overset{+}{N}H_2{-}\overset{-}{C}Cl_2 \rightarrow R{-}NH{-}CHCl_2$$

$$R{-}NH{-}CHCl_2 + 2OH^- \rightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C} + 2Cl^- + 2H_2O$$

Tetrachloromethane (carbon tetrachloride) is manufactured by the chlorination of carbon disulphide. Aluminium chloride is used as a catalyst.

$$CS_2 + 3Cl_2 \xrightarrow{AlCl_3\text{ as cat.}} CCl_4 + \underset{\substack{\text{Disulphur}\\ \text{dichloride}}}{S_2Cl_2}$$

It is a colourless liquid which is insoluble in water but soluble in all organic solvents. It is inert to most reagents; for example, it is not hydrolysed by alkali. It is used as a fire-extinguisher (Pyrene) because it is non-inflammable and its dense vapour prevents oxygen getting to the flame.

9.5
Unsaturated halides

Chloroethene (vinyl chloride), $CH_2{=}CHCl$, is the most important of the unsaturated halides.

It is manufactured from ethyne (7.2) and, to an increasing extent, from ethene (6.3). Its principal use is for the manufacture of PVC (poly(chloroethene)) (p. 330).

The reactions of chloroethene are strikingly different from those of alkyl chlorides in that it does not react with nucleophilic reagents; for example, it is not hydrolysed by sodium hydroxide.

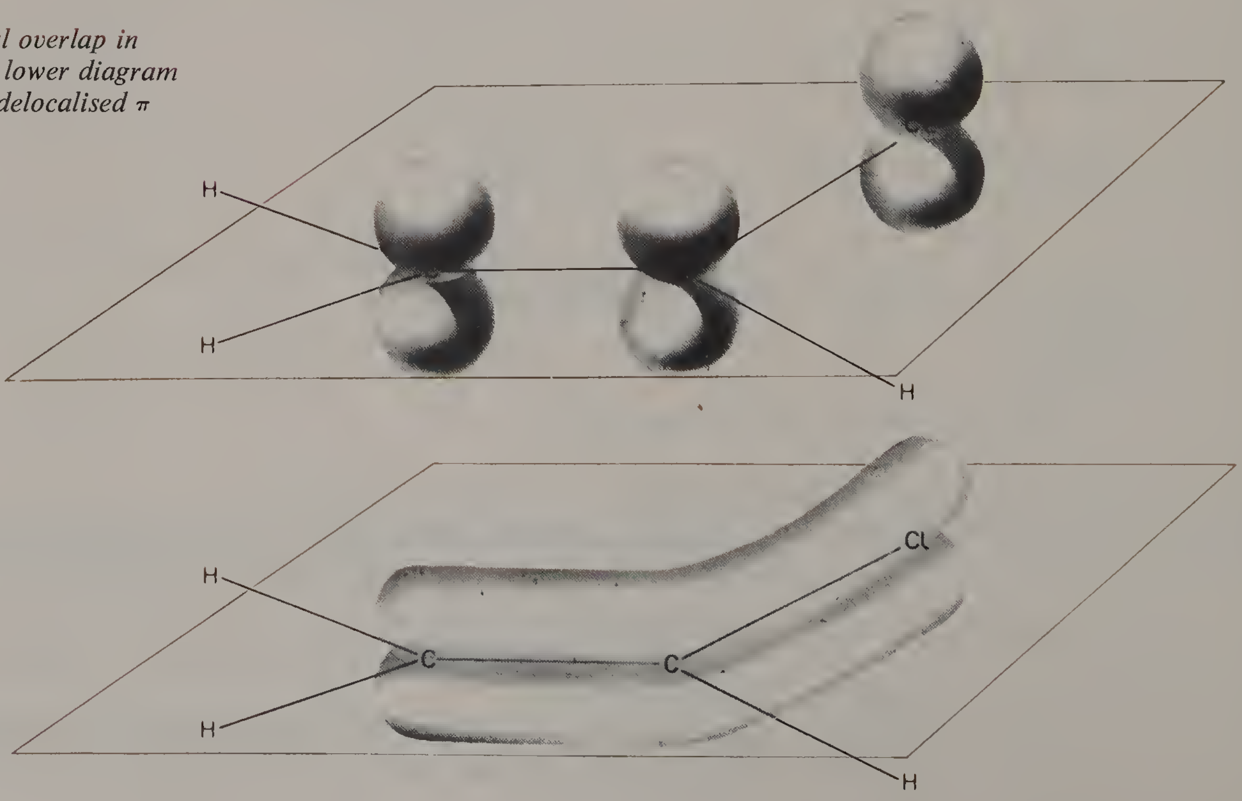


FIG. 9.4. p-*Orbital overlap in chloroethene; the lower diagram shows one of the delocalised π orbitals*

The reason for this difference is that the C—Cl bond in chloroethene is stronger than one in an alkyl chloride such as chloroethane and is therefore less readily broken. This in turn is because, in chloroethene, a *p* orbital on chlorine interacts with the *p* orbital on the adjacent carbon atom (Fig. 9.4), providing additional bonding as compared with an alkyl chloride.

Trichloroethene, $CHCl{=}CCl_2$, is manufactured by the chlorination of 1,2-dichloroethane (p. 85) in presence of a catalyst:

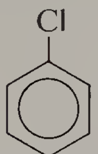
$$CH_2Cl{-}CH_2Cl + 2Cl_2 \xrightarrow[300^\circ C]{\text{cat.}} CHCl{=}CCl_2 + 3HCl$$

It resembles chloroethene in being unreactive towards nucleophilic reagents, and because of its chemical stability and its property of dissolving oils and greases, it is used as a cleaning agent. Surfaces are cleaned by suspending the object (for example, an aeroplane wing or large engine) in the vapour of trichloroethene, which condenses on the surface and 'strips off' the grease and dirt.

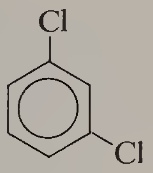
9.6
Aromatic halides

There are two types of halides which contain an aromatic ring, examples of which are given in Table 9.2.

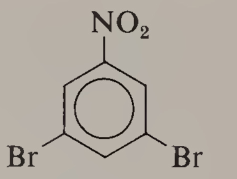
(a) **Aryl halides** have the halogen atom attached to the aromatic ring. They are named as the halogen derivatives of the aromatic compound, for example:



Chlorobenzene



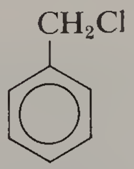
1,3-Dichlorobenzene



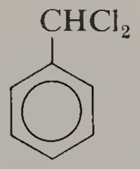
3,5-Dibromonitrobenzene

Aryl halides (aryl, from aromatic) have different properties from alkyl halides.

(b) Some aromatic halides have the halogen atom in a side-chain, for example:



(Chloromethyl)-benzene



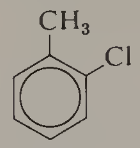
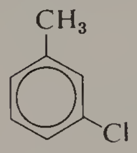
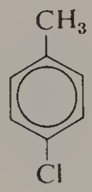
(Dichloromethyl)-benzene

These behave like aliphatic halides, and their reactions are compared with those of alkyl and aryl halides in the practical section (p. 137).

Preparation of aryl halides

1. Chlorobenzene and bromobenzene are prepared by the reaction of the halogen with benzene at room temperature in the presence of a 'halogen carrier' (8.3); iron, or aluminium chloride or bromide, are usually employed. The mechanism of the reaction is discussed on p. 104, and details of the laboratory preparation of bromobenzene are given on p. 136.

Table 9.2. Some aromatic halides

NAME	FORMULA	B.P./°C
Fluorobenzene	$C_6H_5—F$	85
Chlorobenzene	$C_6H_5—Cl$	132
Bromobenzene	$C_6H_5—Br$	156
Iodobenzene	$C_6H_5—I$	189
Chloro-2-methylbenzene		159
Chloro-3-methylbenzene		162
Chloro-4-methylbenzene		162
(Chloromethyl)benzene	$C_6H_5—CH_2Cl$	179
(Dichloromethyl)benzene	$C_6H_5—CHCl_2$	206
(Trichloromethyl)benzene	$C_6H_5—CCl_3$	221

2. All aryl halides can be prepared from the corresponding aromatic amine *via* the diazonium salt (16.8).

Manufacture of chlorobenzene

Chlorobenzene is now manufactured by the chlorination of benzene in the liquid phase using iron(III) chloride as the 'halogen carrier' (8.3).

Chemical properties of aryl halides

1. They are unreactive towards nucleophilic reagents under ordinary laboratory conditions. Thus, they resemble unsaturated halides and differ from alkyl halides. However, some reactions with nucleophiles can be effected under very vigorous conditions, and one which is of industrial importance is the hydrolysis of chlorobenzene with sodium hydroxide solution at 200°C under a pressure of 200 atmospheres:

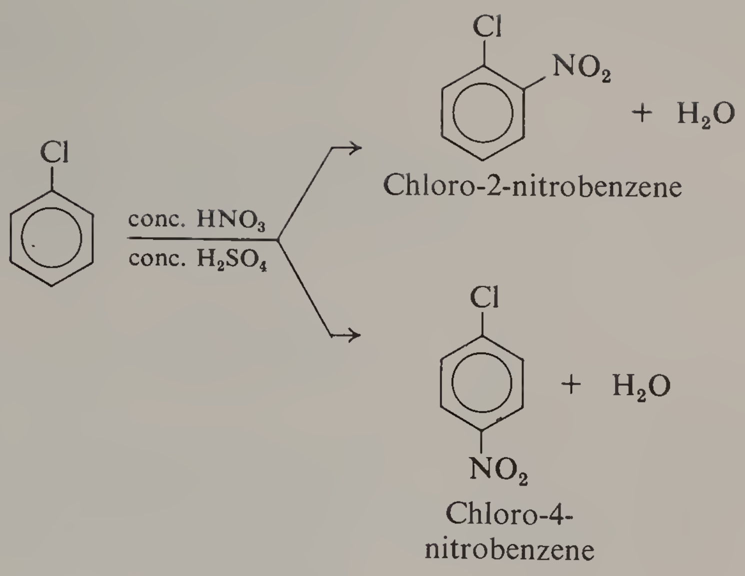
$$C_6H_5—Cl + 2NaOH \rightarrow C_6H_5—O^-Na^+ + H_2O + NaCl$$

Phenol is liberated on the addition of acid:

$$C_6H_5—O^-Na^+ + H^+ \rightarrow C_6H_5—OH + Na^+$$

2. Aryl halides undergo substitution in the aromatic ring with electrophilic reagents (8.5). The 2- and 4-derivatives are the major products, for

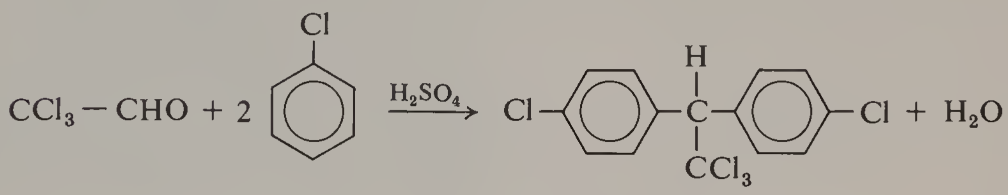
example:



3. Bromobenzene and iodobenzene form Grignard reagents with magnesium (9.8). Details of the preparation of phenylmagnesium bromide are given on p. 203.

Uses of chlorobenzene

Chlorobenzene is used in the manufacture of phenol (10.8) and the important insecticide D.D.T., by reaction with trichloroethanal in the presence of concentrated sulphuric acid.



9.7 Fluorocarbons

For convenience, the alkyl fluorides, R—F, and other fluorine derivatives of the hydrocarbons are discussed together. They are much less reactive than the other halides because of the much greater strength of the C—F bond (485 kJ mol^{-1}) than C—Cl (339 kJ mol^{-1}), C—Br (284 kJ mol^{-1}) or C—I (213 kJ mol^{-1}). In general, they behave like alkanes (hydrocarbons), so that they are usually referred to as fluorocarbons. Many have become of industrial importance during the last 20 years.

Physical properties

Fluorine derivatives have physical properties (for example, boiling points) which are similar to those of the parent alkane:

	$n = 1$	2	3	4
C_nH_{2n+2} B.p. °C	−162	−89	−42	−0·5
C_nF_{2n+2} B.p. °C	−128	−79	−38	−5

Preparations

1. *By fluorination of alkanes.* Fluorine reacts far more vigorously with the alkanes than do the other halogens, and it is necessary to use nitrogen as a diluent for the fluorine to help remove the heat evolved in the reaction. A complex mixture of products is formed and the carbon skeleton of the alkane is often broken down.

2. *By substitution of fluorine for other halogens.* (a) A halogen atom is replaced by fluorine when an alkyl halide is heated with anhydrous potassium fluoride in ethane-1,2-diol, for example:

$$CH_3{-}Cl + KF \rightarrow CH_3{-}F + KCl$$

(b) Antimony trifluoride, in the presence of antimony pentachloride, can also be used as a fluorinating agent, for example:

$$3CCl_4 + 2SbF_3 \rightarrow 3CF_2Cl_2 + 2SbCl_3$$

Addition of anhydrous hydrogen fluoride regenerates antimony trifluoride from the antimony trichloride.

3. *By substitution of fluorine for oxygen.* Sulphur tetrafluoride replaces oxygen by fluorine in alcohols ($R{-}OH \rightarrow R{-}F$), ketones ($R_2C{=}O \rightarrow R_2CF_2$) and acids ($R{-}CO_2H \rightarrow R{-}CF_3$).

4. *By electrolysis.* When an organic compound in pure hydrogen fluoride is electrolysed with nickel electrodes at 0°C, it undergoes fluorination at the anode. For example, diethyl ether gives $C_2F_5{-}O{-}C_2F_5$, and ethanoic acid gives $CF_3{-}CO{-}F$, which on hydrolysis gives trifluoroethanoic acid, $CF_3{-}CO_2H$.

Chemical properties

Unlike the other halogen derivatives of alkanes, the alkyl fluorides are chemically stable. They do not react with oxidising or reducing agents, or with strong acids and alkalis. They react slowly with sodium or potassium metal at elevated temperatures. However, Grignard reagents have been prepared, but the magnesium compound is only stable below −20°C.

The fluorocarbons are regarded as parents of a new branch of chemistry, similar to the organic compounds formed from hydrocarbons. Chains of $—CF_2—$ are stable, similar to $—CH_2—$ chains. Thus there is a wide range of fluorocarbon derivatives of the type R_FZ, where R_F is the fluorocarbon group ($CF_3—$, $CHF_2—$, $CH_2F—$, etc.), and the functional group Z can be $—CO_2H$, $—CHO$, $—CH_2OH$, $—OH$, etc., and a vast new series of compounds is now being developed.

Uses

1. Fluorocarbons are generally very stable. They are used as oils, sealing liquids and coolants.

2. Tetrafluoroethene, C_2F_4, is the fluorine analogue of ethene, C_2H_4. It is prepared by the fluorination of trichloromethane, generally by antimony trifluoride; reaction occurs in two stages:

$$2CHCl_3 \xrightarrow{SbF_3} 2CHF_2Cl \xrightarrow{700°C} CF_2{=}CF_2 + 2HCl$$

In the presence of a catalyst, tetrafluoroethene undergoes a free-radical polymerisation (21.2) to give a plastic, poly(tetrafluoroethene) (PTFE), marketed as Teflon, which is highly resistant to all chemicals.

3. The fluorochloro derivatives of methane and ethane, for example CF_2Cl_2 and $CFCl_3$, are used as refrigerants (sold under the name of Freons) and as aerosol propellants in dispensers for fly-killers, shaving cream, etc.

4. 1-Bromo-1-chloro-2,2,2-trifluoroethane is used as an anaesthetic (Fluothane).

9.8
Grignard reagents

The preparation of organic compounds containing magnesium was first described by Grignard in 1900. The importance of the compounds lies in their usefulness in organic synthesis, and Grignard was awarded the Nobel Prize for his work in 1912.

Preparation of Grignard reagents

A Grignard reagent is prepared by refluxing an alkyl or aryl bromide or iodide, dissolved in dry ether, with small magnesium turnings. A small crystal of iodine is sometimes added to initiate the reaction:

$$\mathrm{R{-}Br + Mg \rightarrow R{-}MgBr}$$

Grignard reagents cannot be isolated. The ethereal solution of the reagent is used for further reaction.

Alkyl chlorides also form Grignard reagents, though less readily than the bromides or iodides, but aryl chlorides react too slowly. Iodides react more readily than bromides, and are used in the following examples.

Reactions of Grignard reagents

The Grignard reagent, dissolved in ether, is usually kept in the apparatus used for its preparation, and the other reagent, which is sometimes dissolved in ether, is added from a tap-funnel.

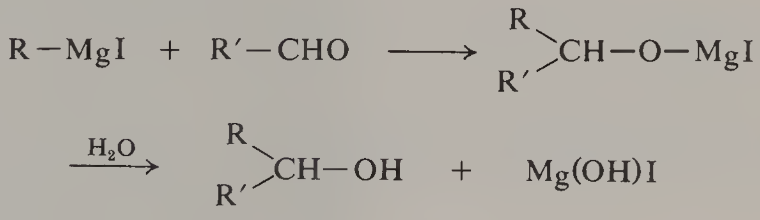
1. With water, to form an **alkane**:

$$\mathrm{R{-}MgI + H_2O \rightarrow R{-}H + Mg(OH)I}$$

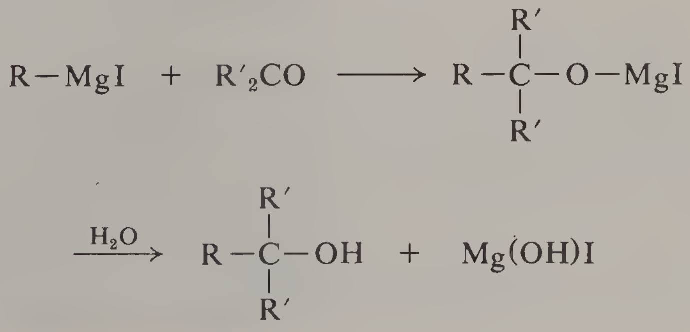
2. With methanal, to form a **primary alcohol**. Methanal gas is passed into the solution of the Grignard reagent, and the mixture is then hydrolysed with dilute acid:

$$\mathrm{R{-}MgI + CH_2{=}O \rightarrow R{-}CH_2{-}O{-}MgI}$$
$$\mathrm{R{-}CH_2{-}O{-}MgI + H_2O \rightarrow R{-}CH_2{-}OH + Mg(OH)I}$$

3. With other aldehydes, to form a **secondary alcohol**:

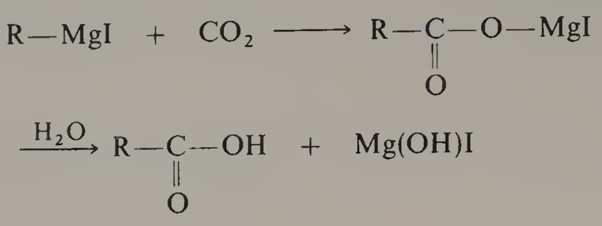


4. With ketones, to form a **tertiary alcohol**:



$$\mathrm{R{-}MgI + R'_2CO \longrightarrow R{-}\underset{R'}{\overset{R'}{C}}{-}O{-}MgI}$$
$$\xrightarrow{\mathrm{H_2O}} \mathrm{R{-}\underset{R'}{\overset{R'}{C}}{-}OH + Mg(OH)I}$$

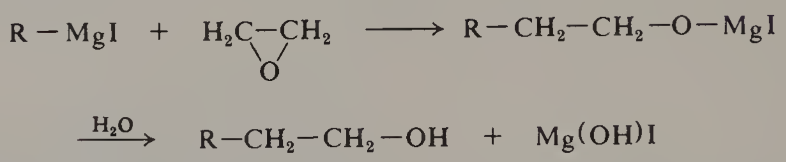
5. When carbon dioxide is passed through the solution of the Grignard reagent and the mixture is then hydrolysed, a **carboxylic acid** is formed:



$$R{-}MgI + CO_2 \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O{-}MgI \xrightarrow{H_2O} R{-}\underset{\underset{O}{\|}}{C}{-}OH + Mg(OH)I$$

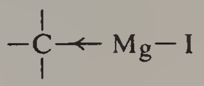
Details of this reaction are given on p. 203.

6. With epoxyethane, to form a **primary alcohol**:

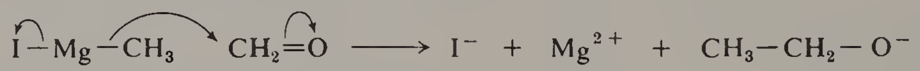


In this method for primary alcohols, *two* carbon atoms are introduced into the Grignard reagent, whereas when methanal is used *one* carbon atom is added.

The reactions of Grignard reagents described above share a common feature in their mechanisms. The C—Mg bond in the Grignard reagent is strongly polarised by the electropositive metal:



As a result, the carbon atom tends to break away with the bonding pair of electrons; that is, it behaves as a nucleophilic reagent, for example:



9.9 Practical work

Small-scale preparation of bromoethane

Place 6 cm³ of ethanol in the flask, immerse the flask in cold water and add, slowly, 7 cm³ of *concentrated* sulphuric acid. Shake the mixture gently while adding the acid. Add 6 g of potassium bromide and set up the apparatus (Fig. 9.5).

Heat the flask very gently until all the alkyl halide has distilled over into the receiver, which should be surrounded by ice.

Transfer the distillate to a separating funnel, add about 3 cm³ of a dilute solution of sodium hydrogencarbonate, fit the stopper and shake. Remove the stopper several times to relieve the pressure.

Allow the mixture to settle and run off the lower organic layer. After discarding the upper layer, wash the alkyl halide in the separating funnel with water and then run it into a test-tube. Add some anhydrous calcium chloride, stopper the test-tube and shake it.

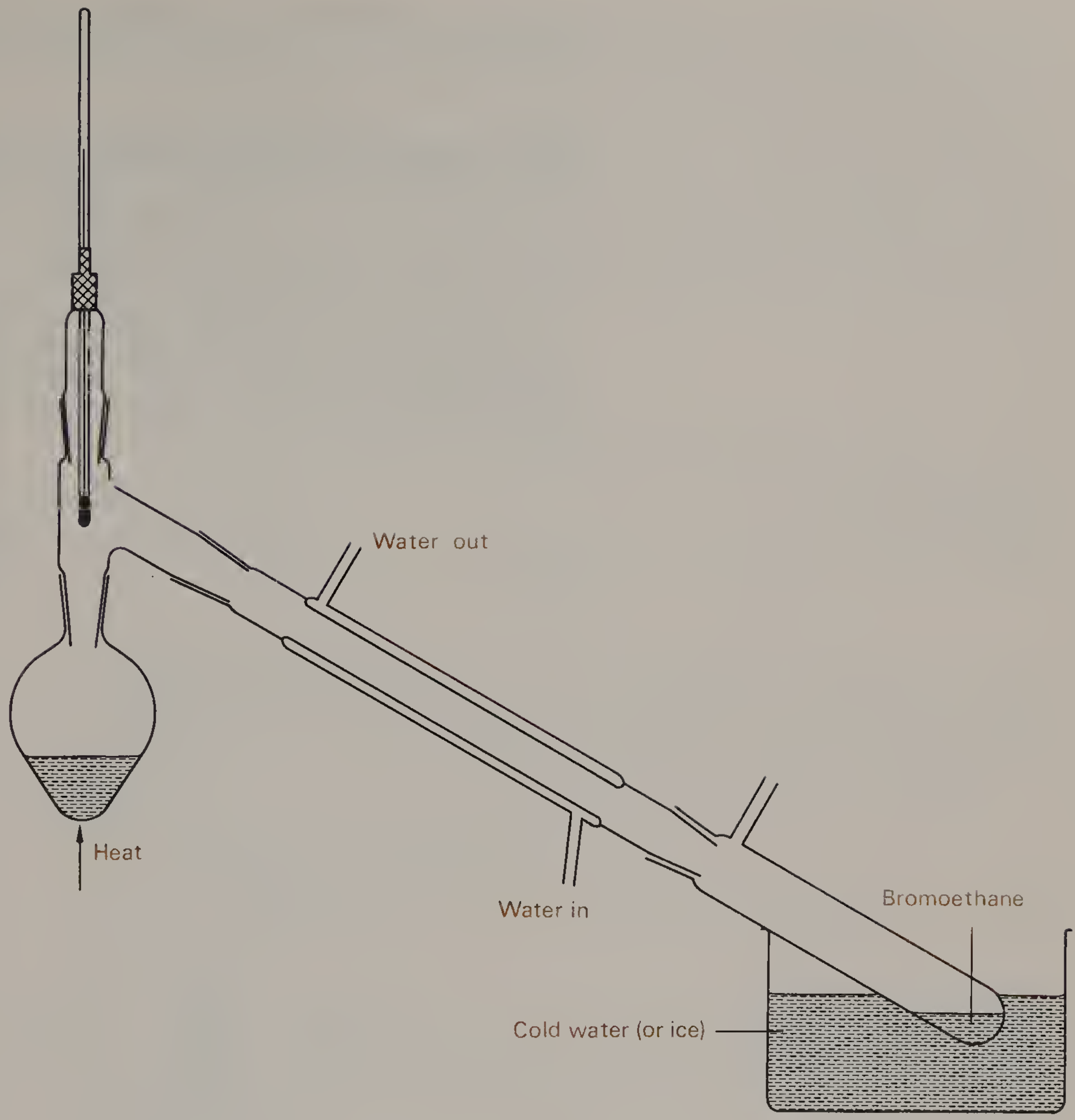
Redistil the dry bromoethane, collecting the fraction boiling between 35 and 40°C (Fig. 2.2); heat the flask with a beaker of hot water.

Small-scale preparation of 1-bromobutane

Place 6 g of potassium bromide in about 6 cm³ of water in the flask and add 6 cm³ of butan-1-ol. Immerse the flask in cold water and add, slowly, 6 cm³ of *concentrated* sulphuric acid. Shake the mixture gently while adding the acid. Reflux the mixture using a small bunsen flame for 30 minutes (Fig. 2.1).

Rearrange the apparatus (Fig. 2.2). Distil the halogenoalkane until no

FIG. 9.5. *Preparation of bromoethane*



more oily drops come over.

If a pure sample is required, transfer the impure compound to a test-tube and add about 2 cm^3 of *concentrated* hydrochloric acid. Shake the mixture to remove unchanged butan-1-ol and then remove the acid layer (using a dropping pipette).

Add, *slowly,* about 5 cm^3 of a saturated solution of sodium carbonate (to remove any excess acid) and remove the aqueous layer (with a dropping pipette). Finally, shake the mixture with 5 cm^3 of water. Remove the water layer yet again, and add 2 or 3 lumps of anhydrous calcium chloride to the halogenoalkane (to remove the last traces of water).

Redistil (Fig. 2.2) and collect the fraction boiling between 99 and 103°C.

Small-scale preparation of 2-chloro-2-methylbutane

Shake 5 cm^3 of 2-methylbutan-2-ol with 20 cm^3 of *concentrated* hydrochloric acid for 10 minutes in a separating funnel. Run off the lower layer (acid) and add slowly 10 cm^3 of dilute sodium hydrogencarbonate solution. Shake, making sure that you do not allow an excess of pressure of carbon dioxide to build up.

Discard the lower aqueous layer, run the alkyl halide into a test-tube, add a few pieces of anhydrous calcium chloride, stopper the tube and shake.

Decant the dry alkyl halide into a distillation flask and purify it by distillation (Fig. 2.2). Collect the fraction boiling between 84 and 86°C.

Small-scale preparation of bromobenzene

The experiment must be carried out in a fume-cupboard, and take great care not to breathe in the vapour of either benzene or bromine. Benzene is highly toxic and must only be used under supervision.

Set up the apparatus shown in Fig. 9.6, with 6 cm^3 of benzene and 0·2 g of iron filings in the flask. Run 3 cm^3 of bromine slowly into the flask, and *slowly* raise the temperature of the water-bath to 70°C. Maintain this temperature until no more hydrogen bromide is evolved.

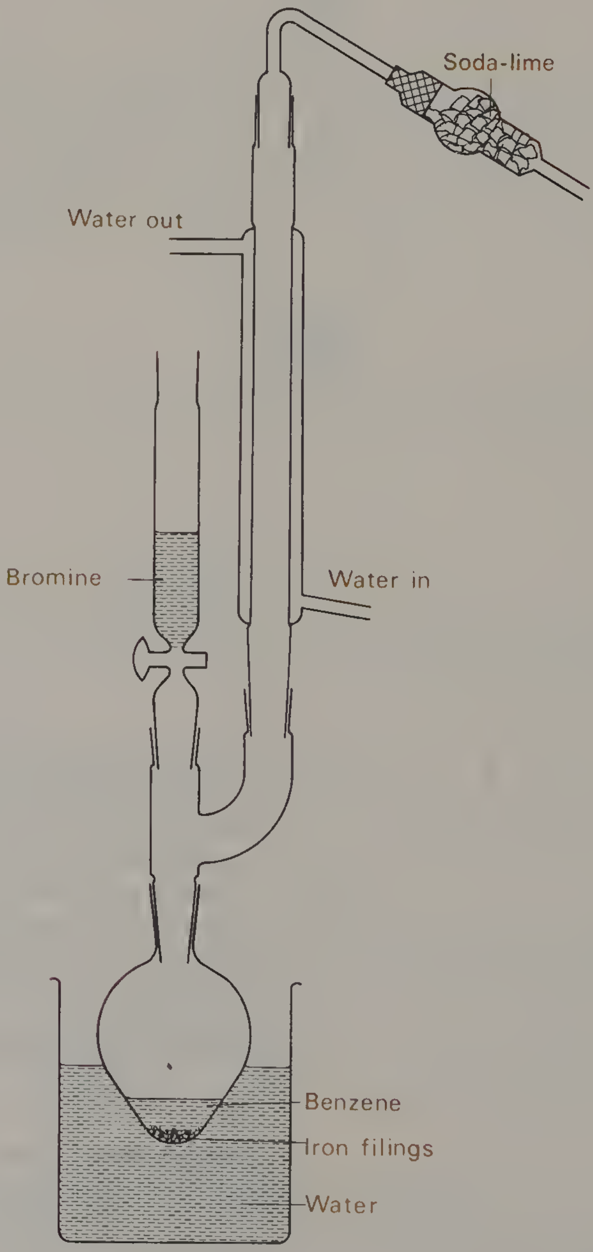


FIG. 9.6. *Preparation of bromobenzene*

Remove the flask, cool it in cold water and pour the mixture into a separating funnel. Purify the aryl halide in a similar way to that described for bromoethane (p. 134), collecting the fraction boiling between 152 and 158°C.

Rates of hydrolysis of some halogen compounds

(a) *To compare the rates of hydrolysis of chloro-, bromo- and iodoalkanes*

To three separate test-tubes, add 2 cm^3 of ethanol and place them in a beaker of water kept at about 60°C. When the ethanol has reached this temperature, using separate dropping pipettes, add 5 drops of 1-chlorobutane to one test-tube, 5 drops of 1-bromobutane to the second and 5 drops of 1-iodobutane to the third. Then, as quickly as possible, add 1 cm^3 of 0·1M silver nitrate solution to each. Shake the test-tubes and observe (a) the order in which the precipitates appear, (b) the colour and density of the precipitates.

(i) What are the precipitates?
(ii) Test whether they occur when the silver nitrate is added to any of the alkyl halides by themselves.
(iii) Deduce why the precipitates are formed. Write equations for the reactions.
(iv) What is the effect on the rate of these reactions arising from changing the halogen in the alkyl halides?

(b) *To compare the rates of hydrolysis of some bromobutanes*

Repeat the experiment above, at room temperature, using 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane. The test-tubes can be placed in a test-tube rack. Add the reagents as quickly as possible with shaking, and observe the test-tubes carefully for at least five minutes.

(i) What are the precipitates?
(ii) Write equations for the reactions.
(iii) What effect does the alkyl group have on the rate of reaction? Suggest reasons.

(c) *To compare the reactivity of the halogen atoms in aliphatic and aromatic halogen compounds* (*Carry out these experiments in a fume-cupboard. (Bromomethyl)benzene is a powerful lachrymator*)

Repeat the experiments given in (a), first at room temperature and then in hot water (at 60°C), with 1-bromobutane, bromobenzene and (bromomethyl)benzene.

(i) What are the precipitates?
(ii) Write equations for the reactions.
(iii) What effect does the phenyl group have on the reactivity of the halogen atom?

Take care that there is enough ethanol present to dissolve the aromatic halogen compounds. A slight turbidity on mixing may be due to an emulsion of the organic compound with water; to test for this, add a few drops of ethanol and shake.

Reactions of 1,1-dichloroethane and 1,2-dichloroethane

1. To 2–3 drops of 1,1-dichloroethane in a test-tube, add 2 cm^3 of dilute sodium hydroxide solution. Shake and gently boil the mixture. Allow the mixture to cool, acidify with dilute nitric acid, then add silver nitrate solution.

(a) Note the smell of the vapour evolved.
(b) Note whether a precipitate is formed.

Write an equation to explain your observations.

Repeat the experiments using 1,2-dichloroethane. Do you observe the same results? Write equations for the reactions.

2. Add a few pellets (about 0·5 g) of potassium hydroxide to 2 cm^3 of ethanol in a test-tube. Warm the test-tube gently until the pellets have dissolved. Add 6 drops of 1,1-dichloroethane to the alcoholic solution of potassium hydroxide. Shake gently, then introduce a plug of Rocksil to absorb the solution. Fit the test-tube with a delivery tube dipping into 2 cm^3 of an ammoniacal solution of copper(I) chloride. Warm the Rocksil plug gently and observe what occurs to the copper(I) chloride solution.

Repeat the experiment with 1,2-dichloroethane, writing equations for both reactions.

Preparation of a Grignard reagent

The preparation of phenylmagnesium bromide from bromobenzene is described on p. 203.

9.10
Further reading

Reaction mechanisms: An introduction. 1980. Open University. S246 7–9

9.11
Films and Videotapes

S_N1 or S_N2 (F,V) Open University. S246/08F

9.12
Questions

1 Outline how iodoethane (ethyl iodide) may be prepared from (a) ethene (ethylene), (b) ethanol. How from iodoethane would you prepare (i) ethane, (ii) ethene, (iii) butane, (iv) diethyl ether?

Give the structural formulae of the isomers of $C_2H_4Cl_2$ and describe the action of aqueous alkali on these isomers. (AEB)

2 Describe a laboratory method for the preparation of a named alkyl halide, giving a diagram and full practical details.

An alkyl bromide, *A* (0·615 g), was boiled under reflux with 100 cm^3 of 0·125M sodium hydroxide solution. The mixture was allowed to cool and then titrated, using methyl orange as indicator, with 0·125M hydrochloric acid, of which 60 cm^3 was required. Assuming that *A* contains only one bromine atom in its molecule, calculate its molecular weight.

The organic product of the hydrolysis of *A* is found to be easily oxidised to a ketone. Suggest the probable structural formula of *A* and indicate the reasoning by which you arrive at this result. ($H = 1$, $C = 12$, $Br = 80$.) (L(X))

3 Describe how you would prepare a pure specimen of bromoethane from ethanol (ethyl alcohol). Draw a sketch of the apparatus you would use to obtain the crude product.

How and under what conditions does bromoethane react with: (a) silver oxide, (b) potassium cyanide, (c) sodium hydroxide? Describe the experiments you would carry out to identify the organic product in one of these reactions. (O)

4 How would you prepare a pure sample of bromoethane from ethanol?

Outline the reactions by which bromoethane may be used in the preparation of (i) propanonitrile, (ii) ethane, (iii) ethylbenzene.

Chloroethane reacts with an alloy of sodium and lead to produce a liquid compound of the composition C, 29·7 per cent; H, 6·2 per cent; Pb, 64·1 per cent. Suggest a structural formula for this compound. (C(T))
(H = 1·0, C = 12, Pb = 207.)

5 Assume that the chemical properties of 1-bromopropane are the same as those of bromoethane. Deduce what products are formed when 1-bromopropane reacts with (a) hydrogen, (b) potassium hydroxide, (c) sodium, (d) sodium ethoxide. In each case give the essential conditions of reaction and name the chief product formed.

Give outline schemes of reactions for converting 1-bromopropane into (i) an acid, (ii) a primary amine, each containing the original number of carbon atoms per molecule. (AEB)

6 By means of equations with brief notes on reagents and experimental conditions show how an alkyl halide may be converted into (a) the corresponding hydrocarbon, (b) an alcohol, (c) an alkene, (d) a nitrile, and (e) a primary amine.

What prevents a good yield of the primary amine in (e)? (JMB)

7 Describe two methods of introducing a chlorine atom into (a) an aliphatic compound and (b) an aromatic compound. Give one example of each method.

By consideration of the reaction between methylbenzene and chlorine illustrate the importance of experimental conditions in determining the reaction products. Discuss the mechanism operating in each case.

Describe the reactivity of typical aliphatic monohalogen compounds towards (i) potassium hydroxide, (ii) potassium cyanide, and (iii) ammonia. Discuss the mechanisms of these reactions. (JMB (Syllabus B) Specimen question)

8 Give reasons for the items that are **underlined** in the following directions for the laboratory preparation of approximately 30 g of bromoethane.

Fit a 500 cm^3 round-bottomed flask with a bent tube connected to a double-surface condenser set for downward distillation. To the lower end of the condenser attach an adapter. (These parts must be fitted together with tight-fitting joints.) Arrange for the end of the adapter to dip below the surface of about 50 cm^3 of water contained in a 250 cm^3 flask which is surrounded by an ice/water mixture.

Place 37 cm^3 (30 g) of ethanol in the round-bottomed flask and add slowly 40 cm^3 (74 g) of concentrated sulphuric acid. When the mixture has cooled add 50 g of powdered potassium bromide, reconnect the flask to the condenser and heat gently, at the same time ensuring that a copious supply of cold water is passing through the condenser. Continue heating until no more droplets pass from the end of the condenser.

Pour the contents of the receiving flask into a separating funnel and run off and retain the lower layer. Discard the upper layer. Return the lower layer to the separating funnel and wash it first with dilute aqueous sodium carbonate and then with water, retaining the lower layer each time. Add a few pieces of anhydrous calcium chloride to the lower layer and leave for 20 min in a stoppered flask.

Filter the solution through a fluted filter paper directly into a 50 cm^3 distilling flask containing a few chips of unglazed porcelain. Fit the flask with a 100° thermometer and a double-surface condenser having as before a copious supply of cold water running through it. Collect the fraction b.p. 36–40°C.

The bromoethane obtained in this way contains approximately 15 per cent diethyl ether. How do you account for the presence of this impurity?

Given that the product contains 30 g of bromoethane, calculate the percentage yield for the overall reaction. (JMB)

9 (a) Chloromethane reacts with an alloy of aluminium and sodium to form the compound *J*.

J has the following composition by mass; C = 50%, H = 12·5%, Al = 37·5%.
0·24g of *J* react with excess water to produce 0·224 dm^3 of the gas, *K*, and a white gelatinous precipitate, *L*.
L dissolves in hydrochloric acid and in sodium hydroxide solution.
25 cm^3 of *K* require 50 cm^3 of oxygen for complete combustion. (All gas volumes

were measured at s.t.p.)

[H = 1·0, C = 12·0, Al = 27·0; molar volume of a gas at s.t.p. = 22·4 $dm^3\ mol^{-1}$.]

(i) Calculate the empirical formula of *J*.
(ii) Suggest a structural formula for *J*.
(iii) Identify the compounds *K* and *L*.
(iv) Write equations for:
the reaction of chloromethane with the Al/Na alloy;
the reaction of *J* with excess water;
the complete combustion of *K*;
the reaction of *L* with hydrochloric acid;
the reaction of *L* with sodium hydroxide solution.

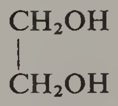
(b) How, and under what conditions, does bromoethane react with

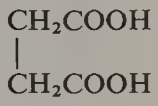
(i) potassium hydroxide;
(ii) silver ethanoate (acetate);
(iii) benzene?

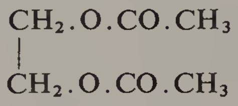
Write equations for the reactions described. (SUJB)

10 Given a supply of ethanol and the usual laboratory reagents, describe how you would prepare a sample of 1,2-dibromoethane (ethylene dibromide).

Outline methods for the conversion of the dibromoethane into

(a) 
$CH_2OH{-}CH_2OH$

(b) 
$CH_2COOH{-}CH_2COOH$

(c) 
$CH_2.O.CO.CH_3{-}CH_2.O.CO.CH_3$

(L)

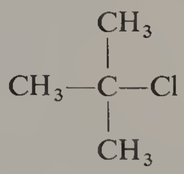
11 Give the structural formulae of the isomers represented by $C_2H_4Cl_2$ and outline how each may be prepared.

Describe how and under what conditions each isomer reacts with potassium hydroxide and name the chief products formed. (AEB)

12 Outline schemes of reactions for the preparations of (chloromethyl)benzene and chlorobenzene from benzene, and for the preparation of chloroethane from methane.

How do these products react with (i) aqueous sodium hydroxide, (ii) alcoholic ammonia, (iii) lithium aluminium hydride? (AEB)

13 The hydrolysis of chloroethane C_2H_5Cl is a *nucleophilic, bimolecular* substitution reaction, whereas the hydrolysis of 2-chloro-2-methylpropane,


$(CH_3)_3C{-}Cl$

is a *nucleophilic, unimolecular* reaction.

(a) Explain the terms in italics.
(b) Discuss the mechanisms of the two reactions.
(c) Describe in outline one experiment to show that the tertiary halogen compound hydrolyses at a faster rate than the primary.
(d) Give, and explain the results of, the reactions of each of the halogen compounds with sodium ethoxide in ethanol solution. L(S)

14 Write the names and structural formulae of the products of mono-nitration of bromobenzene. Indicate any necessary conditions for the nitration.

Compare the chemical reactivity of bromoethane and bromobenzene to aqueous sodium hydroxide.

Outline how bromobenzene may (a) be obtained from benzene and 4-bromobenzaldehyde respectively, (b) be converted to methylbenzene. (W)

15 Suggest possible structural formulae for aromatic compounds of empirical formula C_7H_7Cl. What (if any) would be the reactions of each of these compounds with sodium hydroxide?

Describe, giving essential experimental details, how you would detect the presence of chlorine in one of these isomers. How, and why, would you modify your method if the compound also contained nitrogen?

Which isomer would you use as a starting material for the preparation of benzoic acid? Describe briefly how you would perform the conversion in the laboratory. (AEB)

16 Explain the meaning of the terms *nucleophile*, *electrophile*, and *free radical*, giving **one** example of each, and emphasising those structural features which are responsible for their behaviour.

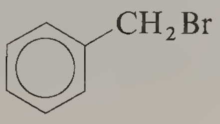
Give **two** examples of electrophilic addition, **two** examples of electrophilic substitution, and **two** examples of nucleophilic addition.

Why do many gas phase reactions involve free radicals rather than ions? (O and C(S))

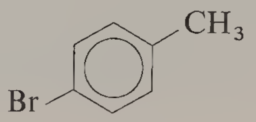
17 (a) Describe the meaning of the terms *homolytic* and *heterolytic* with reference to the reactions of chlorine with (i) ethene, (ii) methane. Indicate the mechanisms of the reactions you choose.

(b) Calculate the weight of bromine needed to convert 4.6 g of methylbenzene into compound **K** below.

(c) Describe test-tube experiments which would enable you to distinguish chemically between **K** and **L**.



K



L

18 The following results are those from an experiment in which equal volumes of equimolar solutions of a bromoalkane of formula C_4H_9Br and of potassium hydroxide were mixed and then 20 cm^3 samples taken at intervals, the reaction quenched in an excess of ice cold water, and titrated against a standard acid solution.

Time (seconds × 10^3)	0	0·45	0·9	1·8	2·7	3·6	4·5	5·4	6·3	7·2	8·1
Titre (cm^3 of acid)	20	11·5	8·0	5·0	3·55	2·8	2·35	2·0	1·75	1·55	1·4

(a) Use these results to find the overall order of the reaction.

(b) From your result in (a), deduce the most probable mechanism for the hydrolysis, explaining your deduction.

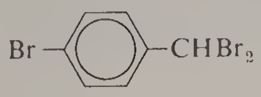
(c) What is the most probable formula for the bromoalkane? Explain your reasoning carefully. (L (Nuffield trial) (S))

19 Devise experiments to determine:

(a) the structure of the product(s) obtained by addition of hydrogen bromide to propene $CH_3—CH{=}CH_2$;

(b) the structure of the product(s) obtained by elimination of hydrogen bromide from 2-bromobutane $CH_3—CHBr—CH_2—CH_3$. (O Schol.)

20 Discuss the differences in chemical properties between chloroethane and chlorobenzene. How would you expect the following compound to behave:



21 Write equations for some of the reactions of alkyl halides giving examples of as many different types of reaction as possible. How could you distinguish chemically between 1-chloropropane and 2-chloropropane?

When 1-chloropropane is further chlorinated the ratio of 1,2-dichloropropane to 1,3-dichloropropane in the product is 9:7. How does this result differ from that which might have been expected? (O Schol.)

22 Write an essay on nucleophilic substitution reactions of haloalkanes and the uses of these reactions in synthesis.

Explain how the products of the reactions of the haloalkanes with alkali vary with the conditions used.

(JMB)

Chapter 10

Alcohols and phenols

General formula

R—OH

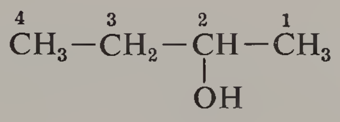
10.1 Introduction

Alcohols are compounds containing one or more hydroxyl groups attached to saturated carbon atoms. Those with one hydroxyl group are known as **monohydric** alcohols; examples are ethanol, C_2H_5—OH (an aliphatic monohydric alcohol) and phenylmethanol, C_6H_5—CH_2—OH (an aromatic monohydric alcohol). There are also **polyhydric** alcohols, which contain more than one hydroxyl group; examples are ethane-1,2-diol, $HOCH_2$—CH_2OH (an aliphatic dihydric alcohol) and propane-1,2,3-triol, $HOCH_2$—CH(OH)—CH_2OH (an aliphatic trihydric alcohol).

Phenols are compounds containing one or more hydroxyl groups attached to aromatic carbon atoms; the parent member of the series is phenol itself, C_6H_5—OH. Many of the properties of phenols are different from those of alcohols, and they are described separately (10.8).

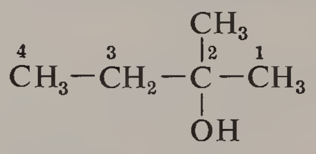
10.2 Nomenclature of monohydric alcohols

Monohydric alcohols are named by replacing the final **-e** in the corresponding alkane by **-ol**. The position of the hydroxyl group in the carbon chain is given by numbering the carbon atoms as for alkanes. For example:



$$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\underset{|}{\overset{2}{\mathrm{CH}}}}-\overset{1}{\mathrm{CH_3}}$$

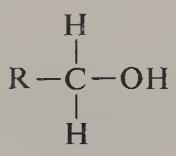
Butan-2-ol



$$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|\,2}{\mathrm{C}}}}}-\overset{1}{\mathrm{CH_3}}$$

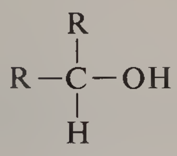
2-Methylbutan-2-ol

There are three classes of alcohol. They differ in the number of alkyl groups attached to the hydroxyl-bearing carbon atom:



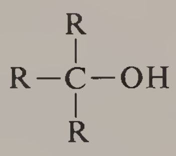
$$\mathrm{R}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}}-\mathrm{OH}$$

Primary



$$\mathrm{R}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}}}-\mathrm{OH}$$

Secondary



$$\mathrm{R}-\underset{\mathrm{R}}{\underset{|}{\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}}}-\mathrm{OH}$$

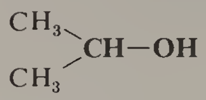
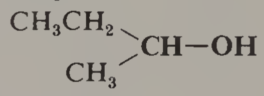
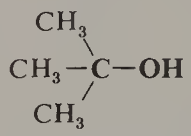
Tertiary

The three classes have many similar chemical properties, owing to the presence of the same functional group, —OH. However, there are also differences which are due to the different numbers of hydrogen atoms on the hydroxyl-bearing carbon atom.

The names and structural formulae of some alcohols are in Table 10.1.

There are two isomers with formula C_3H_7OH, one a primary and the other a secondary alcohol. There are four isomers of C_4H_9OH, two of which are primary alcohols, for 2-methylpropan-1-ol is a primary alcohol as it possesses a —CH_2OH group, even though it contains a branched alkyl chain.

Table 10.1. The structural formulae, class and physical properties of some alcohols

NAME	FORMULA	STRUCTURAL FORMULA	CLASS	M.P./°C	B.P./°C
Methanol	CH_3OH	$H{-}CH_2{-}OH$	Primary	–97	64
Ethanol	C_2H_5OH	$CH_3CH_2{-}OH$	Primary	–117	78
Propan-1-ol	C_3H_7OH	$CH_3CH_2CH_2{-}OH$	Primary	–127	98
Propan-2-ol	C_3H_7OH	 $\begin{matrix}CH_3\diagdown & \\ & CH{-}OH\\ CH_3\diagup & \end{matrix}$	Secondary	–89	82
Butan-1-ol	C_4H_9OH	$CH_3CH_2CH_2CH_2{-}OH$	Primary	–90	118
2-Methylpropan-1-ol	C_4H_9OH	 $\begin{matrix}CH_3\diagdown & \\ & CHCH_2{-}OH\\ CH_3\diagup & \end{matrix}$	Primary	–108	108
Butan-2-ol	C_4H_9OH	 $\begin{matrix}CH_3CH_2\diagdown & \\ & CH{-}OH\\ CH_3\diagup & \end{matrix}$	Secondary		100
2-Methylpropan-2-ol	C_4H_9OH	 $\begin{matrix} & CH_3 & \\ CH_3{-} & C & {-}OH\\ & CH_3 & \end{matrix}$	Tertiary	25	83
Pentan-1-ol	$C_5H_{11}OH$	$CH_3CH_2CH_2CH_2CH_2{-}OH$	Primary	–79	138
Hexan-1-ol	$C_6H_{13}OH$	$CH_3CH_2CH_2CH_2CH_2CH_2{-}OH$	Primary	–51	157
Phenylmethanol	$C_6H_5CH_2OH$	$C_6H_5CH_2{-}OH$	Primary	–15	205

10.3 Physical properties of monohydric alcohols

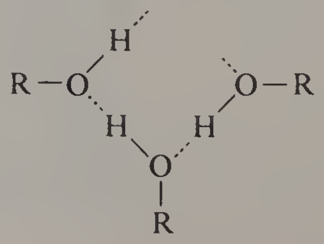
As with alkanes, the boiling points of the alcohols increase fairly regularly on the addition of each methylene ($—CH_2—$) group; the increment is about 20°C among the lower homologues (Table 10.1). Again, as with the alkanes, and for the same reason (5.2), increase in branching of the carbon chain is accompanied by decrease in boiling point; this is illustrated by the four isomeric alcohols, C_4H_9OH (Table 10.1).

However, the boiling points of alcohols are considerably higher than those of alkanes of approximately the same formula weight, as illustrated in Table 10.2.

Table 10.2. The boiling points of alkanes and alcohols of similar formula weight

ALKANE	F. WT.	B.P./°C	ALCOHOL	F. WT.	B.P./°C
Ethane	30	–89	Methanol	32	64
Propane	44	–42	Ethanol	46	78
Butane	58	–0·5	Propan-1-ol	60	98

This is because of the occurrence of strong attractive forces, known as **hydrogen-bonds**, between the molecules of the alcohol in the liquid phase. The bonds are electrostatic in nature; the proton in the hydroxyl group of one molecule is attracted by an unshared pair of electrons on the oxygen atom of another:



The hydrogen-bonds, represented by dotted lines, are longer than covalent bonds and are not as strong. A typical value for the strength of a hydrogen-bond is 20 kJ mol^{-1}, which is much larger than the usual attractive forces between molecules, which are generally of the order of 1–2 kJ mol^{-1}. These differences in the attractive forces are reflected in the higher temperatures needed to separate the molecules of an alcohol compared with the molecules of an alkane. Hydrogen-bonding in a liquid alcohol can be detected by infrared spectroscopy (Fig. 10.1).

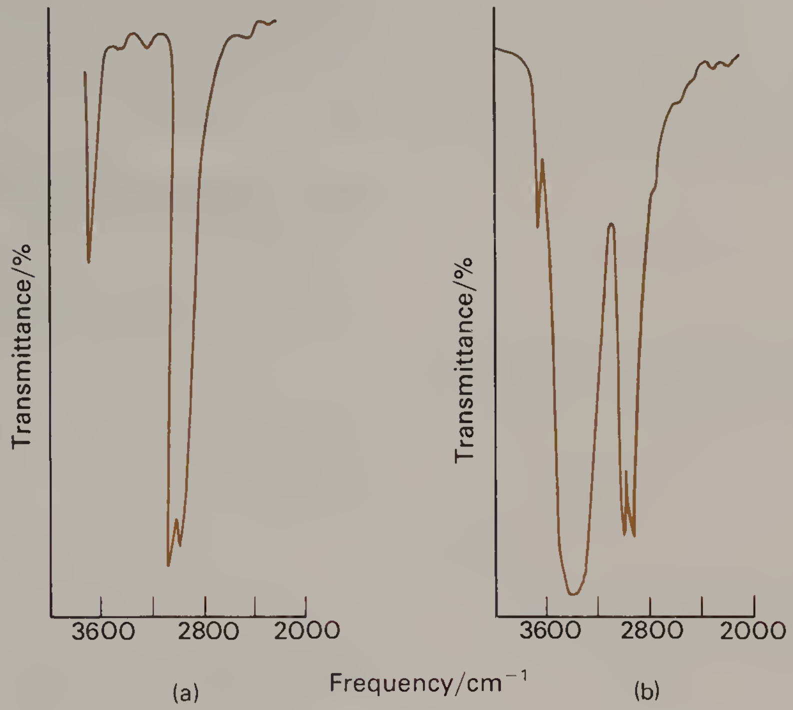
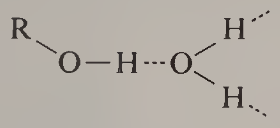


FIG. 10.1. *Part of the infrared absorption spectrum of ethanol. In (a), ethanol is in the vapour phase, and the —OH group is absorbing radiation at 3700 cm*$^{-1}$. *In (b), ethanol is dissolved in an inert solvent and the —OH group is absorbing radiation at 3300 cm*$^{-1}$. *The reduction in frequency indicates that the bond strength is reduced due to hydrogen-bonding between the molecules of ethanol*

The smaller alcohols are miscible with water, but as the number of carbon atoms increases, solubility decreases, for example:

Alcohol	Methanol	Ethanol	Propan-1-ol
Solubility (g 100 cm^{-3})	Miscible	Miscible	Miscible
Alcohol	Butan-1-ol	Pentan-1-ol	Hexan-1-ol
Solubility (g 100 cm^{-3})	8·3	2·6	1·0

Alcohols are more soluble in water than are alkanes of similar formula weight because of the attractive forces (hydrogen-bonds) between molecules of the alcohol and molecules of water:



10.4
Methods of preparation of monohydric alcohols

General methods

1. By the hydration of an alkene (6.3), for example:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3{-}CH_2{-}O{-}SO_2{-}OH$$

$$CH_3{-}CH_2{-}O{-}SO_2{-}OH + H_2O \rightarrow CH_3{-}CH_2{-}OH + H_2SO_4$$

2. By the hydrolysis of an alkyl halide with an aqueous solution of an alkali (9.3), for example:

$$(CH_3)_2CH—Cl + NaOH \rightarrow (CH_3)_2CH—OH + NaCl$$

3. By the reaction of a Grignard reagent with an aldehyde or ketone (9.8). Methanal yields a primary alcohol, other aldehydes yield secondary alcohols and ketones yield tertiary alcohols.

4. By the reduction of an aldehyde (giving a primary alcohol) or a ketone (giving a secondary alcohol) (12.5).

5. By the reduction of a carboxylic acid with lithium tetrahydridoaluminate, giving a primary alcohol (13.5).

Manufacture of methanol

From natural gas. Methane, obtained from natural gas (19.2), is passed with steam over nickel at about 900°C and under pressure:

$$CH_4 + H_2O \xrightarrow{\text{Ni as cat.}} CO + 3H_2$$

This mixture of gases, known as **synthesis gas**, can be converted into methanol. The gases are passed over a heated copper catalyst under pressure:

$$CO + 2H_2 \xrightarrow{250^\circ C;\ 70\ \text{atm. pressure}} CH_3OH$$

Manufacture of ethanol

1. Ethene is passed under pressure through concentrated sulphuric acid at 80°C to form ethyl hydrogensulphate:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3—CH_2—O—SO_2—OH$$

The mixture is then diluted with water and distilled to give an aqueous solution of ethanol:

$$CH_3—CH_2—O—SO_2—OH + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

2. A more recent method is to hydrate ethene directly by passing a mixture of the alkene and steam over a solid acid catalyst (phosphoric acid on silica) at 300°C and a pressure of about 70 atmospheres:

$$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$$

Only about 4 per cent of the ethene reacts, but the remaining ethene and steam are recirculated over the catalyst many times to obtain a good yield of ethanol.

3. An older method is by the fermentation of starch (18.3).

Absolute ethanol

Regardless of the method of manufacture, all aqueous solutions of ethanol yield, on fractional distillation, a ‘constant boiling mixture’ of 96 per cent ethanol and 4 per cent water, known as **rectified spirit**. This means that further fractionation would remove no more water, since the distillate has the same composition as the liquid.

In the laboratory, the rectified spirit is stored over quicklime (freshly prepared by heating calcium carbonate). Subsequently the mixture is refluxed over quicklime for about 6 hours, and then allowed to stand overnight. The pure product, known as **absolute ethanol**, is then distilled off, precautions being taken to prevent absorption of water vapour by the hygroscopic alcohol.

In industry, benzene is added to the rectified spirit. Distillation yields three fractions:

At 65°C, a constant boiling mixture of ethanol, benzene and water (a 'ternary azeotrope').

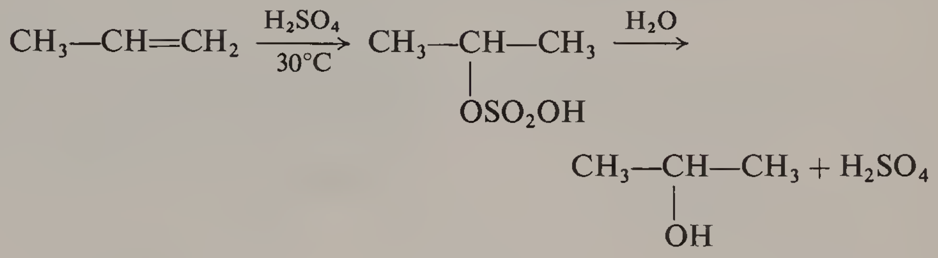
At 68°C, a constant boiling mixture of ethanol and benzene (a 'binary azeotrope').

At 78°C, pure ethanol.

Manufacture of propan-2-ol

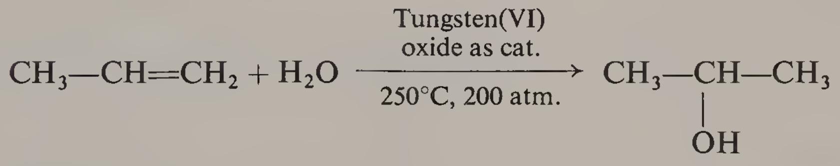
Propan-2-ol is made from propene (obtained from petroleum (20.4)) by methods analogous to those for the manufacture of ethanol from ethene:

1.



$$CH_3{-}CH{=}CH_2 \xrightarrow[30°C]{H_2SO_4} CH_3{-}\underset{\underset{OSO_2OH}{|}}{CH}{-}CH_3 \xrightarrow{H_2O} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 + H_2SO_4$$

2.



$$CH_3{-}CH{=}CH_2 + H_2O \xrightarrow[250°C,\ 200\ atm.]{\text{Tungsten(VI) oxide as cat.}} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$$

10.5
Chemical properties of monohydric alcohols

The reactions of alcohols can be grouped in three classes:

(a) Reactions of the —OH group.

(b) Oxidation reactions, which depend on whether the alcohol is primary, secondary or tertiary.

(c) Elimination reactions, which depend on whether or not the alcohol contains at least one hydrogen atom attached to the carbon atom next to the C—OH group.

(a) Reactions of the —OH group

1. Alcohols react with sodium to form salts (sodium alkoxides) and hydrogen, for example:

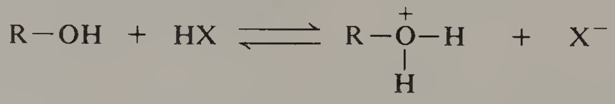
$$2C_2H_5OH + 2Na \rightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5O^-Na^+} + H_2$$

2. Alcohols react with the hydrogen halides to form alkyl halides:

$$R—OH + HCl \rightarrow R—Cl + H_2O$$
$$R—OH + HBr \rightarrow R—Br + H_2O$$
$$R—OH + HI \rightarrow R—I + H_2O$$

The reaction with hydrogen chloride is catalysed by zinc chloride. A test (Lucas test) to distinguish between simple primary, secondary and tertiary alcohols is based on this reaction and the fact that tertiary alcohols react faster than secondary alcohols which in turn react faster than primary alcohols. The alcohol is shaken with a solution of zinc chloride in concentrated hydrochloric acid. Immediate cloudiness (due to formation of the alkyl chloride) indicates a tertiary alcohol; if the solution turns cloudy within about five minutes, a secondary alcohol is indicated; while primary alcohols show no cloudiness at room temperature.

The mechanism of the reaction with a hydrogen halide depends on whether the the alcohol is primary, secondary or tertiary. In each case, the first step is the same: the alcohol reacts reversibly with the hydrogen halide:

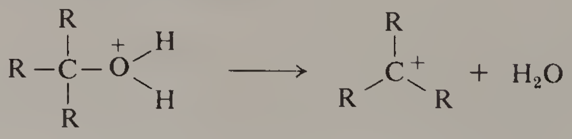


$$R-OH + HX \rightleftharpoons R-\overset{+}{O}(H)-H + X^-$$

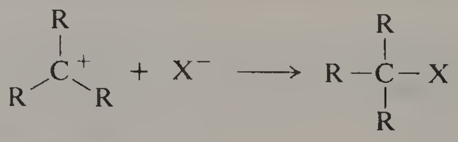
That is, in the presence of a strong acid, the oxygen atom of the alcohol is acting as a base, accepting a proton from the hydrogen halide. Alcohols are very weak bases and the equilibrium lies to the left.

With *primary* alcohols, the next step is displacement by the halide ion of a molecule of water. This is an S_N2 reaction, analogous to the reaction of a primary alkyl halide with hydroxide ion (9.3):

With *tertiary* alcohols, the second step is heterolysis:



and this is followed by reaction of the carbonium ion with the halide ion:



Tertiary alcohols differ from primary alcohols because a tertiary carbonium ion, R_3C^+, is relatively more stable, and is formed more rapidly, than a primary carbonium ion, RCH_2^+ (9.3).

Secondary alcohols are intermediate in behaviour between primary and tertiary alcohols.

3. Alcohols react with phosphorus tribromide and phosphorus tri-iodide to form alkyl bromides and alkyl iodides:

$$3R—OH + PBr_3 \rightarrow 3R—Br + H_3PO_3$$
$$3R—OH + PI_3 \rightarrow 3R—I + H_3PO_3$$

These phosphorus trihalides are conveniently prepared *in situ* from red phosphorus and the halogen.

Alkyl chlorides can be obtained from the alcohol with phosphorus pentachloride or with sulphur dichloride oxide at room temperature:

$$\text{R—OH} + \text{PCl}_5 \rightarrow \text{R—Cl} + \text{POCl}_3 + \text{HCl}$$
$$\text{R—OH} + \text{SOCl}_2 \rightarrow \text{R—Cl} + \text{SO}_2 + \text{HCl}$$

The liberation of hydrogen chloride from an alcohol and phosphorus pentachloride is typical of the behaviour of organic compounds containing the hydroxyl group.

4. Alcohols react with concentrated sulphuric acid to form products which depend on the nature of the alcohol and the reaction conditions.

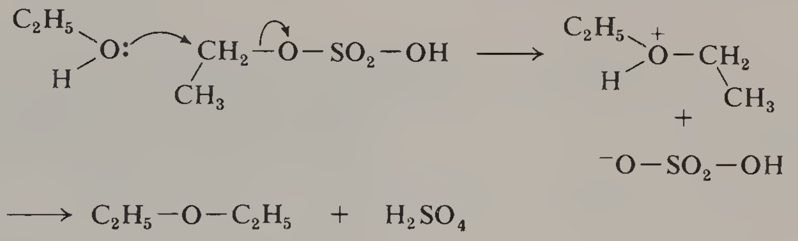
At 0°C, an alkyl hydrogensulphate is formed:

$$\text{R—OH} + \text{H}_2\text{SO}_4 \rightarrow \text{R—O—SO}_2\text{—OH} + \text{H}_2\text{O}$$

When the acid is added to an excess of a primary alcohol and the mixture is heated to about 140°C, an ether is formed, for example:

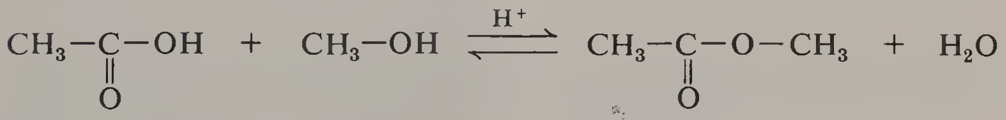
$$2\text{C}_2\text{H}_5\text{—OH} \xrightarrow[140°\text{C}]{\text{H}_2\text{SO}_4} \underset{\text{Diethyl ether}}{\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5} + \text{H}_2\text{O}$$

The reaction occurs by displacement of the hydrogensulphate group by the excess of the alcohol, as in the S_N2 substitution of an alkyl halide (9.3):



However, when there is an excess of the acid and a still higher temperature is used, elimination can occur and an alkene is formed (p. 150).

5. Alcohols react with organic acids to form esters. The reaction is slow unless an acid catalyst is used; hydrogen chloride or concentrated sulphuric acid are suitable catalysts. For example:



$$\text{CH}_3\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—OH} + \text{CH}_3\text{—OH} \xrightleftharpoons{\text{H}^+} \text{CH}_3\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—O—CH}_3 + \text{H}_2\text{O}$$

Ethanoic acid Methyl ethanoate

This type of reaction (esterification) is discussed on p. 212.

Alcohols also form esters when treated with acid halides or acid anhydrides (14.3, 14.4), for example:

$$\text{CH}_3\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—Cl} + \text{CH}_3\text{—OH} \longrightarrow \text{CH}_3\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—O—CH}_3 + \text{HCl}$$

Ethanoyl chloride Methyl ethanoate

(b) Oxidation reactions

Primary and secondary alcohols are readily oxidised to aldehydes and ketones, respectively. Tertiary alcohols are resistant to oxidation.

Oxidation in solution can be brought about with acidified sodium or potassium dichromate:

$$RCH_2\text{—}OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} RCH\text{=}O$$

$$R_2CH\text{—}OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} R_2C\text{=}O$$

In the case of the primary alcohol, the resulting aldehyde undergoes further oxidation to the carboxylic acid unless precautions are taken to prevent it (12.3).

Potassium manganate(VII) in acid solution also effects these oxidations.

Oxidation in the gas phase can be brought about either by passing the vapour of the alcohol, together with oxygen, over silver at about 500°C, for example,

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[500°C]{\text{Ag as cat.}} HCHO + H_2O$$

or by passing the vapour of the alcohol alone over heated copper, for example:

$$CH_3CH_2OH \xrightarrow[500°C]{\text{Cu as cat.}} CH_3CHO + H_2$$

$$(CH_3)_2CHOH \xrightarrow[500°C]{\text{Cu as cat.}} (CH_3)_2CO + H_2$$

Secondary alcohols which contain the grouping $CH_3\text{—}CH(OH)\text{—}$ are oxidised by iodine in the presence of sodium hydroxide to tri-iodomethane:

$$CH_3\text{—}CH(OH)\text{—}R + I_2 + 2NaOH \rightarrow CH_3\text{—}CO\text{—}R + 2NaI + 2H_2O$$

$$CH_3\text{—}CO\text{—}R + 3I_2 + 4NaOH \rightarrow CHI_3 + R\text{—}CO_2^-Na^+ + 3NaI + 3H_2O$$

One primary alcohol, ethanol, also undergoes this reaction:

$$CH_3\text{—}CH_2\text{—}OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCO_2^-Na^+ + 5NaI + 5H_2O$$

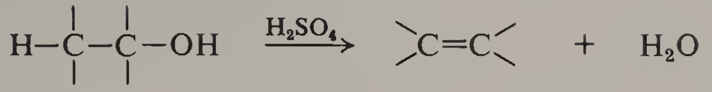
Other primary and secondary alcohols are also oxidised and iodinated but do not then give tri-iodomethane, for example:

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}OH + I_2 + 2NaOH \rightarrow CH_3\text{—}CH_2\text{—}CH\text{=}O + 2NaI + 2H_2O$$

$$CH_3\text{—}CH_2\text{—}CH\text{=}O + 2I_2 + 2NaOH \rightarrow CH_3\text{—}CI_2\text{—}CH\text{=}O + 2NaI + 2H_2O$$

(c) Elimination reactions

Alcohols which possess at least one hydrogen atom on the carbon atom next but one to the hydroxyl group undergo **dehydration** (elimination of water) when heated with concentrated sulphuric acid:



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH \xrightarrow{H_2SO_4} {>}C{=}C{<} + H_2O}$$

The reaction occurs via the alkyl hydrogensulphate, for example:

$$C_2H_5OH + H_2SO_4 \longrightarrow CH_3—CH_2—O—SO_2—OH + H_2O$$

$$CH_3—CH_2—O—SO_2—OH \xrightarrow{170°C} CH_2{=}CH_2 + H_2SO_4$$

This elimination reaction competes with the substitution reaction which occurs (p. 149), for example:

$$CH_3—CH_2—O—SO_2—OH + C_2H_5OH \rightarrow CH_3CH_2—O—CH_2CH_3 + H_2SO_4$$

The substitution reaction is promoted by the presence of an excess of the alcohol, and the elimination reaction is promoted by the use of higher temperatures.

An alternative dehydrating agent is phosphoric acid. A practical example, the dehydration of cyclohexanol, is given on p. 88.

Alcohols can also be dehydrated by passing their vapour over aluminium oxide at about 300°C, for example:

$$CH_3—CH_2—OH \xrightarrow{Al_2O_3\text{ as cat.}} CH_2{=}CH_2 + H_2O$$

Summary of the differences between primary, secondary and tertiary alcohols

1. *Oxidation.* Primary alcohols give aldehydes, secondary alcohols give ketones and tertiary alcohols are resistant to oxidation by mild oxidising agents in solution such as acidified potassium dichromate.

2. *Elimination.* All three types of alcohols containing the grouping $\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH}$ are dehydrated by sulphuric acid to alkenes, but tertiary alcohols react far more readily than secondary alcohols which in turn react more readily than primary alcohols.

3. *Reaction with halogen acids.* All three types of alcohol react, but tertiary alcohols react the most readily (e.g. with concentrated hydrochloric acid, p. 117) and primary alcohols the least readily (anhydrous conditions, with zinc chloride as a catalyst, are necessary).

10.6
Uses of monohydric alcohols

Methanol

1. In the manufacture of methanal, which is used to make thermosetting plastics such as Bakelite (p. 333).

2. To make methyl 2-methylpropenoate, which is used in the manufacture of Perspex (p. 331).

3. In the manufacture of methanoic and ethanoic acids, using carbon monoxide as the other starting material (p. 191).

4. In the manufacture of single-cell protein animal foodstuffs. Methanol is used as the food for the micro-organisms (p. 345).
5. As a solvent for varnishes and paints.

Ethanol

1. In the manufacture of ethanal (12.3).
2. In the manufacture of ethyl esters (p. 214).
3. As a solvent for many organic compounds.

Propan-2-ol

1. In the manufacture of propanone (20.4) and of hydrogen peroxide (20.4).
2. As a solvent for spirit polishes and varnishes.

10.7 Polyhydric alcohols

Dihydric alcohols

According to the I.U.P.A.C. nomenclature, these are known as **diols**, for example:

		B.P./°C
Ethane-1,2-diol	$HO-CH_2-CH_2-OH$	197
Propane-1,2-diol	$HO-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_3$	189
Propane-1,3-diol	$HO-CH_2-CH_2-CH_2-OH$	215

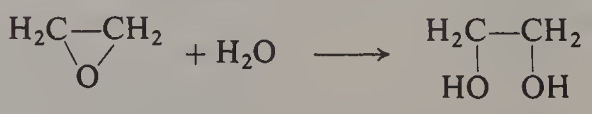
The older name is **glycol**; for example, ethane-1,2-diol is often referred to as ethylene glycol or simply as glycol.

Physical properties of diols

The lower members are viscous, colourless liquids which are soluble in water. Their boiling points are very much higher not only than those of alkanes of similar formula weight but also than those of monohydric alcohols of similar formula weight; this is because the presence of two hydroxyl groups gives rise to very extensive hydrogen-bonding. This is also the reason for their high viscosity, since neighbouring molecules in the liquid, being bonded by hydrogen-bonds, cannot move freely relative to each other. Finally, their solubility in water stems from their forming hydrogen-bonds with water molecules.

Manufacture of ethane-1,2-diol

Ethane-1,2-diol is manufactured by hydration of epoxyethane (11.6):

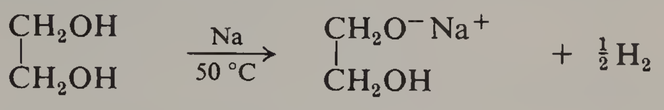


This is carried out in acid solution at about 60°C or with water at 200°C under pressure.

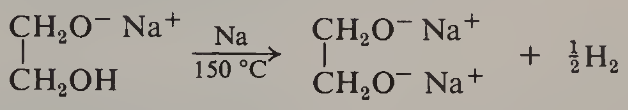
Chemical properties of diols

Ethane-1,2-diol (ethylene glycol) is taken as a typical example. Its two primary alcohol groups behave in the same way as the one such group in a monohydric primary alcohol, except that more vigorous conditions are sometimes needed for reaction of the second of the two groups. For example:

1. It reacts with sodium to form a monoalkoxide and, at higher temperatures, a dialkoxide:

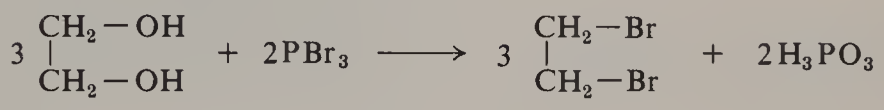


$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} \xrightarrow[50\ ^\circ C]{Na} \begin{array}{l}CH_2O^-Na^+\\|\\CH_2OH\end{array} + \tfrac{1}{2}H_2$$



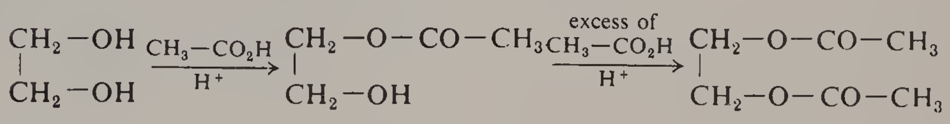
$$\begin{array}{l}CH_2O^-\ Na^+\\|\\CH_2OH\end{array} \xrightarrow[150\ ^\circ C]{Na} \begin{array}{l}CH_2O^-\ Na^+\\|\\CH_2O^-\ Na^+\end{array} + \tfrac{1}{2}H_2$$

2. It reacts with phosphorus halides:



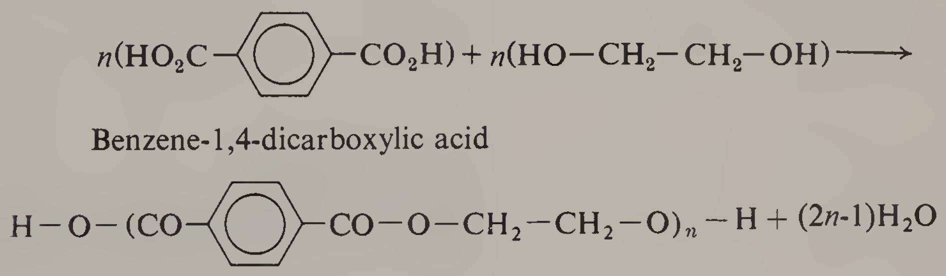
$$3\begin{array}{l}CH_2-OH\\|\\CH_2-OH\end{array} + 2PBr_3 \longrightarrow 3\begin{array}{l}CH_2-Br\\|\\CH_2-Br\end{array} + 2H_3PO_3$$

3. It reacts with carboxylic acids to form esters:



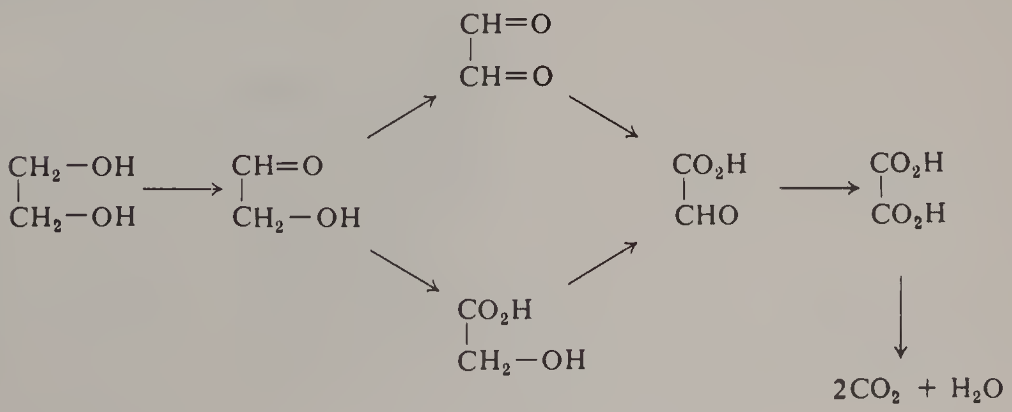
$$\begin{array}{l}CH_2-OH\\|\\CH_2-OH\end{array} \xrightarrow[H^+]{CH_3-CO_2H} \begin{array}{l}CH_2-O-CO-CH_3\\|\\CH_2-OH\end{array} \xrightarrow[H^+]{\text{excess of } CH_3-CO_2H} \begin{array}{l}CH_2-O-CO-CH_3\\|\\CH_2-O-CO-CH_3\end{array}$$

When esterified with a dibasic acid, it forms polymers, for example:



Benzene-1,4-dicarboxylic acid

4. On oxidation, with nitric acid, both primary alcohol groups are oxidised, first to aldehyde and then to carboxyl groups. Ethanedioic acid is then oxidised to carbon dioxide and water:

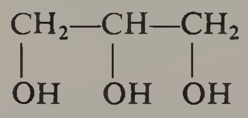


Uses of ethane-1,2-diol

1. In the manufacture of Terylene (p. 337).
2. As an anti-freeze for car radiators and as a de-icing fluid for aeroplane wings. Other chemicals (anti-oxidants) are added to inhibit the formation of acids, by oxidation of the diol, which would cause corrosion.

Propane-1,2,3-triol (glycerol)

Propane-1,2,3-triol is the simplest trihydric alcohol (triol):



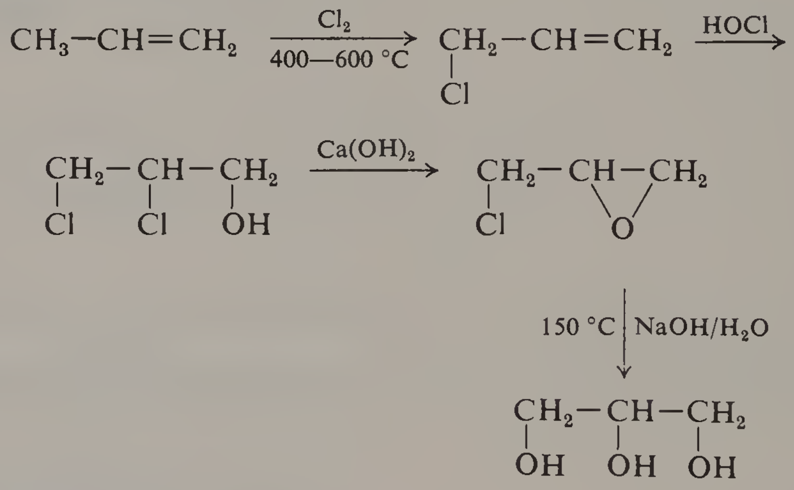
$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

It is a colourless, very viscous liquid which is soluble in water and ethanol. Its chemical properties are similar to those of monohydric alcohols.

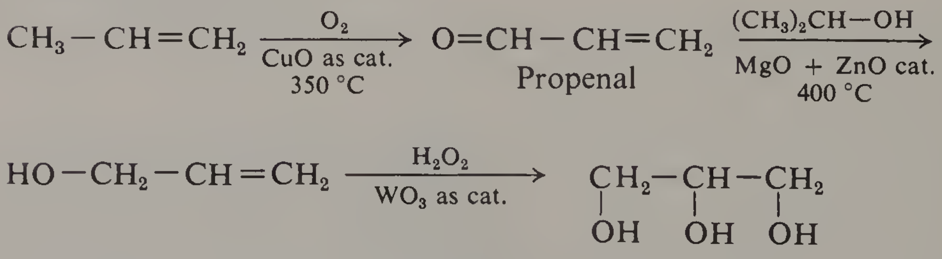
Manufacture of propane-1,2,3-triol

From propene (obtained from petroleum; 20.4) in two ways:

1. *via* 3-Chloropropene:



2. *via* Propenal:



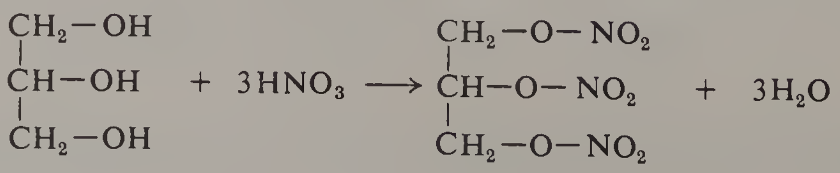
$$CH_3-CH=CH_2 \xrightarrow[\text{CuO as cat. } 350\ °C]{O_2} O=CH-CH=CH_2 \xrightarrow[\text{MgO + ZnO cat. } 400\ °C]{(CH_3)_2CH-OH}$$

$$HO-CH_2-CH=CH_2 \xrightarrow[\text{WO}_3\text{ as cat.}]{H_2O_2} \underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

3. It is a by-product in the manufacture of soap (13.10).

Uses of propane-1,2,3-triol

1. In the manufacture of nitroglycerin, a constituent of several explosives:



$$\begin{matrix}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{matrix} + 3HNO_3 \longrightarrow \begin{matrix}CH_2-O-NO_2\\|\\CH-O-NO_2\\|\\CH_2-O-NO_2\end{matrix} + 3H_2O$$

Nitroglycerin

It should be noted that nitroglycerin is not a nitro-compound as its name may suggest. It is a nitrate ester (propane-1,2,3-triyl trinitrate).

Nitroglycerin is a colourless, oily liquid which is violently detonated on slight shock. Oxygen is present in the molecule, and carbon dioxide, water vapour and nitrogen are liberated to produce a very large pressure.

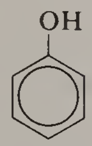
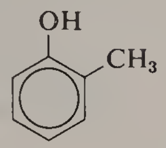
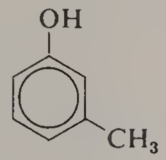
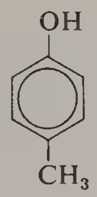
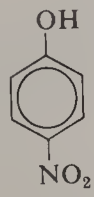
Dynamite, invented by the Swedish chemist, Nobel, is made by allowing kieselguhr to absorb nitroglycerin. Although it retains its explosive properties, the nitroglycerin is less sensitive to shock. Nobel also introduced gun-cotton (cellulose trinitrate), and blasting gelatin, a mixture of 90 per cent nitroglycerin and 10 per cent gun-cotton.

Cordite is a slower burning powder (30 per cent nitroglycerin and 65 per cent gun-cotton) and is used as a propellant for shells, bullets, etc.

2. In the manufacture of glyptal plastics (p. 335).

10.8 Phenols

Phenols are the hydroxy-derivatives of aromatic compounds. Examples of some monohydric phenols:

NAME	FORMULA	M.P./°C	B.P./°C
Phenol		43	181
2-Methylphenol		30	191
3-Methylphenol		11	201
4-Methylphenol		36	201
4-Nitrophenol		114	279

Phenol itself is chosen as a typical member of the group.

Physical properties of phenol

Phenol is a colourless, crystalline solid which becomes discoloured on exposure to air and light. It is only slightly soluble in water but is very soluble in organic solvents.

Preparation of phenol

1. From benzenesulphonic acid (obtained by the sulphonation of benzene; 8.3). The sodium salt of the acid is fused with sodium hydroxide at 300°C:

$$C_6H_5{-}SO_2O^-Na^+ + NaOH \rightarrow C_6H_5{-}OH + Na_2SO_3$$

$$C_6H_5{-}OH + NaOH \rightarrow \underset{\text{Sodium phenoxide}}{C_6H_5{-}O^-Na^+} + H_2O$$

Phenol is released from sodium phenoxide with dilute acid:

$$C_6H_5{-}O^-Na^+ + H_2SO_4 \rightarrow \underset{\text{Phenol}}{C_6H_5{-}OH} + NaHSO_4$$

2. By warming an aqueous solution of benzenediazonium chloride (16.8).

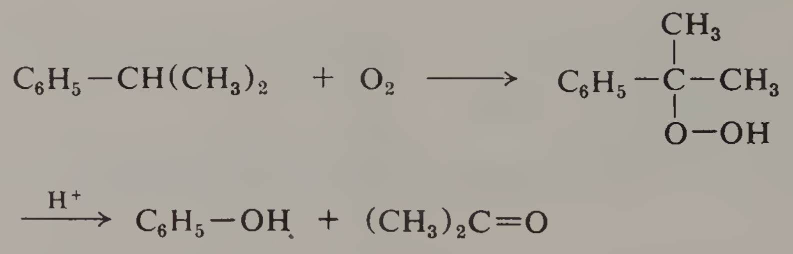
Manufacture of phenol

The process *via* (1-methylethyl)benzene (cumene) now accounts for about 80 per cent of the total phenol produced, the older processes *via* benzenesulphonic acid and chlorobenzene having been largely superseded.

1. *The Cumene process.* Benzene is alkylated with propene, either in the liquid phase with aluminium chloride as catalyst or in the gas phase with phosphoric acid on an inert solid as catalyst:

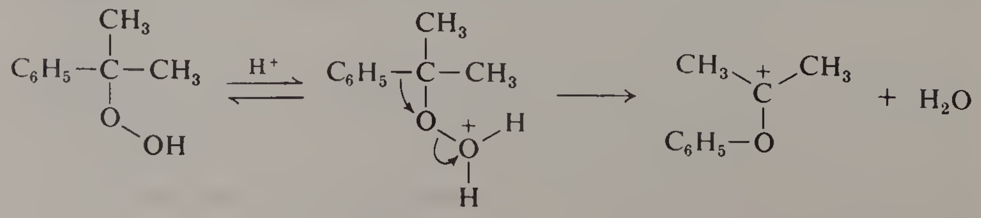
$$C_6H_6 + CH_3{-}CH{=}CH_2 \rightarrow \underset{\text{(1-Methylethyl)benzene}}{C_6H_5{-}CH(CH_3)_2}$$

Air is passed through (1-methylethyl)benzene (often called cumene) to form its hydroperoxide which is then decomposed with warm, dilute sulphuric acid:

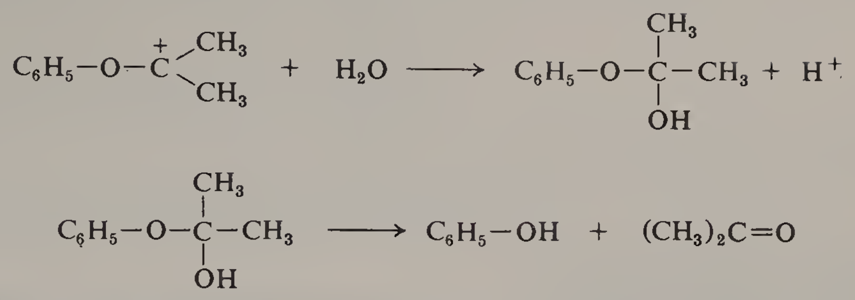


$$C_6H_5{-}CH(CH_3)_2 + O_2 \longrightarrow C_6H_5{-}\overset{\displaystyle CH_3}{\underset{\displaystyle O{-}OH}{C}}{-}CH_3 \xrightarrow{H^+} C_6H_5{-}OH + (CH_3)_2C{=}O$$

The final reaction involves a rearrangement: as the O—O bond in the protonated hydroperoxide breaks, so the phenyl group migrates from carbon to oxygen:



The carbonium ion reacts with water to form the products:



$$C_6H_5-O-\underset{OH}{\overset{CH_3}{C}}-CH_3 \longrightarrow C_6H_5-OH + (CH_3)_2C{=}O$$

This process is particularly valuable because of the formation of propanone as well as phenol.

2. *Chlorobenzene process.*

$$C_6H_6 \xrightarrow[\text{FeCl}_3\text{ cat.}]{Cl_2} C_6H_5{-}Cl \xrightarrow[330^\circ C]{NaOH} C_6H_5{-}O^-Na^+ \xrightarrow{H^+} C_6H_5{-}OH$$

3. *Benzenesulphonic acid process* (p. 156).

The continued superiority of the Cumene process over the others is dependent on there being a ready market for the propanone which is also produced, for in terms of selling phenol *alone*, it is a relatively expensive method.

Chemical properties of phenol

Like alcohols, phenol reacts with acid chlorides to form esters, for example:

$$C_6H_5{-}OH + CH_3{-}CO{-}Cl \rightarrow \underset{\text{Phenyl ethanoate}}{C_6H_5{-}O{-}CO{-}CH_3} + HCl$$

In the following respects, phenol behaves differently from both aliphatic and aromatic alcohols. In Section 10.9 experiments are suggested which compare and contrast the reactions of phenol with those of ethanol and phenylmethanol.

1. Phenol does not react with hydrogen halides to form aryl halides.
2. Phenol does not react with phosphorus tribromide or tri-iodide to form bromobenzene or iodobenzene.
3. Phenol is not oxidised in the same way as alcohols. Oxidation occurs readily, but the products are generally complex, polymeric materials.
4. Phenol does not undergo elimination reactions.
5. Phenol is a considerably stronger acid than an alcohol; thus, K is $1{\cdot}3 \times 10^{-10}$ for phenol and 10^{-16} for methanol.

This can be understood by considering the bonding in the phenoxide ion. One of the p orbitals on the oxygen atom, which contains two electrons, interacts with the singly occupied p orbital on the adjacent carbon atom. The latter also takes part in the p-orbital interactions which are characteristic of the benzene ring (p. 60), so that a total of seven π molecular orbitals is formed. The eight p electrons—six from carbon atoms and two from the oxygen atom—fill four of these; one is shown in Fig. 10.2. Consequently, the charge on the phenoxide ion is not confined to oxygen but is delocalised and therefore stabilised; in contrast, the charge on an alkoxide ion is confined to the oxygen atom. Thus, phenol has a greater tendency to dissociate than an alcohol.

Phenol is not as strong an acid as carbonic acid or a carboxylic acid. This affords a method for distinguishing phenol from a carboxylic acid, for phenol does not react with an aqueous solution of sodium carbonate, whereas carboxylic acids react to liberate carbon dioxide. The separation of a mixture of phenol and a carboxylic acid is based on the same principle (13.5).

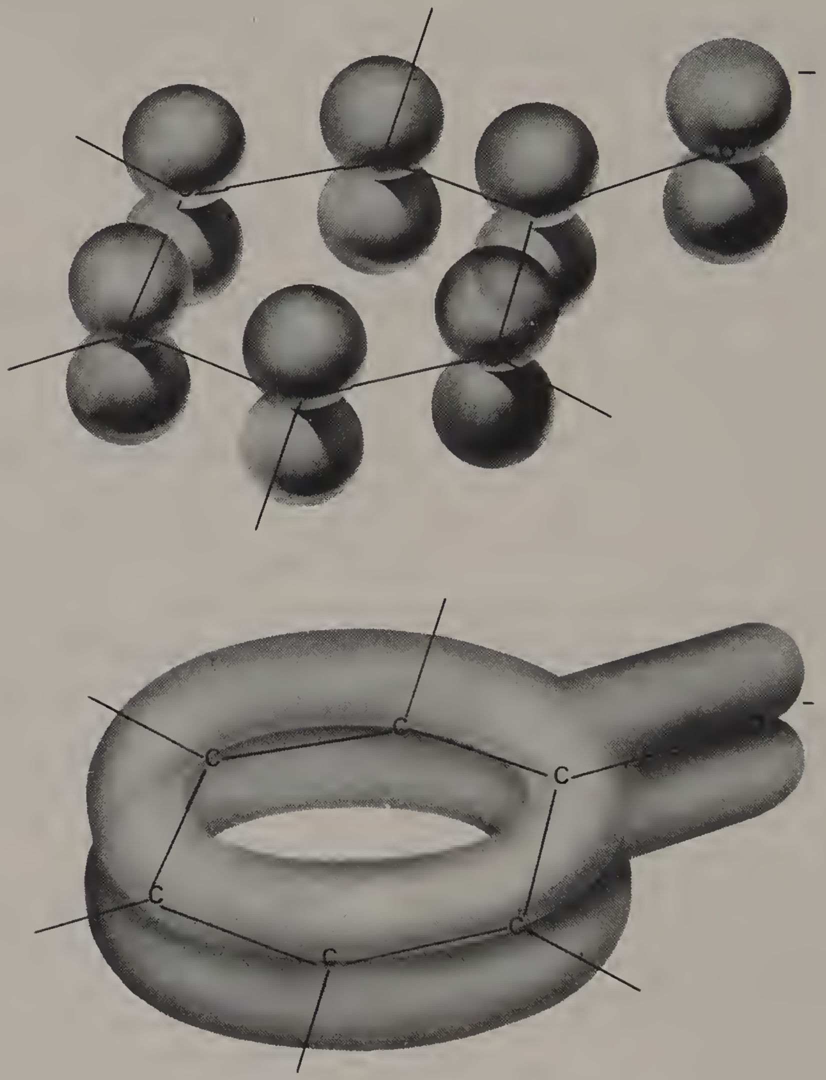
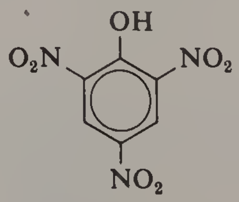


FIG. 10.2. *π-Bonding in the phenoxide ion; the lower diagram shows a delocalised π orbital formed by overlap of the* p *orbitals shown in the upper diagram*

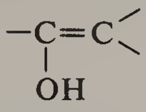
The acidity of a phenol is increased when electron-attracting substituents are introduced into the aromatic ring. For example, 2,4,6-trinitrophenol is quite a strong acid ($K_a = 10^{-1}$), which liberates carbon dioxide from sodium carbonate solution; it is often described as an acid (picric acid) for this reason.



2,4,6-Trinitrophenol
(Picric acid)

6. Phenol reacts with a neutral solution of iron(III) chloride to give a violet colour. This is a characteristic reaction for compounds containing a

hydroxyl group adjacent to an unsaturated carbon atom:

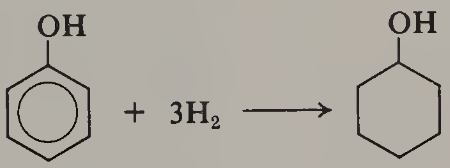


$$-\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}=\mathrm{C}\Big\langle$$

This is known as an **enol** group. Another example of a compound containing an enol group is ethyl 3-oxobutanoate (p. 215).

Reactions of the aromatic ring

1. Phenol is reduced to cyclohexanol when passed over nickel at about 200°C:

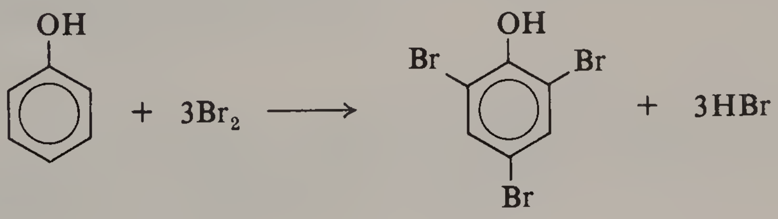


Cyclohexanol

Cyclohexanol is used in the manufacture of nylon (p. 320).

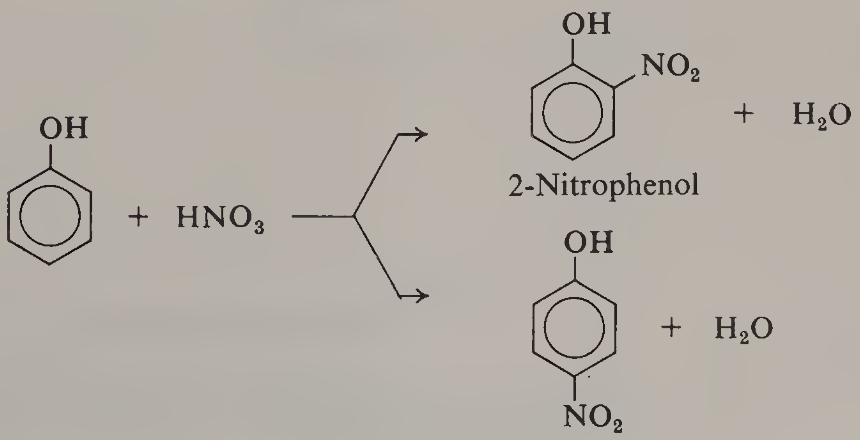
2. Phenol is very reactive towards electrophilic reagents, undergoing substitution at its 2- and 4-positions under mild conditions. The reason for the greater reactivity of phenol than benzene in these reactions has been described earlier (8.5). For example:

(a) With bromine, 2,4,6-tribromophenol is formed:



Likewise, chlorine gives 2,4,6-trichlorophenol.

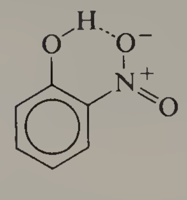
(b) With dilute nitric acid, a mixture of 2- and 4-nitrophenol is formed:



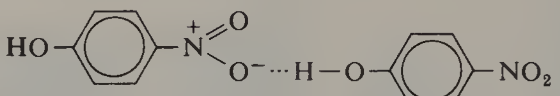
2-Nitrophenol

4-Nitrophenol

2-Nitrophenol possesses an internal hydrogen-bond:



In contrast, the 4-isomer forms hydrogen-bonds by attraction of the hydroxyl hydrogen atom of one molecule to the nitro group of another:

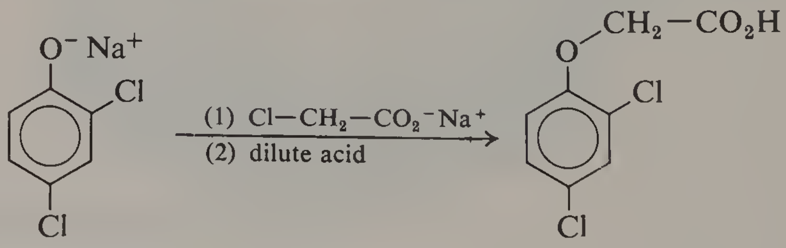


Consequently, more energy is needed to separate the molecules of 4-nitrophenol from each other, so that its boiling point (279°C) is higher than that of the 2-isomer (216°C). This makes it possible to separate the two compounds; a convenient method is by distillation in steam (2.3), the 2-compound having the higher vapour pressure and therefore being the more volatile in the steam.

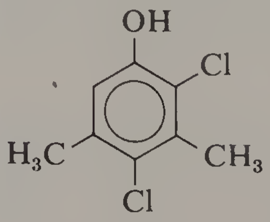
With excess of nitric acid, 2,4,6-trinitrophenol (picric acid) is formed. The dry compound is explosive, but solutions have been used as yellow dyes, and it was probably the first artificial dye (1849).

Uses of phenol

1. In the manufacture of phenol-methanal plastics, e.g. Bakelite (p. 333).
2. As a starting material for the production of cyclohexanol, which is used in the manufacture of nylon (p. 320).
3. To make substituted phenols, which are used to make epoxy resins (p. 335).
4. To make 2,4-dichlorophenol which is used to make 2,4-dichlorophenoxyethanoic acid (known as 2,4-D), a selective weed killer:



5. To make 2,4-dichloro-3,5-dimethylphenol, a powerful antiseptic ('Dettol'):



10.9 Practical work

Reactions of alcohols and phenols

For reactions with alcohols, unless stated, use either ethanol or phenylmethanol (which must be freshly distilled), and use phenol itself as an example of a phenol.

Reactions of the —OH group

1. Dissolve 5 drops of ethanol in 5 cm^3 of water in one test-tube and 0·5 g of phenol in 5 cm^3 of water in another tube. To each solution, add 1 drop of blue litmus solution.

2. (a) To 1 cm^3 of an alcohol in a test-tube, add a small pellet of sodium. Note the effervescence and test the gas evolved with a lighted splint.

(b) When all the sodium has reacted, evaporate the solution to dryness to obtain a white residue. Add 3 drops of water to the residue and test the solution with litmus solution.

Comment on whether these reactions would occur with phenol.

3. Warm a mixture of 5 drops of an alcohol and 5 drops of ethanoic acid with 1 drop of concentrated sulphuric acid. Note the characteristic smell of the product.

Comment on whether this reaction would occur with phenol.

4. To 5 drops of an alcohol in a test-tube, add 2 or 3 drops of ethanoyl chloride. Repeat the experiment with a few crystals of phenol.

5. *Schotten-Baumann reaction.* To 0·5 g of phenol, add 5 cm^3 of 10 per cent sodium hydroxide. Add 5 drops of benzoyl chloride and shake. Filter the precipitate of phenyl benzoate, wash with water and recrystallise from hot ethanol; the product should melt at 69°C:

$$C_6H_5\text{—}OH + NaOH \rightarrow C_6H_5\text{—}O^-Na^+ + H_2O$$

$$C_6H_5\text{—}O^-Na^+ + C_6H_5\text{—}CO\text{—}Cl \rightarrow \underset{\text{Phenyl benzoate}}{C_6H_5\text{—}O\text{—}CO\text{—}C_6H_5} + NaCl$$

Would you expect alcohols to undergo this reaction?

6. To 1 cm^3 of an alcohol in a test-tube, add about 0·1 g of phosphorus pentachloride. Test the fumes evolved by (a) moist blue litmus paper, (b) breathing upon them.

Oxidation reactions

7. To 5 drops of ethanol, add 10 drops of dilute sulphuric acid and 2 drops of potassium dichromate solution. Warm gently, noting (a) the colour of the solution and (b) the smell of the product.

Repeat the experiment with (i) propan-2-ol, (ii) 2-methylpropan-2-ol, (iii) phenylmethanol.

8. Introduce about 10 cm^3 of methanol into a 100-cm^3 beaker. Introduce a red-hot spiral of platinum wire above the alcohol as shown in Fig. 10.3.

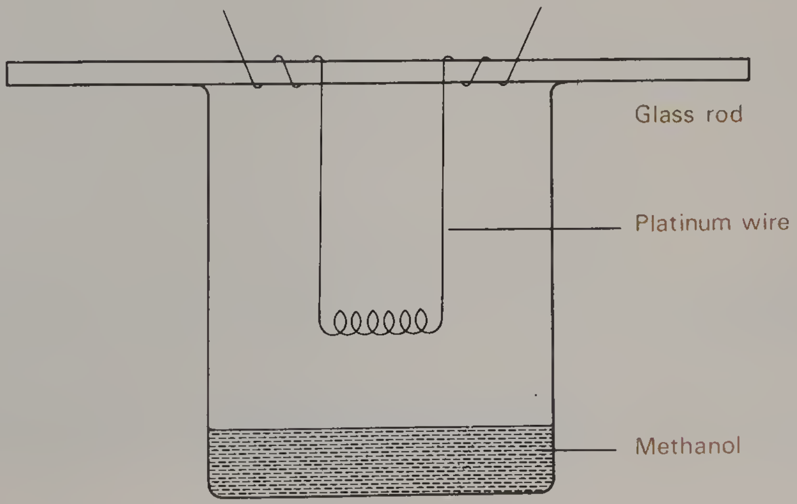


FIG. 10.3. *Catalytic oxidation of methanol*

The spiral continues to glow and the pungent odour of methanal is noticed:

$$2CH_3OH + O_2 \xrightarrow{\text{Pt as cat.}} 2HCHO + 2H_2O$$

9. *The iodoform test.* To 5 drops of ethanol, add 5 drops of iodine solution (Appendix III) and then add dilute sodium hydroxide solution dropwise until the colour of the iodine is discharged. A yellow precipitate of triiodomethane (iodoform) is obtained. Filter, dry and view the crystals under a microscope and note their characteristic shape (hexagonal plates).

Repeat this experiment with (i) methanol and (ii) propan-2-ol.

Elimination reactions

10. The test-tube preparation of ethene in Section 6.5 is an example.

Would you expect (i) methanol, (ii) propan-2-ol, (iii) 2-methylpropan-2-ol, (iv) phenylmethanol, to undergo this reaction?

Substitution in the aromatic ring of phenol

11. To a few crystals of phenol in a test-tube, add 1 cm^3 of water. Shake and warm the solution. Allow to cool and add bromine water dropwise, until a precipitate of 2,4,6-tribromophenol is obtained.

What products would you expect to obtain when bromine water is added to (a) ethanol, (b) phenylmethanol?

12. Phenol is nitrated with *dilute* nitric acid (p. 278).

Test for the enol group in phenol

13. Make up a neutral solution of iron(III) chloride by adding ammonia solution to 2 cm^3 of iron(III) chloride solution, until a precipitate just appears. Add the original iron(III) chloride solution, dropwise, until the precipitate just disappears.

Place 5 drops of this solution in two test-tubes. To one add 3 drops of an alcohol and to the other add 1 crystal of phenol.

Reactions of polyhydric alcohols (choose either ethane-1,2-diol or propane-1,2,3-triol)

14. To 2 cm^3 of the alcohol in a test-tube, add a small clean pellet of sodium. Note whether there is any effervescence, and then warm the mixture gently. Test any gas evolved with a lighted splint.

15. To 2 cm^3 of the alcohol in a test-tube, add ethanoyl chloride dropwise (taking great **CARE**). Test the gas evolved.

16. To 1 cm^3 of a dilute acidified solution of potassium manganate(VII), add 5 drops of the alcohol. Warm the mixture gently.

Preparation of propane-1,2,3-triol from a fat

17. Details of the saponification of a fat are given on p. 227.

10.10 Questions

1 How and under what conditions does ethanol react with (a) sodium, (b) phosphorus trichloride, (c) sulphuric acid, (d) chlorine and (e) ethanoic acid.

Suggest a scheme for preparing from ethanol a compound containing **four** atoms of carbon per molecule. (AEB)

2 Name and give the formula of one aliphatic monohydric alcohol and describe how it behaves with (a) phosphorus pentachloride, (b) concentrated sulphuric acid.

Name and give the formula of one aliphatic dihydric alcohol, and write down the formulae of all its possible oxidation products.

Distinguish between a *primary*, *secondary* and *tertiary* alcohol and explain how each behaves on oxidation. (AEB)

3 Name the four alcohols represented by the molecular formula C_4H_9OH, and write their structural formulae.

What is the effect of oxidation upon each of these compounds? Outline an experiment by which, using an acidified dichromate solution as a relatively mild oxidising agent, you could differentiate as far as possible between these four alcohols by recognition of the character of their oxidation products.

Outline the procedure by which pure ethanol can be obtained industrially from starch. (JMB)

4 Write structural formulae for the isomers corresponding to the molecular formula $C_4H_{10}O$.

One of these isomers, *W*, reacts with sodium. A ketone, *X*, is formed when *W* is oxidised. Dehydration of *W* gives a mixture of two hydrocarbons *Y* and *Z*, each containing 85·7 per cent of carbon. Explain how these reactions enable *W* to be identified and specify an appropriate reagent for its oxidation and dehydration respectively. Predict how hydrogen bromide would react with *Y* and *Z*. (W)

5 Outline how you would prepare a pure sample of ethanol in the laboratory. What evidence would you cite for the presence of (a) a hydroxyl group (—OH), (b) a methyl group (CH_3—) and (c) a methylene group (—CH_2—) in ethanol? (L)

6 60·0 cm^3 of a gaseous hydrocarbon, **A**, was exploded with 400 cm^3 of oxygen. On cooling to room temperature and pressure, the residual gas occupied a volume of 280 cm^3. On shaking with aqueous potassium hydroxide, the volume left occupied 40 cm^3. Treatment of compound **A**, with hydrogen chloride gas, yielded a compound **B**. When **B** was treated with aqueous sodium hydroxide, compound **C** was obtained which when reacted with ethanoic acid, produced a compound **D**. Compound **D** had an empirical formula of C_3H_6O. Compound **C** was found to be resistant to oxidation.

(a) Determine the molecular formula of **A** and write the structures of the possible isomers of this compound.

(b) Give the names and structural formulae of **B**, **C** and **D** and explain, with the aid of equations, the reasons for your deductions.

(c) Explain, using equations, how you would convert

(i) **B** into **A**

(ii) **A** into methanal (formaldehyde)

(iii) **C** into **B**. (AEB(I))

7 A compound *A*, containing C, 60·0; H, 13·3; O, 26·7 per cent, and having molecular weight 60, gave on oxidation *B*, containing C, 62·1; H, 10·3; O, 27·6 per cent. *B* did not reduce Fehling's solution.

When *A* was heated with concentrated sulphuric acid it gave *C*. Addition of bromine to *C* gave *D*, which on boiling with aqueous sodium carbonate gave *E*.

Write down the structural formulae of the compounds *A* to *E*. (O and C)

8 Describe, giving essential reagents and conditions, how phenol can be prepared in the laboratory, starting from nitrobenzene.

(a) How would you confirm that the product is a phenol?

(b) What are the products of the reaction of phenol with (i) ethanoic (*acetic*) anhydride and (ii) benzenecarbonyl (*benzoyl*) chloride? Give equations for these reactions. (JMB)

9 Describe the preparation of phenol from benzenesulphonic acid. Compare and contrast the chemical reactivity of the hydroxyl group in ethanol with that in phenol. (W)

10 Outline (a) **one** process for the manufacture of phenol, (b) a laboratory preparation of phenol from phenylamine.

How, and under what conditions, does phenol react with (i) sodium carbonate, (ii) 50 per cent nitric acid, (iii) concentrated sulphuric acid, (iv) iodomethane (methyl iodide)? (AEB)

11 (a) A polyhydroxylic compound, $C_4H_8O_4$, was heated with excess ethanoic anhydride. On refluxing 2·87 g of the product with 50·00 cm^3 of molar sodium hydroxide solution, the residual alkali required 15·00 cm^3 of molar hydrochloric acid for neutralisation. Calculate the number of hydroxyl groups per molecule of the original compound.

(b) A compound *X* has the following percentage composition by weight: C = 64·9 per cent, H = 13·5 per cent, O = 21·6 per cent. Oxidation yields a neutral compound *Y* which does not react with sodium. Further oxidation of *Y* yields an acid *Z*. When 8 cm^3 of the vapour of *Y* is sparked with excess oxygen, 32 cm^3 of carbon dioxide is formed. *Z* forms only one silver salt which contains 64·7 per cent by weight of silver.

Identify *X*, *Y*, *Z* and explain your reasoning. (SUJB(S))

12 Outline how phenol is manufactured from petroleum. Explain what happens when phenol reacts with (i) iodomethane, (ii) benzoyl chloride, (iii) bromine water, (iv) nitric acid.

13 Compare and contrast the reactions of the —OH group in phenol and in ethanol.

How, and under what conditions, does phenol react with (a) bromine, (b) benzenediazonium chloride?

14 Describe how phenol may be prepared from benzene.

Outline the simplest methods for effecting the following changes: (a) phenol to phenylamine, (b) phenol to phenyl ethanoate. What action has bromine on phenol?

15 Four isomeric liquids stand side by side on a shelf, each with the label $C_4H_{10}O$, and no other information. *Two* are known to be alcohols, but two have been shown by their infrared spectra to lack an —OH group. Suggest formulae for these compounds and *outline* a scheme by which they may each be identified. (C Schol.)

16 By what reactions may ethane-1,2-diol be obtained from ethene? Give the structural formula of ethane-1,2-diol and show how this formula may be justified. What substances may be formed from ethane-1,2-diol by oxidation? Give their structural formulae and show how any one of these may be confirmed by an independent method of formation. What are the uses of ethane-1,2-diol?

17 Describe one method by which methanol is manufactured. How does it react with (a) sodium, (b) phosphorus pentachloride, (c) ethanoic acid?

Describe one chemical test which would enable you to distinguish between methanol and ethanol.

18 A compound, *A*, $C_3H_8O_2$, was ethanoylated; 0·236 g of the ethanoyl derivative was boiled with 50 cm^3 of M/10 sodium hydroxide and the resulting solution required 30 cm^3 of M/20 sulphuric acid for neutralisation. When *A* was oxidised it gave *B*, $C_3H_6O_3$, which could not be ethanoylated, but of which 0·225 g required 25 cm^3 of M/10 sodium hydroxide for neutralisation. Assign possible structures to *A* and *B* and account for the above results. (C Schol.)

19 An optically active compound *W* undergoes the following reactions:

$$\underset{W}{C_9H_{12}O} \xrightarrow[\text{nitric acid}]{\text{dilute}} \underset{X}{C_9H_{10}O} \xrightarrow{\text{NaOBr}} \underset{Y}{C_8H_8O_2} \xrightarrow[\text{potassium manganate(VII)}]{\text{alkaline}} \underset{Z}{C_8H_6O_4}$$

Z is unchanged on heating. Elucidate these reactions and give structures for *W*, *X*, *Y* and *Z*.

20 Compare and contrast the properties of phenol and phenylmethanol in their reactions, if any, with sodium carbonate, sodium hydroxide, potassium, bromine, ethanoic acid and an acidified solution of potassium manganate(VII).

21 How do primary, secondary, and tertiary alcohols differ in their reactions with oxidising agents?

Investigation of the rates of the following reactions of primary, secondary, and tertiary alcohols shows that in (a) the rates are in the order tertiary > secondary > primary, whereas the reverse is true in (b) and (c):

(a) $ROH + HBr = RBr + H_2O$

(b) $2ROH + 2Na = 2RONa + H_2$

(c) $ROH + CH_3COOH = RO.CO.CH_3 + H_2O$

What can you deduce about the esterification reaction (c) from these observations? (O Schol.)

22 Contrast the properties of the hydroxyl groups of ethanol and phenol. Place the following in order of diminishing acidity: C_6H_5OH, C_2H_5OH, CH_3COOH, H_2CO_3, and describe simple tests which would enable you to justify your order. (O Schol.)

Chapter 11

Ethers

General formula

R—O—R′

11.1 Nomenclature

The two R groups in the structural formula R—O—R′ can be the same (the simple ethers) or different (the mixed ethers), and can be either alkyl groups or aromatic groups. According to the I.U.P.A.C. rules, the RO— group is regarded as a substituent of the hydrocarbon R′H; for example, $CH_3—O—CH_2—CH_3$ is methoxyethane. However, it is common practice to use the name compounded from the two groups R and R′ followed by ether, as in Table 11.1.

Table 11.1. Some ethers

NAME	FORMULA	B.P./°C
Dimethyl ether	$CH_3—O—CH_3$	–24
Ethyl methyl ether	$CH_3—O—CH_2—CH_3$	11
Diethyl ether	$CH_3—CH_2—O—CH_2—CH_3$	35
Methyl phenyl ether	$CH_3—O—C_6H_5$	154
Diphenyl ether	$C_6H_5—O—C_6H_5$	259

11.2 Physical properties of ethers

Dimethyl ether is a colourless gas, and the other lower homologues are colourless liquids with the characteristic 'ether' smell. Their boiling points are much lower than those of the isomeric alcohols, but are about the same as those of the alkanes of similar formula weight (Table 11.2). Molecules of ethers are not associated by hydrogen-bonding in the liquid phase, unlike alcohols.

Table 11.2 **The boiling points/°C of alkanes, alcohols and ethers**
(The formula weights are given in brackets)

ALKANE	ALCOHOL	ETHER
Propane (44) –42	Ethanol (46) 78	Dimethyl ether (46) –24
Pentane (72) 36	Butan-1-ol (74) 118	Diethyl ether (74) 35
Heptane (100) 98	Hexan-1-ol (102) 157	Dipropyl ether (102) 91

11.3
Methods of preparation of ethers

Laboratory methods

1. *Simple ethers* can be prepared by the dehydration of an excess of an alcohol with concentrated sulphuric acid at about 140°C (10.5), for example:

$$C_2H_5\text{—}OH + H_2SO_4 \rightarrow C_2H_5\text{—}O\text{—}SO_2\text{—}OH + H_2O$$

$$C_2H_5\text{—}OH + C_2H_5\text{—}O\text{—}SO_2\text{—}OH \rightarrow \underset{\text{Diethyl ether}}{C_2H_5\text{—}O\text{—}C_2H_5} + H_2SO_4$$

2. *Simple* and *mixed ethers* can be prepared by the reaction between an alkyl halide and the sodium derivative of an alcohol (the alkoxide):

$$R\text{—}OH + Na \rightarrow R\text{—}O^-Na^+ + \tfrac{1}{2}H_2$$

$$R\text{—}O^-Na^+ + R'\text{—}X \rightarrow R\text{—}O\text{—}R' + NaX$$

For example:

$$C_2H_5\text{—}O^-Na^+ + CH_3\text{—}I \rightarrow \underset{\substack{\text{Ethyl methyl}\\ \text{ether}}}{C_2H_5\text{—}O\text{—}CH_3} + NaI$$

Manufacture

Diethyl ether is obtained as a by-product during the manufacture of ethanol from ethene and concentrated sulphuric acid.

11.4
Chemical properties of ethers

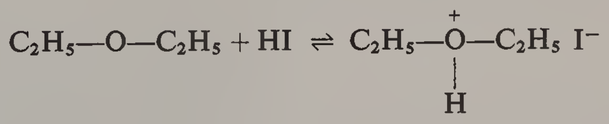
Ethers, like alkanes, are inert towards most inorganic reagents. For example, they are not attacked by sodium or, in the cold, by phosphorus pentachloride, and can therefore be readily distinguished from alcohols. They have three general properties:

1. They are highly flammable, and mixtures with air are dangerously explosive.

2. They react with a hot, concentrated solution of hydriodic acid to form alkyl iodides, for example:

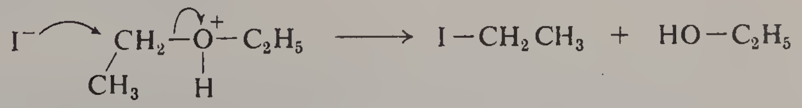
$$C_2H_5\text{—}O\text{—}C_2H_5 + 2HI \rightarrow 2C_2H_5\text{—}I + H_2O$$

Reaction occurs by the reversible protonation of the ether,



$$C_2H_5\text{—}O\text{—}C_2H_5 + HI \rightleftharpoons C_2H_5\text{—}\underset{\displaystyle H}{\overset{+}{O}}\text{—}C_2H_5\ I^-$$

followed by displacement of a molecule of the alcohol by the nucleophilic iodide ion:



The alcohol reacts with a further molecule of hydrogen iodide.

3. They react with phosphorus pentachloride when heated. No hydrogen chloride is evolved, showing that ethers do not contain a hydroxyl group (10.5):

$$R{-}O{-}R' + PCl_5 \rightarrow R{-}Cl + R'{-}Cl + POCl_3$$

11.5
Uses of ethers

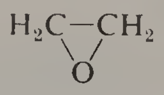
Diethyl ether is used as an anaesthetic. Inhalation of the vapour depresses the activity of the central nervous system.

Ethers, particularly diethyl ether, are used as solvents for fats, oils and resins.

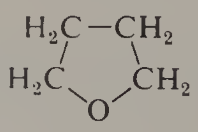
The ability of ethers to dissolve a wide range of organic compounds, coupled with their resistance to chemical reaction, makes them valuable solvents for organic preparations (e.g. Grignard reagents; 9.8) and for the separation and purification of compounds by extraction.

11.6
Cyclic ethers

Cyclic ethers with five or more members in the ring are, like the corresponding cycloalkanes, relatively strainless and have the properties of their non-cyclic analogues. An example is tetrahydrofuran. However, those with three- and four-membered rings are strained and, like cyclopropane and cyclobutane (5.6), are very reactive towards reagents which are capable of opening the ring. An example is epoxyethane (ethylene oxide).



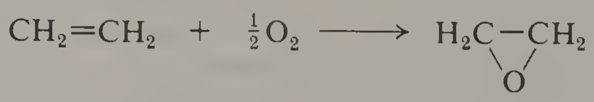
Epoxyethane



Tetrahydrofuran

Manufacture of epoxyethane

By passing ethene and oxygen at 250°C over a silver catalyst:

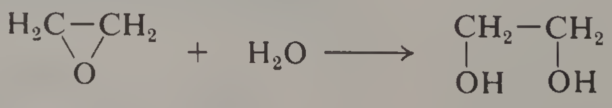


Physical properties of epoxyethane

It is a volatile liquid, b.p. 13°C, which is soluble in water and in organic solvents.

Chemical properties of epoxyethane

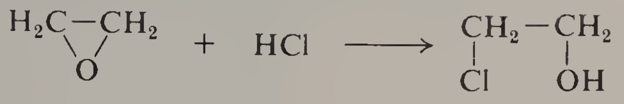
1. It is hydrolysed by steam at 200°C under pressure, or by dilute acids at 60°C and atmospheric pressure:



Ethane-1,2-diol

This is the basis of the manufacture of ethane-1,2-diol.

2. It reacts with the halogen acids, for example:



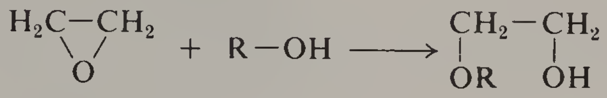
2-Chloroethanol

3. It reacts with Grignard reagents to yield primary alcohols (9.8).

Uses of epoxyethane

1. In the manufacture of ethane-1,2-diol.

2. In the manufacture of diol ethers which are used as de-icing fluids, brake fluids and solvents. The diol ethers have an ether and a primary alcohol group:



3. In the manufacture of non-ionic detergents (13.10).

11.7 Questions

1 Describe the laboratory preparation of diethyl ether.

Deduce the probable structural formula of an ether which contains by weight 60 per cent of carbon and 13·3 per cent of hydrogen, and suggest how it could be prepared.

2 Starting with a sample of radioactive potassium cyanide $K\overset{*}{C}N$, suggest reaction schemes enabling you to label each of the carbon atoms in ethyl methyl ether $CH_3OCH_2CH_3$.

How would you confirm the position of the labelled carbon atom in $CH_3OCH_2\overset{*}{C}H_3$?

3 Describe the preparation of a pure sample of diethyl ether.

Four unlabelled bottles contain samples of diethyl ether, pentane, propanone, and ethanol. What chemical tests would you use to identify each compound? (C(T))

4 Write an equation for the laboratory preparation of diethyl ether from ethanol. Why is an excess of ethanol used in the preparation? What is the main organic impurity in the distillate likely to be and how may it be removed?

Explain why ether is particularly suitable as a solvent for the extraction of an organic compound from an aqueous solution. What is the main disadvantage in using ether for this purpose?

Calculate the weight of phenylamine which would be extracted from 100 cm^3 of an aqueous solution containing 5·0 g phenylamine by shaking with

(a) 50 cm^3 of ether is one portion,

(b) two successive 25 cm^3 portions of ether.

Comment on the results.

(Partition coefficient of phenylamine between ether and water = 5.) (L(X))

5 *A* is a liquid containing carbon, hydrogen and iodine only. 0·150 g of *A* in a Victor Meyer's apparatus displaced 25·3 cm^3 of air, collected over water at 15°C and 763 mm pressure.

Another compound, *B*, containing carbon, hydrogen and oxygen only, reacts vigorously with metallic sodium when hydrogen is liberated and a white solid, *C*, is formed.

When *A* was heated under reflux with *C* and the mixture subsequently distilled, a compound *D*, containing carbon, hydrogen and oxygen only was obtained. *D* contained C, 64·9 per cent and H, 13·5 per cent and it was not attacked by sodium even on warming.

Identify *A* and then show that there are two possible compounds for each of *B*, *C* and *D*.

The saturated vapour pressure of water at 15° is 13·0 mm. (L)

6 16 cm³ of a gaseous aliphatic compound *A*, $C_nH_{3n}O_m$, was mixed with 60 cm³ of oxygen at room temperature and sparked. At the original temperature again, the final gas mixture occupied 44 cm³. After treatment with potassium hydroxide solution the volume of gas remaining was 12 cm³. Deduce the molecular and structural formulae of *A*, and name it.

Give the name and structural formula of a compound *B* isomeric with *A*, and state briefly how *A* and *B* react separately with (a) sodium, (b) hydrogen iodide, (c) phosphorus trichloride.

(If there is no reaction in any one case, make this clear.)

Outline a reaction scheme, stating reagents, by which *A* might be prepared from *B*. (SUJB)

7 A neutral compound, *P*, $C_9H_{12}O_2$, fumes when treated with phosphorus pentachloride and, when heated with acidified sodium dichromate solution another neutral compound, *Q*, is formed. *Q* produces a characteristic orange-red precipitate with a solution of 2,4-dinitrophenylhydrazine but *Q* does not react with an ammoniacal solution of silver oxide.

P gives a yellow precipitate with iodine and alkali and if the filtrate from this reaction is acidified, an acid, *R*, $C_8H_8O_3$, is produced. *R*, on boiling with hydrogen iodide, gives a further acid, *S*. A familiar smell of oil of wintergreen is produced if *S* is warmed with methanol containing a little concentrated sulphuric acid as catalyst.

Deduce the nature of the compounds *P*, *Q*, *R* and *S* and explain fully all the reactions.

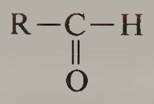
What is the significance of the reaction between *S* and ethanoic anhydride? (S(S))

Chapter 12

Aldehydes and ketones

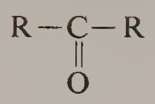
12.1 Introduction

General formula



$$R-\underset{\underset{O}{\|}}{C}-H$$

Aldehyde



$$R-\underset{\underset{O}{\|}}{C}-R$$

Ketone

Both aldehydes and ketones contain the **carbonyl group** ($>C=O$). This group has characteristic properties which are shown by both classes of compound, so that it is convenient for the two homologous series to be considered together. However, the attachment of a hydrogen atom to the carbonyl group in an aldehyde gives aldehydes certain properties which ketones do not possess and which enable the two classes of compound to be distinguished from one another.

The I.U.P.A.C. nomenclature uses the suffixes **-al** for aldehydes and **-one** for ketones; the main carbon chain is named as usual and, for ketones, the position of the carbonyl group is specified by inserting the number of its carbon atom from the nearer end of the chain. For example:

$$CH_3-CH_2-CH_2-CH_2-CHO \qquad \overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}O-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

Pentanal — Hexan-3-one

12.2 Nomenclature

The simpler members of the series are often known by their original names. Some examples, with the original names in parentheses, together with their boiling points, are in Table 12.1.

Table 12.1. Some aldehydes and ketones

NAME	STRUCTURAL FORMULA	B.P./°C
Methanal (formaldehyde)	$H-CHO$	−21
Ethanal (acetaldehyde)	CH_3-CHO	21
Propanal (propionaldehyde)	CH_3-CH_2-CHO	49
Benzaldehyde	C_6H_5-CHO	179
Propanone (acetone)	$CH_3-CO-CH_3$	56
Butanone (ethyl methyl ketone)	$CH_3-CO-CH_2-CH_3$	80
Pentan-3-one (diethyl ketone)	$CH_3-CH_2-CO-CH_2-CH_3$	102
Phenylethanone (acetophenone)	$C_6H_5-CO-CH_3$	202
Diphenylmethanone (benzophenone)	$C_6H_5-CO-C_6H_5$	306

12.3 Physical properties of aldehydes and ketones

Methanal is a gas, other aldehydes and ketones of relatively low formula weight are liquids and the remainder are solids. Methanal dissolves readily in water; a 40 per cent solution is known as formalin. The liquid aldehydes and ketones of low formula weight are also readily soluble in water (for example, ethanal and propanone are miscible with water), but solubility decreases as the formula weight increases.

12.4
Methods of preparation of aldehydes and ketones

General methods

1. Aldehydes are obtained by the oxidation of primary alcohols, and ketones by the oxidation of secondary alcohols.

A convenient oxidising agent is an acidified solution of sodium dichromate. For example:

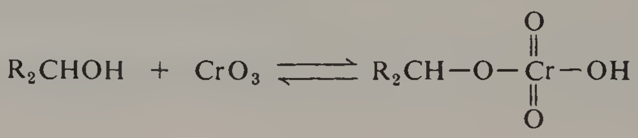
$$3CH_3CH_2OH + Na_2Cr_2O_7 + 4H_2SO_4 \rightarrow \underset{\text{Ethanal}}{3CH_3CHO} + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$3(CH_3)_2CHOH + Na_2Cr_2O_7 + 4H_2SO_4 \rightarrow \underset{\text{Propanone}}{3CH_3COCH_3} + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

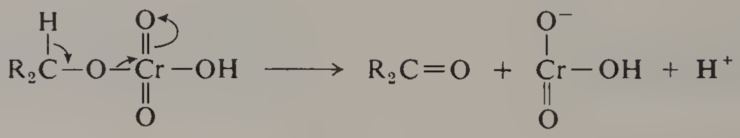
Sodium dichromate can be regarded as a solution of chromium(VI) oxide:

$$Na_2Cr_2O_7 + H_2O \rightleftharpoons 2CrO_3 + 2NaOH$$

Reaction with the alcohol occurs by formation of an unstable chromium(VI) ester which breaks down to give the carbonyl compound and a chromium(IV) ion:



$$R_2CHOH + CrO_3 \rightleftharpoons R_2CH{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}{-}OH$$



$$R_2\overset{\overset{\displaystyle H}{|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}{-}OH \longrightarrow R_2C{=}O + \overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}{-}OH + H^+$$

Three chromium(IV) ions disproportionate to give two chromium(III) ions and one chromium(VI) species:

$$3HCrO_3^- + 9H^+ \rightarrow CrO_3 + 2Cr^{3+} + 6H_2O$$

A difficulty arises in the preparation of aldehydes in this way: the aldehyde is itself readily oxidised (12.5). It is necessary to remove the aldehyde as soon as it is formed in order to prevent this happening, and this can readily be done because aldehydes have lower boiling points than the corresponding alcohols (whose boiling points are relatively high because of their hydrogen-bonded structure; 10.3). Thus, the alcohol is added slowly to the hot oxidising agent so that the aldehyde boils off as fast as it is formed whereas the higher boiling alcohol remains in solution until it is oxidised.

Details of the laboratory preparation of ethanal (p. 183) and propanone (p. 183) are given.

2. Aldehydes and ketones are formed by the hydrolysis of *gem*-dichlorides ($RCHCl_2$ and R_2CCl_2), for example:

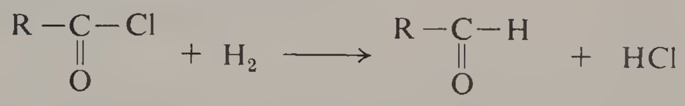
$$C_6H_5{-}CHCl_2 + H_2O \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5{-}CHO} + 2HCl$$

This method is of limited use for aliphatic compounds because of the difficulty of obtaining the dichloro-compounds; in fact, these compounds are usually made from the corresponding aldehyde or ketone with phosphorus pentachloride (12.5). However, the method is particularly useful for aromatic aldehydes because the dichloro-compounds can be obtained by the free-radical chlorination of the corresponding methyl compound (8.4), so that to obtain benzaldehyde, methylbenzene would be the starting material:

$$C_6H_5{-}CH_3 + 2Cl_2 \xrightarrow[\text{heat}]{\text{u.v. light}} C_6H_5{-}CHCl_2 + 2HCl$$

Specific method for aldehydes

Acid chlorides are reduced to aldehydes by hydrogen on palladium which is supported on barium sulphate:



$$R{-}\underset{\displaystyle\overset{\|}{O}}{C}{-}Cl + H_2 \longrightarrow R{-}\underset{\displaystyle\overset{\|}{O}}{C}{-}H + HCl$$

Sulphur and quinoline are added as a poison to prevent the reduction of the aldehyde to the primary alcohol.

Specific method for aromatic ketones

Many aromatic compounds react with acid chlorides in the presence of aluminium chloride to give aromatic ketones (Friedel-Crafts reaction; 8.3), for example:

$$C_6H_6 + CH_3{-}CO{-}Cl \xrightarrow{AlCl_3 \text{ as cat.}} \underset{\text{Phenylethanone}}{C_6H_5{-}CO{-}CH_3} + HCl$$

$$C_6H_6 + C_6H_5{-}CO{-}Cl \xrightarrow{AlCl_3 \text{ as cat.}} \underset{\text{Diphenylmethanone}}{C_6H_5{-}CO{-}C_6H_5} + HCl$$

Manufacture of ethanal

1. *Wacker process.* By oxidising ethene with palladium(II) chloride in water:

$$CH_2{=}CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + 2HCl + Pd$$

By carrying out the reaction in the presence of a copper(II) salt, the palladium which is formed is oxidised back to palladium(II) ion:

$$Pd + 2Cu^{2+} \rightarrow Pd^{2+} + 2Cu^{+}$$

In the presence of air, the copper(I) ion is oxidised back to copper(II) ion:

$$4Cu^{+} + O_2 + 4HCl \rightarrow 4Cu^{2+} + 2H_2O + 4Cl^{-}$$

Therefore, the reaction requires only catalytic amounts of palladium and copper salts, so that the principal cost is that of ethene. Since the Wacker process is essentially one-stage from ethene, and ethene is cheaper than ethyne, this process has superseded the two older routes, outlined below.

2. By passing ethyne through dilute sulphuric acid, with mercury(II) sulphate as catalyst, at 60°C:

$$CH{\equiv}CH + H_2O \xrightarrow{HgSO_4 \text{ as cat.}} CH_3{-}CHO$$

3. By oxidation of ethanol (which is manufactured from ethene) in the gas phase over a silver or a copper catalyst:

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \xrightarrow[500°C]{\text{Ag as cat.}} CH_3CHO + H_2O$$

$$CH_3CH_2OH \xrightarrow[500°C]{\text{Cu as cat.}} CH_3CHO + H_2$$

Manufacture of methanal

By the oxidation of methanol vapour over heated copper or silver:

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[500°C]{\text{Ag as cat.}} HCHO + H_2O$$

Manufacture of propanone

1. As a co-product from the Cumene process for the manufacture of phenol (10.8).
2. By passing the vapour of propan-2-ol over copper at 500°C. The alcohol is obtained from propene (10.4).

$$(CH_3)_2CHOH \xrightarrow[500°C]{\text{Cu as cat.}} (CH_3)_2CO + H_2$$

3. By oxidation of propan-2-ol in the liquid phase (20.4).
4. As a by-product in the manufacture of ethanoic acid from naphtha (13.4).

12.5
Chemical properties of aldehydes and ketones

The reactions can be divided into three types:

(a) Reactions of the carbonyl group.
(b) Reactions of the alkyl group(s) adjacent to the carbonyl group.
(c) Oxidation reactions. Reactions of this type constitute the principal difference between aldehydes and ketones.

Many of the reactions which follow are shown by all aldehydes and ketones, but some members of each series show exceptional behaviour which is mentioned below and also in a section on anomalous properties (p. 182).

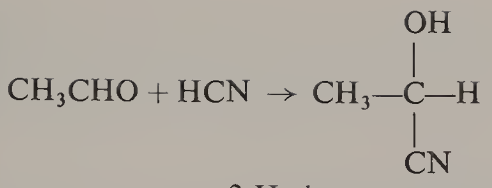
(a) Reactions of the carbonyl group

These can be subdivided into (i) **addition reactions** and (ii) **condensation reactions**.

(i) Addition reactions

Both aldehydes and ketones undergo addition reactions. The following are examples:

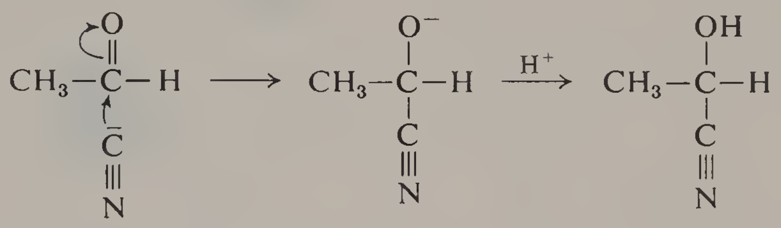
1. They react with hydrogen cyanide to form **2-hydroxynitriles (cyanohydrins)**, for example:



$$CH_3CHO + HCN \rightarrow CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}H$$

2-Hydroxypropanenitrile

These reactions occur very slowly, but their rates are greatly increased by the addition of some alkali. This is because the slow step is the addition of the cyanide ion to the carbonyl group; the resulting anion then takes up a proton, for example:



Thus, hydrogen cyanide itself adds slowly because, being a very weak acid ($K_a = 5 \times 10^{-10}$), its solution contains only a very small proportion of cyanide ions, whereas in the presence of alkali a much larger concentration of cyanide ions is present since the equilibrium,

$$HCN + OH^- \rightleftharpoons CN^- + H_2O$$

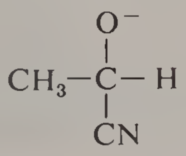
lies to the right.

In practice, in the laboratory, it is more convenient, and safer, to replace hydrogen cyanide and alkali by an alkali-metal cyanide like KCN (whose solution contains a high proportion of cyanide ions) and acid; but too much acid must be avoided for otherwise the concentration of cyanide ion is reduced to so low a level that the rate of reaction is again too slow for practical purposes.

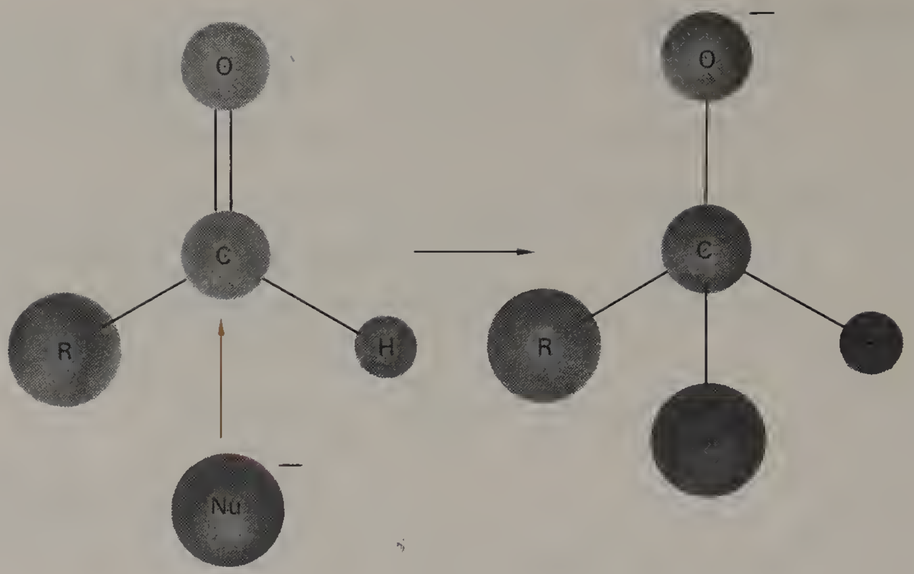
It was the observation that alkali catalyses the addition of hydrogen cyanide to carbonyl compounds that led to the reaction mechanism described above. This was the first organic mechanism to be elucidated, in 1902. The carbonyl compound chosen for study was a coloured one which gave a colourless addition product so that it was possible to assess the rate, roughly, by following the loss of colour by eye. It was found that reaction between the ketone and hydrogen cyanide alone took 8–10 hours to go to completion, and when some mineral acid was added there was no detectable reaction even after 14 days; but the addition of a drop of an aqueous solution of potassium hydroxide caused the reaction to go to completion in a matter of seconds.

The mechanism of formation of cyanohydrins is typical of all nucleophilic additions to aldehydes and ketones: that is, reaction occurs by addition of a nucleophile to form an anion (Fig. 12.1) followed by uptake of a proton.

An understanding of the mechanism enables us to understand why the double bond in an aldehyde or ketone is reactive towards nucleophilic reagents whereas that in an alkene is not. In the anion formed by addition to a carbonyl group, the negative charge resides on oxygen:



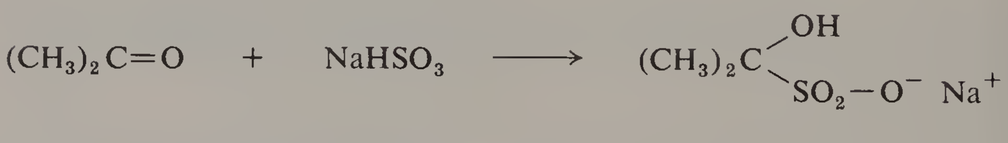
$$CH_3{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}H$$



However, if a nucleophile adds to an alkene, the negative charge resides on carbon; since carbon is much less strongly electron-attracting than oxygen, this species is less stable and less readily formed.

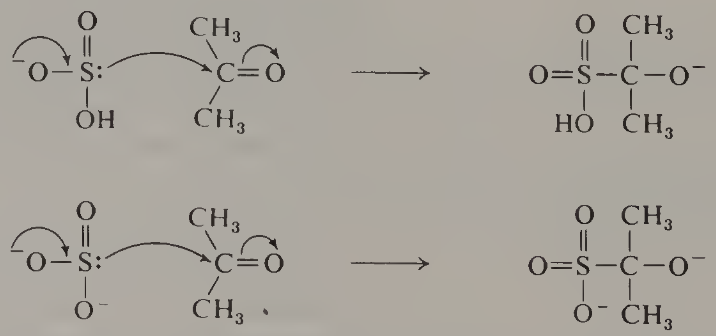
Aromatic aldehydes, such as benzaldehyde, react with potassium cyanide in a different manner from other aldehydes or ketones (p. 183).

2. Aldehydes and ketones react with sodium hydrogensulphite to form addition compounds, for example:



$$(CH_3)_2C{=}O \quad + \quad NaHSO_3 \longrightarrow (CH_3)_2C\begin{matrix}\diagup OH \\ \diagdown SO_2{-}O^- \ Na^+\end{matrix}$$

In this reaction, both the hydrogensulphite and the sulphite ions act as nucleophilic reagents:



The sulphite ion reacts the more rapidly, but hydrogensulphite ion is a weak acid ($K_a = 1{\cdot}1 \times 10^{-7}$), so that the equilibrium

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$$

lies well to the left and under the usual reaction conditions $[HSO_3^-]$ is much greater than $[SO_3^{2-}]$, serving to offset to some extent the greater reactivity of the sulphite ion. Which of the two ions makes the more important contribution to the overall reaction depends on a variety of factors, including the structure of the carbonyl compound and the pH.

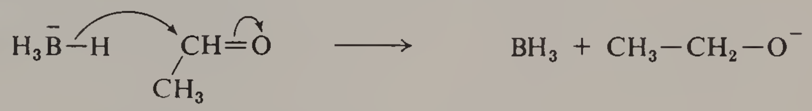
Ketones only undergo this reaction if at least one of the two groups attached to the carbonyl group is methyl. The probable reason is that methyl is the smallest group, and when two larger groups are attached, their size hinders the approach of the nucleophilic reagent to the carbonyl group.

3. Aldehydes and ketones are reduced to **alcohols** by treatment with sodium tetrahydridoborate in water. Aldehydes give primary alcohols and ketones give secondary alcohols, for example:

$$4CH_3{-}CH{=}O + NaBH_4 \rightarrow (CH_3{-}CH_2{-}O)_4B^-Na^+$$

$$(CH_3{-}CH_2{-}O)_4B^-Na^+ + 3H_2O \rightarrow 4CH_3{-}CH_2{-}OH + NaH_2BO_3$$

The reducing agent is the tetrahydridoborate anion, BH_4^-. It acts as a nucleophile by transferring a hydride ion to the carbonyl group:



$$H_3\bar{B}{-}H \quad \underset{CH_3}{CH}{=}O \longrightarrow BH_3 + CH_3{-}CH_2{-}O^-$$

The species BH_3 immediately reacts with the alkoxide ion,

$$CH_3{-}CH_2{-}O^- + BH_3 \rightarrow CH_3{-}CH_2{-}O{-}\bar{B}H_3$$

and the resulting anion then reduces another carbonyl group. Further reactions of this type occur until all four hydrogens of the BH_4^- anion have been replaced.

Lithium tetrahydridoaluminate, $LiAlH_4$, can be used in place of sodium tetrahydridoborate. It is a much more powerful reducing agent and reacts violently with water, so that it is necessary to use an inert solvent such as ether. The product of the reaction is a salt of the alcohol, $(R_2CHO)_4Al^-Li^+$; excess of $LiAlH_4$ is destroyed by adding ethyl ethanoate (which acts by being reduced to ethanol), and the alcohol is then liberated from the salt by addition of dilute sulphuric acid:

$$4R_2CO + LiAlH_4 \rightarrow (R_2CHO)_4Al^-Li^+$$

$$2(R_2CHO)_4Al^-Li^+ + 4H_2SO_4 \rightarrow 8R_2CHOH + Al_2(SO_4)_3 + Li_2SO_4$$

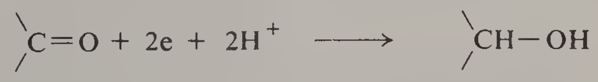
The aldehyde or ketone reacts with the tetrahydridoaluminate anion, AlH_4^-, in a similar way to the tetrahydridoborate anion.

4. Aldehydes and ketones are also reduced with sodium amalgam and water, with sodium and ethanol or with zinc and ethanoic acid, for example:

$$C_2H_5CH{=}O + 2Na + 2C_2H_5OH \rightarrow C_2H_5CH_2OH + 2C_2H_5O^-Na^+$$

$$(CH_3)_2C{=}O + Zn + 2CH_3CO_2H \rightarrow (CH_3)_2CHOH + (CH_3CO_2)_2Zn$$

These reactions do not occur by nucleophilic attack but by the transfer of electrons from the electropositive metal to the carbonyl group and the uptake of two protons from the water, ethanol, or acid; a simple representation is:



$$>C{=}O + 2e + 2H^+ \longrightarrow\ >CH{-}OH$$

Sodium provides one electron, so that two atoms of sodium per molecule of carbonyl compound are required, whereas one atom of zinc, which can provide two electrons (giving Zn^{2+}), reduces one molecule of carbonyl compound.

5. Aldehydes and ketones react with phosphorus pentachloride to give **gem-dichloro compounds**, for example:

$$\mathrm{CH_3{-}CH{=}O + PCl_5 \rightarrow \underset{\text{1,1-Dichloroethane}}{CH_3{-}CHCl_2} + POCl_3}$$

$$\mathrm{CH_3{-}CO{-}CH_3 + PCl_5 \rightarrow \underset{\text{2,2-Dichloropropane}}{CH_3{-}CCl_2{-}CH_3} + POCl_3}$$

(ii) Condensation reactions

Aldehydes and ketones react with compounds which contain the $-NH_2$ group with the elimination of water.

Hydroxylamine forms **oximes**, for example:

$$\mathrm{CH_3CH{=}O + NH_2OH \rightarrow \underset{\text{Ethanal oxime}}{CH_3CH{=}N{-}OH} + H_2O}$$

$$\mathrm{(CH_3)_2C{=}O + NH_2OH \rightarrow \underset{\text{Propanone oxime}}{(CH_3)_2C{=}N{-}OH} + H_2O}$$

Hydrazine forms **hydrazones** which, since they still contain an $-NH_2$ group, can react with more of the carbonyl compound to give **azines**, for example:

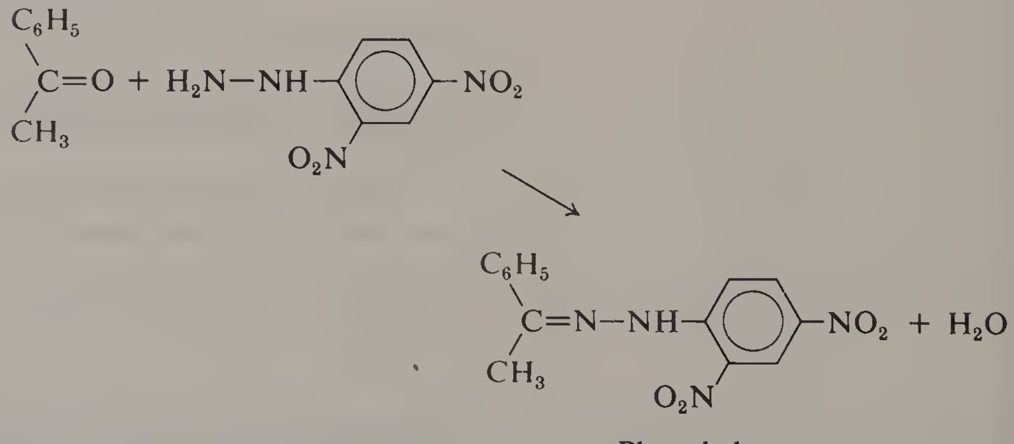
$$\mathrm{CH_3CH{=}O + NH_2NH_2 \rightarrow CH_3CH{=}N{-}NH_2 + H_2O}$$

$$\mathrm{CH_3CH{=}N{-}NH_2 + CH_3CH{=}O \rightarrow CH_3CH{=}N{-}N{=}CHCH_3 + H_2O}$$

Phenylhydrazine forms **phenylhydrazones**, for example:

$$\mathrm{C_6H_5CH{=}O + \underset{\text{Phenylhydrazine}}{H_2N{-}NH{-}C_6H_5} \rightarrow \underset{\substack{\text{Benzaldehyde}\\ \text{phenylhydrazone}}}{C_6H_5CH{=}N{-}NH{-}C_6H_5} + H_2O}$$

2,4-Dinitrophenylhydrazine forms **2,4-dinitrophenylhydrazones**, for example:



Phenylethanone
2,4-dinitrophenylhydrazone

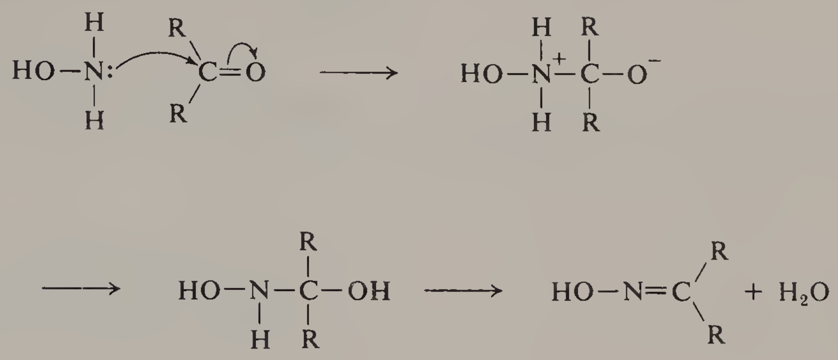
Primary amines form **imines** (also called Schiff bases), for example:

$$\mathrm{C_6H_5CH{=}O + H_2N{-}C_6H_5 \rightarrow C_6H_5CH{=}N{-}C_6H_5 + H_2O}$$

However, many of the derivatives with amines are unstable.

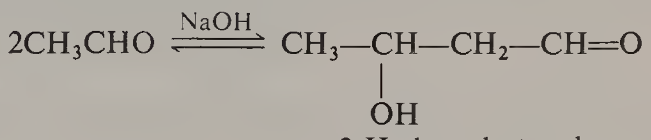
The reactions with hydroxylamine, phenylhydrazine and 2,4-dinitrophenylhydrazine are used for the characterisation of aldehydes and ketones because the products are mostly crystalline solids and the melting points of the derivatives from closely similar aldehydes or ketones are usually sufficiently different to enable the carbonyl compound to be recognised.

The reactions all occur by nucleophilic addition to the carbonyl group followed by the movement of a proton from one atom to another and then the elimination of water, for example:



(b) Reactions of the akyl group(s)

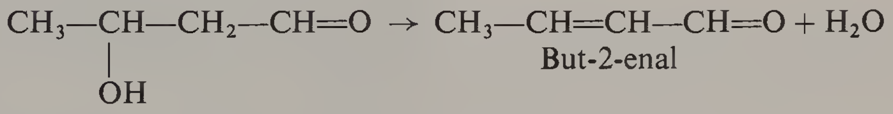
1. Aldehydes and ketones which possess at least one hydrogen atom on the carbon atom adjacent to the carbonyl group (i.e. >CH—CO—, etc.) undergo condensation reactions in the presence of a base. For example, ethanal and dilute alkali give 3-hydroxybutanal:



$$2CH_3CHO \underset{}{\overset{NaOH}{\rightleftharpoons}} \underset{\displaystyle OH}{CH_3—\underset{|}{C}H}—CH_2—CH{=}O$$

3-Hydroxybutanal

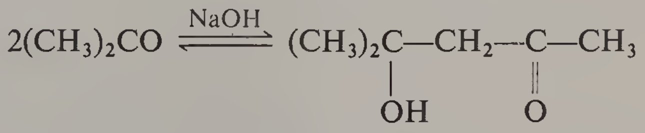
If the solution is warmed, water is eliminated:



$$\underset{\displaystyle OH}{CH_3—\underset{|}{C}H}—CH_2—CH{=}O \rightarrow CH_3—CH{=}CH—CH{=}O + H_2O$$

But-2-enal

Propanone gives 4-hydroxy-4-methylpentan-2-one:



$$2(CH_3)_2CO \overset{NaOH}{\rightleftharpoons} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}—CH_2—\underset{\displaystyle O}{\underset{\|}{C}}—CH_3$$

With concentrated alkali, ethanal forms a resin which precipitates from the solution. It is a polymeric compound of structure

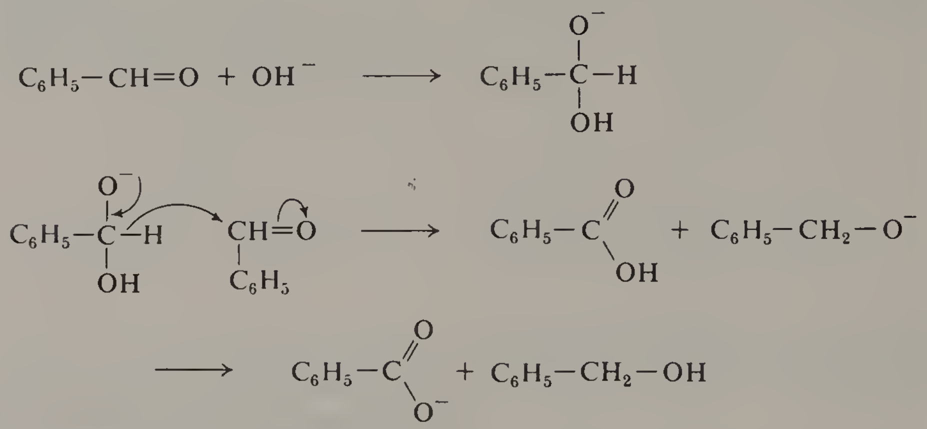
$$CH_3\text{+}CH{=}CH\text{)}_xCH{=}O$$

where x is large and varies with the conditions of the reaction.

However, those aldehydes which do not contain at least one hydrogen atom on the carbon next to the carbonyl group (e.g. methanal and benzaldehyde) do not undergo condensation reactions with alkali (see above) but instead, with concentrated alkali, undergo the **Cannizzaro reaction** in which one half of the quantity of the aldehyde is oxidised and the other half is reduced, for example:

$$2C_6H_5{-}CH{=}O + NaOH \rightarrow \underset{\text{Sodium benzoate}}{C_6H_5{-}CO_2^-Na^+} + \underset{\text{Phenylmethanol}}{C_6H_5{-}CH_2OH}$$

Reaction occurs by addition of hydroxide ion to the carbonyl group of one molecule of the aldehyde, to give an intermediate which transfers a hydride ion to a second molecule of the aldehyde. Reaction is completed by transference of a proton:



2. Aldehydes and ketones which possess at least one hydrogen atom on the carbon atom adjacent to the carbonyl group react with the halogens in the presence of dilute acid or alkali; one or more of these hydrogen atoms is replaced by halogen atoms. In the acid-catalysed reaction, it is possible to isolate the monohalogenated product, since introduction of a second halogen atom occurs more slowly than that of the first, for example:

$$CH_3{-}CH_2{-}CO{-}CH_2{-}CH_3 + I_2 \xrightarrow{H^+} CH_3{-}CHI{-}CO{-}CH_2{-}CH_3 + HI$$

However, in the base-catalysed reaction, the reaction rate increases as each halogen atom is introduced, so that it is possible to isolate only the product in which all the appropriate hydrogen atoms have been replaced, for example:

$$CH_3{-}CH_2{-}CO{-}CH_2{-}CH_3 + 4I_2 \xrightarrow{OH^-} CH_3{-}CI_2{-}CO{-}CI_2{-}CH_3 + 4HI$$

If the carbonyl compound contains the group $-CO-CH_3$ (i.e. ethanal or a methyl ketone), reaction in the presence of alkali leads first to the replacement of all three hydrogen atoms in the methyl group by halogen atoms, for example,

$$CH_3{-}CH_2{-}CO{-}CH_3 + 3Cl_2 + 3NaOH \rightarrow CH_3{-}CH_2{-}CO{-}CCl_3 + 3H_2O + 3NaCl$$

and then, with excess of alkali, to breakage of a C—C bond:

$$CH_3{-}CH_2{-}CO{-}CCl_3 + NaOH \rightarrow CH_3{-}CH_2{-}CO_2^-\,Na^+ + \underset{\text{Trichloromethane}}{CHCl_3}$$

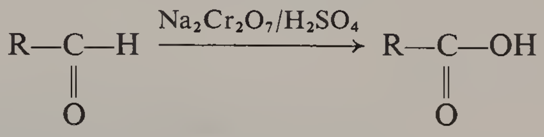
Similarly, bromine gives tribromomethane, $CHBr_3$, and iodine gives tri-iodomethane, CHI_3. Tri-iodomethane is a yellow crystalline solid which is easily recognised, and its formation from a carbonyl compound indicates that this must have been either ethanal or a methyl ketone, since no others contain the group $—CO—CH_3$. This reaction is known as the **iodoform test**, after the original name for tri-iodomethane. Since alcohols which contain the group $—CH(OH)—CH_3$ (e.g. ethanol and propan-2-ol) are oxidised by iodine to give the group $—CO—CH_3$, these also give a positive iodoform test (p. 150).

(c) Oxidation reactions

The principal difference between an aldehyde and a ketone is that the $—CH{=}O$ group of an aldehyde is readily oxidised to the carboxylic acid group, $—CO_2H$, whereas ketones are difficult to oxidise in solution.

Oxidation of aldehydes

Aldehydes are oxidised to carboxylic acids by sodium (or potassium) dichromate in acidic solution:



$$R—\underset{\underset{O}{\|}}{C}—H \xrightarrow{Na_2Cr_2O_7/H_2SO_4} R—\underset{\underset{O}{\|}}{C}—OH$$

Likewise, they are oxidised by potassium manganate(VII).

The ready oxidation of aldehydes compared with ketones enables the two types of carbonyl compound to be simply distinguished. Three reactions for this purpose (details for two of which are on p. 185) are:

1. A solution of silver nitrate in an excess of a solution of ammonia, which contains the complex ion, $Ag(NH_3)_2{}^+$, is reduced by an aldehyde to silver, which deposits on the wall of a test-tube as an easily recognised mirror.

2. Fehling's solution, which is made by mixing a solution of copper(II) sulphate with an alkaline solution of a salt of 2,3-dihydroxybutanoic (tartaric) acid and which contains a deep-blue complexed copper(II) ion, is reduced by an aldehyde to copper(I) oxide, which deposits as a red precipitate.

However, some aldehydes, such as benzaldehyde, do not react in this way, so that a negative result must be interpreted with care.

3. Fuchsin is a pink dye which forms a colourless complex when treated with sulphur dioxide. The addition of an aldehyde to this colourless solution restores the pink colour of the dye (Schiff's test).

Oxidation of ketones

Ketones are oxidised by strong oxidising agents, such as alkaline potassium manganate(VII) and hot nitric acid. The bond between the carbonyl group and the adjacent carbon atom is broken, for example:

$$CH_3—CH_2—CO—CH_2—CH_3 \xrightarrow{HNO_3} CH_3—CH_2—CO_2H + CH_3—CO_2H$$

The acids formed contain *fewer* carbon atoms than the ketone. The acid formed on oxidation of an aldehyde contains the *same* number of carbon atoms.

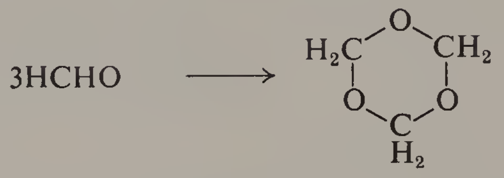
Specific reactions of aldehydes and ketones

Methanal, $HCHO$, differs from other aldehydes in the following ways:

1. When an aqueous solution of methanal is gently evaporated, a linear polymer, polymethanal, is formed. Polymethanal has the structure

$$HO\left(CH_2-O\right)_x CH_2OH$$

When it is distilled from an acidified solution, methanal forms the cyclic trimer:

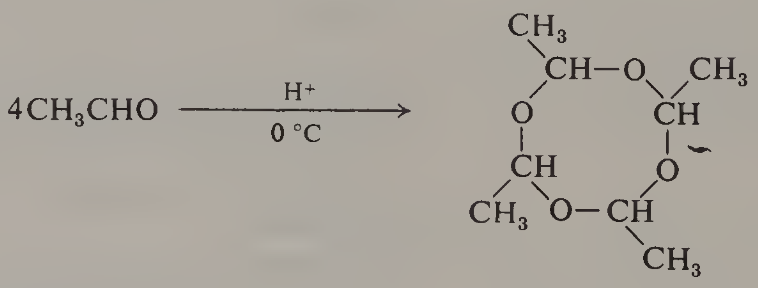


2. It does not undergo a condensation reaction of the type ethanal undergoes when treated with alkali, but with concentrated alkali it undergoes the Cannizzaro reaction:

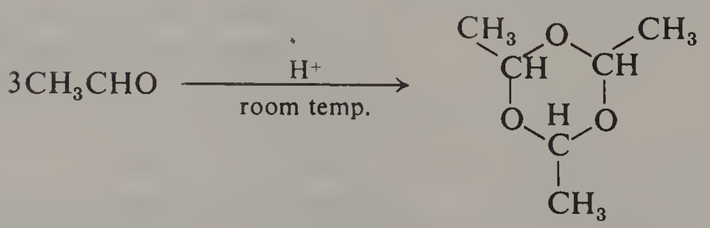
$$2HCHO + NaOH \rightarrow H-CO_2^-Na^+ + CH_3OH$$

This behaviour of methanal is typical of that of aldehydes which do not have a hydrogen atom attached to the carbon atom next to the carbonyl group.

Ethanal, CH_3CHO, forms cyclic polymers with acids:



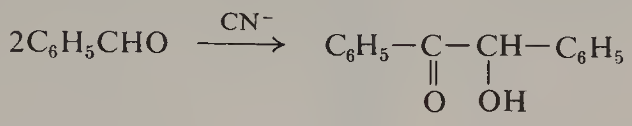
Ethanal tetramer



Ethanal trimer

Benzaldehyde, C_6H_5CHO, does not reduce Fehling's solution or undergo condensations with alkali, but it undergoes the Cannizzaro reaction. In these respects it is typical of aldehydes which do not have a C—H bond adjacent to carbonyl.

Benzaldehyde is peculiar in not giving a cyanohydrin with potassium cyanide. Instead, it undergoes a condensation reaction to form 2-hydroxy-1,2-diphenylethanone, in which cyanide ion acts as a catalyst:



$$2C_6H_5CHO \xrightarrow{CN^-} C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-C_6H_5$$

2-Hydroxy-1,2-diphenylethanone

12.6 Uses of aldehydes and ketones

Methanal

1. In the manufacture of thermosetting plastics, in particular Bakelite, carbamide-methanal resins and polyoxymethylene (p. 332, 333).
2. In solution (formalin) it is used as a disinfectant and to preserve animal specimens.

Ethanal

In the manufacture of ethanoic acid (p. 191).

However, ethene (from which ethanal is made) is becoming progressively more expensive relative to the starting materials for other routes to ethanoic acid (p. 191), and these are now displacing the route *via* ethanal.

Propanone

1. In the manufacture of Perspex (p. 331).
2. In the manufacture of ethenone, used to make ethanoic anhydride (14.4).
3. As a solvent for plastics, varnishes and greases.

12.7 Practical work

Small-scale preparation of ethanal

To 6 cm^3 of water in a flask, add 2 cm^3 of *concentrated* sulphuric acid, and set up the apparatus as shown in Figure 12.2.

Make up a solution containing 5 g of sodium dichromate in 5 cm^3 of water, add 4 cm^3 of ethanol and pour the solution into the dropping funnel.

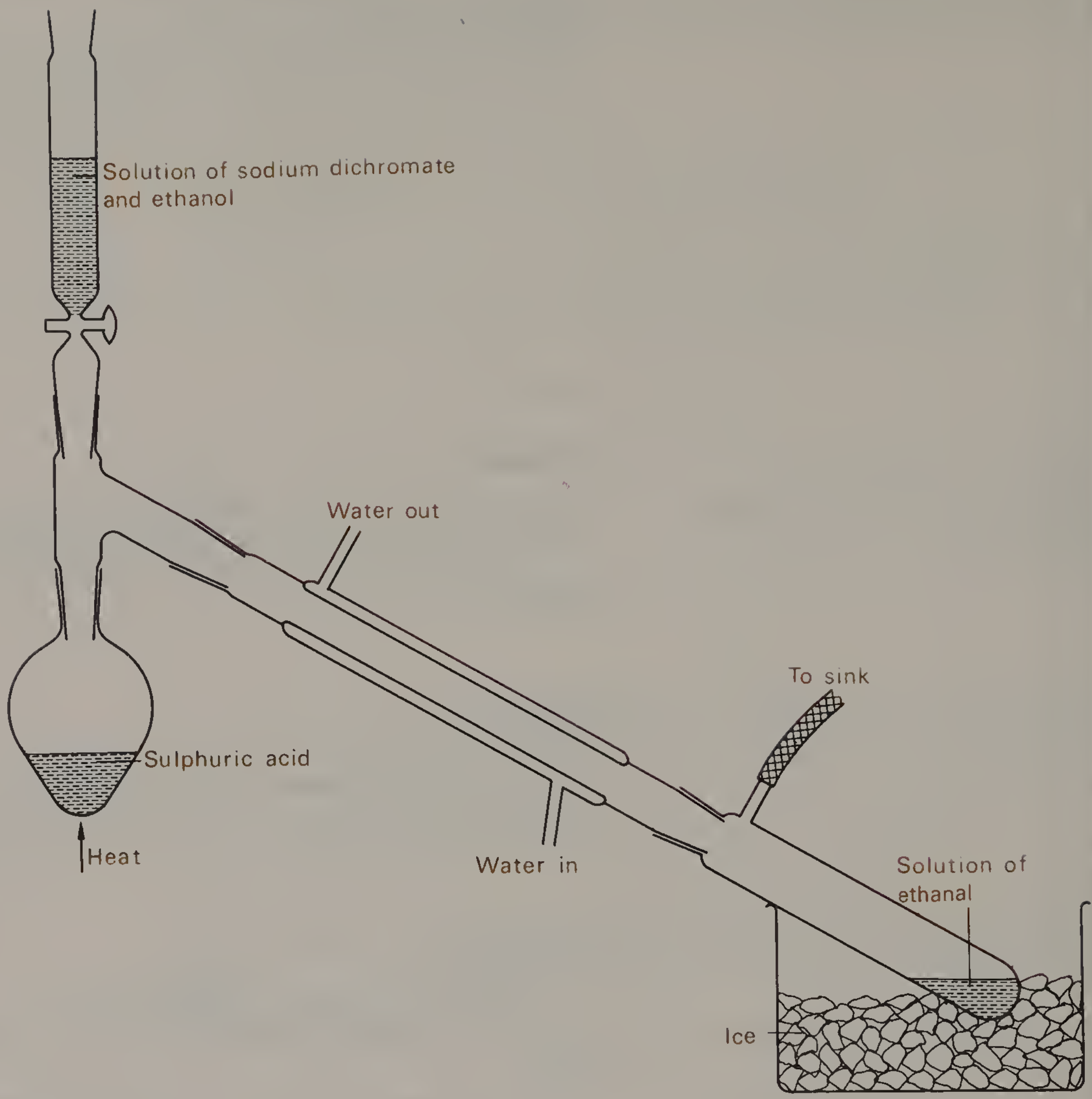
Boil the acid in the flask and then turn out the bunsen flame. Add the mixture containing ethanol slowly so that the dilute acid remains near its boiling point.

Collect the distillate and redistil (Fig. 2.2), using a hot-water bath. Collect the fraction boiling between 20 and 23°C.

Small-scale preparation of propanone

Repeat the experiment above, using 4 cm^3 of propan-2-ol in place of 4 cm^3 of ethanol. Collect the distillate and redistil it, collecting the fraction boiling between 54 and 57°C.

FIG. 12.2. *Preparation of ethanal*



Reactions of methanal, ethanal, benzaldehyde propanone, pentan-3-one and phenylethanone

(a) Reactions of the carbonyl group

Addition reactions

1. *Preparation of ethanal hydrogensulphite.* Make up 10 cm^3 of a saturated solution of sodium metabisulphite, in a flask, and pass sulphur dioxide through it for about 3 minutes. Add 1 cm^3 of ethanal, shake, stopper the flask and leave for 1–2 hours. Crystals of the addition product, ethanal hydrogensulphite, are formed.

The experiment can be repeated with other aldehydes and ketones, for example with propanone (1 cm^3) or benzaldehyde (1 cm^3), instead of ethanal.

Condensation reactions

2. To 5 drops of one of the aldehydes or ketones in a test-tube, add methanol until the compound just dissolves. Add 5 cm^3 of the solution of 2,4-dinitrophenylhydrazine (see Appendix III, p. 374, for the preparation

of this solution). Cork the test-tube and shake the mixture. Allow it to stand. If a precipitate is not formed within 5 minutes, add dilute sulphuric acid dropwise.

Filter the precipitate using a small Buchner funnel and flask and wash it with a minimum amount of methanol. Transfer the precipitate to a filter paper and squeeze it between two papers to dry it. Recrystallise the solid from the minimum quantity of a (1 : 1) mixture of ethanol and water. Filter, dry the crystals and obtain the melting point (p. 379).

(b) Reactions of the alkyl group

3. To 3 drops of ethanal in a test-tube, cautiously add concentrated sodium hydroxide solution drop by drop. A brown resin is formed with a characteristic smell.

4. To 5 drops of propanone, add 10 drops of iodine solution and 10 drops of 2M hydrochloric acid. Warm the mixture gently.

Repeat the experiment with pentan-3-one.

5. *The iodoform reaction.* In four separate test-tubes, add 5 drops of (i) ethanal, (ii) propanone, (iii) benzaldehyde and (iv) phenylethanone, followed by 10 drops of iodine solution in each (Appendix II). Add dilute sodium hydroxide solution dropwise until the brown colour just disappears.

Observe what happens (a) in the cold, (b) when the mixtures are gently warmed.

(c) Oxidation reactions

6. *Silver mirror test.* Clean 3 test-tubes by washing them thoroughly with distilled water and then with propanone and drying them.

To 3 cm^3 of a solution of silver nitrate, add 1 drop of a dilute solution of sodium hydroxide. Add dilute ammonia solution dropwise until the brown precipitate of silver oxide just redissolves. Divide this solution into three test-tubes.

To one of the test-tubes, add 3 drops of ethanal, to the second 3 drops of propanone and to the third 3 drops of benzaldehyde.

Warm the test-tubes in a beaker of boiling water for about 5 minutes.

7. *Fehling's test.* Make up some Fehling's solution by adding solution II (an alkaline solution of sodium potassium 2,3-dihydroxybutanedioate) to 5 cm^3 of solution I (a solution of copper(II) sulphate) until a deep blue solution is formed (Appendix III). Divide the solution equally between 3 test-tubes.

To one, add 3 drops of ethanal, to the second, 3 drops of propanone and to the other, 3 drops of phenylethanone. Boil the mixtures for a few minutes.

8. *Reaction with potassium manganate(VII).* To 10 cm^3 of dilute sulphuric acid in a test-tube, add 2 cm^3 of a 1 per cent solution of potassium manganate(VII) and divide the solution between 5 test-tubes. Add 3 drops of the following to the test-tubes: (i) methanal, (ii) ethanal, (iii) propanone, (iv) benzaldehyde, (v) phenylethanone. At first shake the mixtures without warming, then warm them very gently.

In particular, contrast the behaviour of (a) ethanal and propanone, (b) propanone and phenylethanone.

(d) Specific reactions of some aldehydes and ketones

9. Pour 1–2 cm^3 of methanal solution (formalin) on a watch-glass, and place it on a beaker containing water that is boiling gently.

10. Pour 1–2 cm^3 of ethanal into a test-tube and place the tube in a beaker containing an ice-salt freezing mixture. Add two drops of concentrated sulphuric acid and stir the mixture gently. Observe whether there is a rise in temperature (why?) and whether a new compound is formed.

11. *The Cannizzaro Reaction.* To a cool solution of potassium hydroxide (5 g in 5 cm^3 of water) in a boiling tube, add about 5 cm^3 of benzaldehyde. Cork the boiling tube, shake and allow it to stand overnight. Add about 20 cm^3 of water to dissolve the potassium benzoate, and extract the aqueous layer with ether. To the aqueous portion, add dilute hydrochloric acid to precipitate benzoic acid. Filter and recrystallise from hot water (m.p. 121°C). Dry the ethereal extract over solid potassium carbonate. Fractionate the dry extract and collect phenylmethanol (b.p. 204–207°C). Benzaldehyde does not form a resin (cf. reaction 3 with ethanal).

(e) To identify an aldehyde or ketone

12. You are given a compound which is either an aldehyde or ketone.

(i) Test the compound with Fehling's solution (reaction 7) to see whether it is either an aldehyde or ketone.

(ii) Prepare a solid derivative of the compound, the 2,4-dinitrophenylhydrazone (reaction 2), and determine its melting point. A list of melting points of 2,4-dinitrophenylhydrazones is given in Appendix VI (p. 379).

12.8 Questions

1 Give the structural formulae of the compounds obtained when propanone reacts with

(a) hydroxylamine,
(b) sodium hydrogensulphite,
(c) concentrated sulphuric acid,
(d) lithium tetrahydridoaluminate.

2 To a solution of propanone (*y* g) in water was added an excess of bromine water followed by sodium hydroxide solution. The tribromomethane, $CHBr_3$, obtained weighed 4·365 g. Calculate the value of *y*. (O and C)

3 (a) State the conditions, name the organic product and write its structural formula, for the reactions of each of ethanal and propanone with:
(i) sodium tetrahydridoborate(III),
(ii) 2,4-dinitrophenylhydrazine.
(b) Describe one simple reaction to distinguish between the members of each of the following pairs of compounds.
(i) Ethanal and benzaldehyde.
(ii) Propanone and phenylethanone (phenyl methyl ketone).
(iii) Aqueous solutions of ethanal and methanal.
State what is observed for *both* compounds in each pair. (AEB)

4 What do you understand by (a) *homologous series*, (b) *isomerism*?

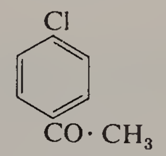
Give the full structural formulae for (i) **all** compounds having the molecular formula $C_4H_{10}O$, (ii) **two** compounds having the molecular formula C_3H_6O. Name **four** of the compounds in (i) and describe two experimental methods by which you could distinguish between the two compounds in (ii). (C(N, T))

5 Compare the reactions of ethanal, benzaldehyde and propanone with (a) hydrogen cyanide, HCN, (b) aqueous sodium hydroxide, (c) concentrated hydrochloric acid, (d) ammoniacal silver nitrate, (e) phenylhydrazine, $C_6H_5NHNH_2$. (O)

6 Outline the preparation of propanone starting from ethanol.
Write the structural formulae of all compounds with the general formula $C_4H_{10}O$. Indicate which of these compounds give the iodoform reaction.
How is the iodoform test performed? (C(N))

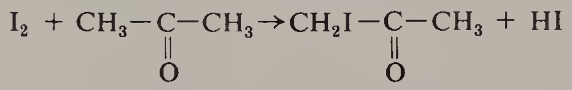
7 (a) Illustrate the similarities and differences in the chemical properties of aldehydes and ketones by considering the reactions of ethanal and propanone with:
   (i) hydrogen cyanide in the presence of a trace of potassium cyanide;
   (ii) potassium manganate(VII);
   (iii) sodium tetrahydridoborate, $NaBH_4$;
   (iv) ammoniacal silver oxide.
(b) Name **one** naturally-occurring compound containing both aldehyde and hydroxyl groups.
(c) Describe what is meant by an *addition-elimination* reaction, using a reaction of ethanal as your example.
(d) Explain why ethanal reacts with hydrogen cyanide but ethanoic acid does not. (O)

8 Describe analytical and synthetic methods you would employ to establish that the product of a reaction possessed the structural formula:



(W(S))

9 Propanone reacts with iodine in aqueous solution according to the following reaction, which is catalysed by H^+:

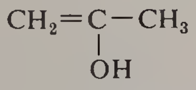


$$I_2 + CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 \rightarrow CH_2I-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + HI$$

In three experiments the rate of the reaction was studied in aqueous acidic solutions using concentrations of propanone much larger than that of the iodine. The results are given below:

	Initial concentrations		$[I_2]$ in *millimoles* per dm³ at time *t* in minutes					
	[Propanone]	$[H^+]$	0	5	9	12	14	15
Exp. 1	1·00 M	0·100 M	2·50	1·65	0·97	0·46	0·12	0
Exp. 2	1·00 M	0·150 M	3·20	1·93	0·90	0·14	0	0
Exp. 3	2·00 M	0·100 M	6·00	4·30	2·94	1·92	1·24	0·90

Plot the concentrations of iodine against time.
How does the reaction rate depend on the concentrations of the various species? Can you express all the data with one rate expression containing only one rate constant?
Given that



$$CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$$

is an intermediate in the reaction, devise a mechanism which will explain the data. (O Schol.)

10 (a) Name **two** reagents which will add to alkenes and **two** which will add to aldehydes. Write an equation for each reaction.
(b) Compare the electronic structure of ethene (ethylene) with that of methanal (formaldehyde).
(c) Make a mechanistic comparison between the addition reactions of alkenes and the addition reactions of aldehydes, illustrating your answer with suitable reactions. (O and C)

11 Discuss the chemistry of phenylethanone, $C_6H_5COCH_3$, by considering the following:

(a) a method of synthesis,

(b) addition and addition-elimination reactions of the carbonyl group,

(c) a method of preparing benzenecarboxylic (*benzoic*) acid from phenylethanone. (JMB)

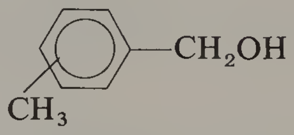
12 Three different compounds, each of molecular formula C_8H_8O, give yellow precipitates with 2,4-dinitrophenylhydrazine and are reduced to compounds of formula $C_8H_{10}O$ by lithium tetrahydridoaluminate ($LiAlH_4$). Given that these compounds do not differ merely by substituent orientation around a ring, suggest structures for each one.

How, using chemical tests, would you decide which compound is which?

Suggest how the following compounds could be synthesised, assuming all three of the above compounds are available as the only organic starting materials.

(a) benzoic acid

(b) one of the isomeric methylphenylmethanols



(c) $C_6H_5CH_2CH(OH)CH(C_6H_5)CHO$. (O and C)

Chapter 13

Carboxylic acids

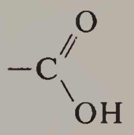
13.1

Introduction

General formula

$$R{-}CO_2H$$

Carboxylic acids contain the **carboxyl group**



which is a combination of the **carb**onyl group, $>C{=}O$, and the hydro**xyl** group, —OH. It will be seen that the properties of each group separately are modified when they are combined.

There are compounds with one carboxylic acid group (monocarboxylic acids), two (dicarboxylic acids) and more than two.

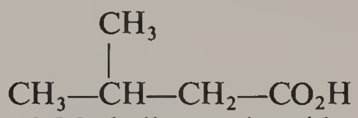
13.2

Nomenclature of monocarboxylic acids

Monocarboxylic acids are named, according to the I.U.P.A.C. system, by replacing the final **e** of the corresponding hydrocarbon by **oic acid**, for example:

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CO_2H$$

Pentanoic acid



$$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CO_2H$$

3-Methylbutanoic acid

The two lowest members, methanoic and ethanoic acid, are often known by their original names: formic acid and acetic acid.

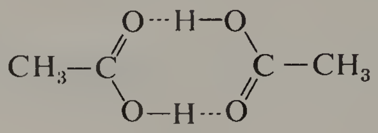
Table 13.1. Some monocarboxylic acids

NAME	FORMULA	M.P./°C	B.P./°C
Methanoic acid	$H{-}CO_2H$	8	101
Ethanoic acid	$CH_3{-}CO_2H$	17	118
Propanoic acid	$CH_3CH_2{-}CO_2H$	–22	141
Butanoic acid	$CH_3CH_2CH_2{-}CO_2H$	–5	163
2-Methyl-propanoic acid	$(CH_3)_2CH{-}CO_2H$	–47	154
Benzoic acid	$C_6H_5{-}CO_2H$	121	

13.3
Physical properties of monocarboxylic acids

The lowest members are liquids with pungent odours. Ethanoic acid smells of vinegar, and the higher acids smell of rancid butter, which is partly butanoic acid. Methanoic acid and ethanoic acid are miscible with water, but as the formula weight increases the solubility decreases.

The formula weight of lower members of the series as determined by, for example, the depression of freezing point of a solvent such as benzene is about twice that expected for the molecular formula $R{-}CO_2H$. This is because carboxylic acids exist as dimers: pairs of molecules are linked by two hydrogen bonds, for example:



A further consequence of this is that the boiling points of carboxylic acids are much higher than those of alkanes of similar formula weight, since more energy is required in order to break the hydrogen bonds in the vaporisation of carboxylic acids; for example, ethanoic acid (formula weight, 60) boils at 118°C whereas butane (formula weight, 58) boils at −0·5°C.

13.4
Methods of preparation of monocarboxylic acids

General methods

1. By the oxidation of primary alcohols and aldehydes with acidified sodium dichromate solution (10.5, 12.5):

$$R{-}CH_2OH \xrightarrow{Na_2Cr_2O_7} R{-}CHO \xrightarrow{Na_2Cr_2O_7} R{-}CO_2H$$

2. By the hydrolysis, with dilute mineral acid or alkali, of acid nitriles (14.6) and acid amides (14.5):

$$R{-}CN + H_2O \xrightarrow{H^+ \text{ or } OH^-} R{-}CONH_2$$

$$R{-}CONH_2 + H_2O \xrightarrow{H^+ \text{ or } OH^-} R{-}CO_2^-\ NH_4^+$$

$$\begin{tikzcd}
 & R{-}CO_2^-\ Na^+ + H_2O + NH_3 \\
R{-}CO_2^-\ NH_4^+ \arrow[ur, "NaOH"] \arrow[dr, "HCl"'] & \\
 & R{-}CO_2H + NH_4Cl
\end{tikzcd}$$

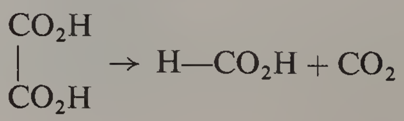
3. By the reaction of carbon dioxide with a Grignard reagent followed by hydrolysis (9.8):

$$R{-}MgX + CO_2 \rightarrow R{-}CO{-}O{-}MgX \xrightarrow{H_2O} R{-}CO_2H + Mg(OH)X$$

Details of the preparation of benzoic acid from phenylmagnesium bromide are given on p. 203.

Methanoic acid

By heating a solution of ethanedioic acid in propane-1,2,3-triol at 150°C:



$$\begin{array}{c} CO_2H \\ | \\ CO_2H \end{array} \rightarrow H{-}CO_2H + CO_2$$

Benzoic acid

By the oxidation of methylbenzene with hot, alkaline potassium manganate(VII) solution, followed by acidification:

$$C_6H_5{-}CH_3 \xrightarrow[NaOH]{KMnO_4} C_6H_5{-}CO_2^-\ Na^+$$

$$C_6H_5{-}CO_2^-\ Na^+ + HCl \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5{-}CO_2H} + NaCl$$

Practical details are described on p. 113.

Manufacture of monocarboxylic acids

Methanoic acid is mainly produced as a by-product of the manufacture of ethanoic acid from naphtha (see below).

It is also manufactured by the carbonylation of methanol, in the liquid phase,

$$CH_3OH + CO \xrightarrow[150^\circ C\ \text{pressure}]{OH^-\ \text{as cat.}} HCO_2CH_3$$

followed by hydrolysis of the ester:

$$HCO_2CH_3 + H_2O \xrightarrow{H^+} HCO_2H + CH_3OH$$

Ethanoic acid is manufactured by three routes:

1. *From butane or naphtha.* They are dissolved in a solvent (ethanoic acid itself) and heated, under pressure, with air at 180–200°C. A catalyst, cobalt(II) ethanoate, is sometimes used. A range of co-products is formed which includes methanoic acid, propanoic acid and propanone. They are separated by fractional distillation.
2. *From methanol*, by carbonylation at 180°C and 30 atmospheres pressure, using a rhodium catalyst:

$$CH_3OH + CO \xrightarrow{\text{cat.}} CH_3CO_2H$$

This is a new process. By the mid-1980s, it is expected to be used to produce half the world's needs for ethanoic acid as, unlike the butane and naphtha routes, it produces a pure product.

3. A small amount of ethanoic acid is produced from ethanal:

$$CH_3{-}CHO + \tfrac{1}{2}O_2 \xrightarrow[60-70^\circ C]{(CH_3CO_2)_2Mn\ \text{as cat.}} CH_3{-}CO_2H$$

Benzoic acid is made by passing air under pressure into methylbenzene at 150°C in the presence of an organic cobalt salt as a catalyst:

$$C_6H_5{-}CH_3 \xrightarrow{O_2} C_6H_5{-}CO_2H$$

13.5 Chemical properties of monocarboxylic acids

1. They are weak acids, dissociating to a small extent (1–2 per cent) in water:

$$R{-}CO_2H \rightleftharpoons R{-}CO_2^- + H^+$$

The dissociation constants, K_a, of some typical members of the series are

	K_a *at* 25°C
$H—CO_2H$	$1{\cdot}7 \times 10^{-4}$
$CH_3—CO_2H$	$1{\cdot}7 \times 10^{-5}$
$CH_3CH_2—CO_2H$	$1{\cdot}3 \times 10^{-5}$
$C_6H_5—CO_2H$	$6{\cdot}3 \times 10^{-5}$
$C_6H_5CH_2—CO_2H$	$4{\cdot}9 \times 10^{-5}$

Thus, the hydroxyl group is far more acidic than in an alcohol, its properties being modified in this respect by the carbonyl group, for a reason described in Section 4.9. They are also stronger acids than phenols, but weaker than sulphonic acids.

2. They react with bases to form salts, for example:

$$R—CO_2H + NaOH \rightarrow R—CO_2^- \, Na^+ + H_2O$$

They react with carbonates and hydrogencarbonates to liberate carbon dioxide:

$$R—CO_2H + NaHCO_3 \rightarrow R—CO_2^- \, Na^+ + H_2O + CO_2$$

The last reaction enables them to be distinguished from simple phenols, for although phenols are acidic enough to turn blue litmus red and to form salts with sodium hydroxide, they are weaker acids than carbonic acid and thus do not liberate carbon dioxide from sodium hydrogencarbonate (10.8).

The reaction with sodium hydrogencarbonate also enables carboxylic acids to be separated from simple phenols. For example, if a mixture of benzoic acid and phenol is partitioned between a solution of sodium hydrogencarbonate and ether, the acid dissolves in the aqueous layer (with liberation of carbon dioxide) and the phenol mainly dissolves in the ether. The two solutions are separated; the ether is evaporated to leave phenol, and hydrochloric acid is added to the aqueous solution to precipitate benzoic acid:

$$C_6H_5—CO_2^- \, Na^+ + HCl \rightarrow C_6H_5—CO_2H + NaCl$$

3. Acids react with alcohols, in the presence of an acid catalyst, to form esters:

$$R—CO_2H + R'—OH \overset{H^+}{\rightleftharpoons} R—CO—O—R' + H_2O$$

The reaction is discussed on p. 212.

4. They react with phosphorus halides to form acid halides:

$$R—CO_2H + PCl_5 \longrightarrow R—CO—Cl + POCl_3 + HCl$$

$$R—CO_2H + PBr_5 \xrightarrow{\text{Red P/Br}_2} R—CO—Br + POBr_3 + HBr$$

Sulphur dichloride oxide (thionyl chloride) can also be used:

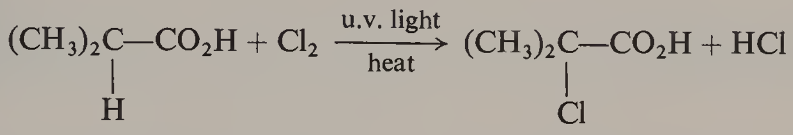
$$R—CO_2H + SOCl_2 \rightarrow R—CO—Cl + SO_2 + HCl$$

5. They are reduced to primary alcohols by lithium tetrahydridoaluminate:

$$\mathrm{R{-}CO_2H \xrightarrow{LiAlH_4} R{-}CH_2OH}$$

However, unlike aldehydes and ketones (p. 177), they are not reduced by sodium tetrahydridoborate.

6. A C—H bond adjacent to the carboxyl group is converted into a C—Cl bond when chlorine gas is passed into the hot acid in the presence of ultraviolet light, for example:



$$\mathrm{(CH_3)_2\underset{\displaystyle H}{\underset{|}{C}}{-}CO_2H + Cl_2 \xrightarrow[heat]{u.v.\ light} (CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}CO_2H + HCl}$$

When there is more than one such C—H bond, further reaction can occur, for example:

$$\mathrm{CH_3{-}CO_2H + Cl_2 \xrightarrow[heat]{u.v.\ light} \underset{\text{Chloroethanoic acid}}{CH_2Cl{-}CO_2H} + HCl}$$

$$\mathrm{CH_2Cl{-}CO_2H + Cl_2 \xrightarrow[heat]{u.v.\ light} \underset{\text{Dichloroethanoic acid}}{CHCl_2{-}CO_2H} + HCl}$$

$$\mathrm{CHCl_2{-}CO_2H + Cl_2 \xrightarrow[heat]{u.v.\ light} \underset{\text{Trichloroethanoic acid}}{CCl_3{-}CO_2H} + HCl}$$

7. Although carboxylic acids contain the carbonyl group, C=O, they do not undergo the addition reactions with, e.g., sodium hydrogensulphite or the condensation reactions with, e.g., hydroxylamine which are characteristic of this group in aldehydes and ketones.

This is because an orbital on the oxygen atom of the hydroxyl group which contains two unshared electrons interacts with the *p* orbital of the adjacent carbon atom (Fig. 13.1). This provides extra delocalisation in the molecule, as compared with that in an aldehyde or ketone, which would be lost by addition of a reagent to the carbonyl group, so that a carboxylic acid is more resistant to addition than an aldehyde or ketone.

Methanoic acid

Methanoic acid, H—CO$_2$H differs in the following respects from the other monocarboxylic acids:

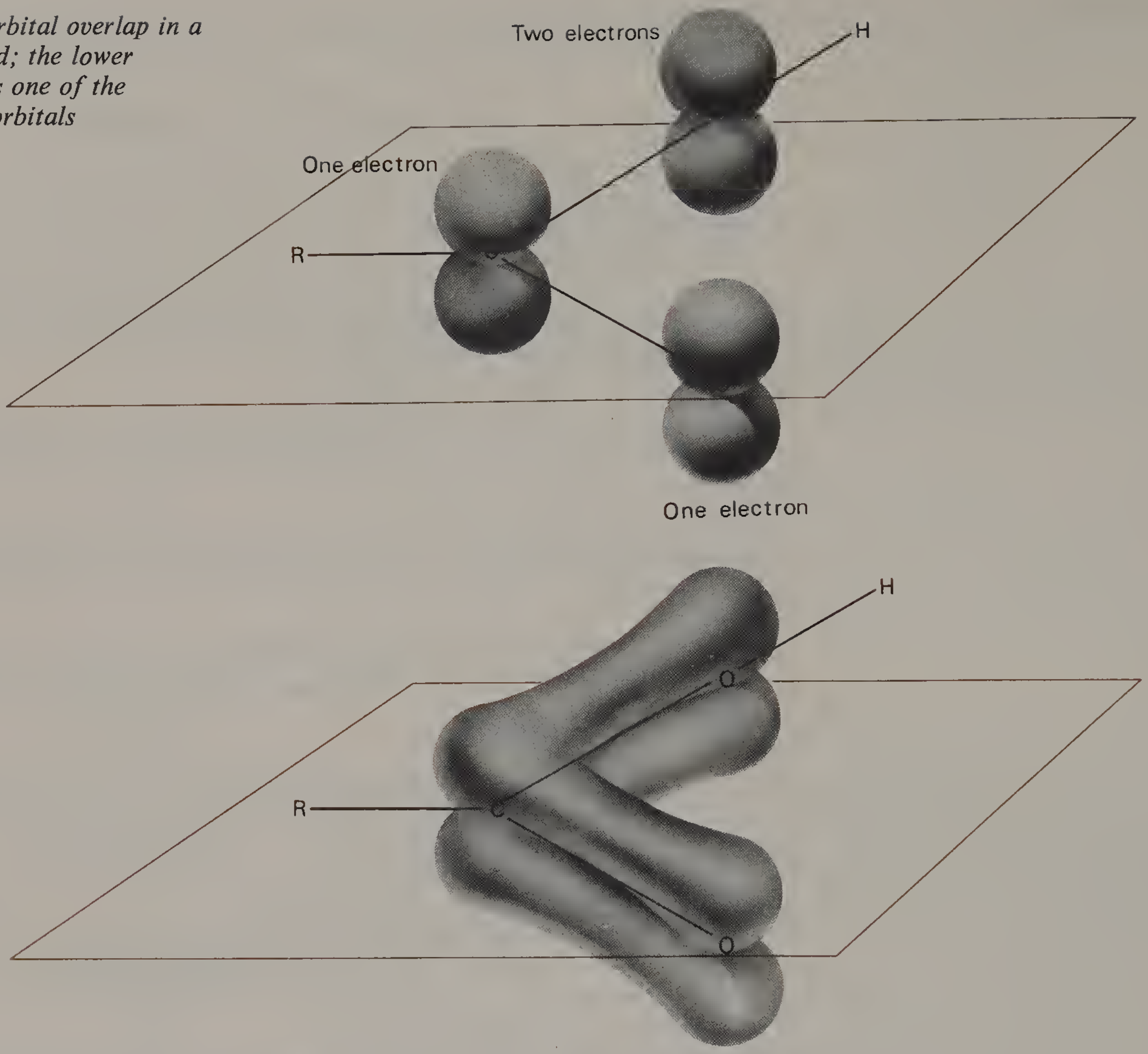
1. It is dehydrated by concentrated sulphuric acid:

$$\mathrm{H{-}CO_2H \xrightarrow{H_2SO_4} CO + H_2O}$$

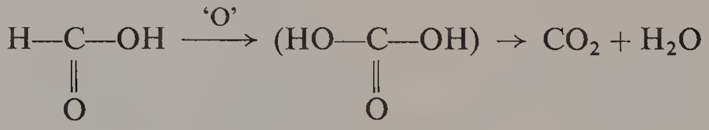
This is the basis of a laboratory preparation of carbon monoxide.

2. It reduces Fehling's solution and gives a silver mirror when warmed with a solution of silver nitrate and ammonia. These are characteristics of

FIG. 13.1. p-*Orbital overlap in a carboxylic acid; the lower diagram shows one of the delocalised π orbitals*



aldehydes (12.5), and it is because methanoic acid contains the readily oxidised aldehydic group (HO—**CH=O**) that it undergoes these reactions, that is:



$$\mathrm{H{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OH} \xrightarrow{\text{'O'}} \mathrm{(HO{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OH)} \rightarrow CO_2 + H_2O$$

3. It does not form acid halides.

13.6 Uses of monocarboxylic acids

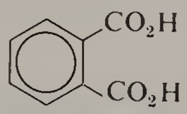
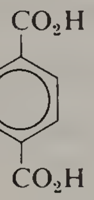
Ethanoic acid is used in the manufacture of ethenyl ethanoate, required for the production of poly(ethenyl ethanoate) (21.2), and ethanoic anhydride (14.4), required for making cellulose ethanoate (18.3) and other ethanoate esters.

Long-chain monocarboxylic acids are used in the manufacture of soaps and detergents (p. 201).

13.7 Dicarboxylic acids

Some examples of dicarboxylic acids, together with their original names, are in Table 13.2.

Table 13.2. Some dicarboxylic acids

NAME	FORMULA	M.P./°C
Ethanedioic acid (oxalic acid)	$HO_2C—CO_2H$	189
Propanedioic acid (malonic acid)	$HO_2C—CH_2—CO_2H$	136 (decomposes)
Butanedioic acid (succinic acid)	$HO_2C—CH_2—CH_2—CO_2H$	185
Hexanedioic acid (adipic acid)	$HO_2C—(CH_2)_4—CO_2H$	149
Benzene-1,2-dicarboxylic acid (phthalic acid)		200 (decomposes)
Benzene-1,4-dicarboxylic acid (terephthalic acid)		300 (sublimes)

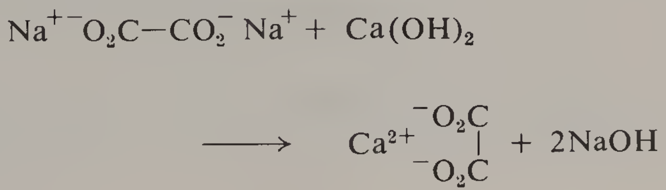
They are white crystalline solids. The lower members are soluble in water and ethanol but are insoluble in ether.

Laboratory preparations of dicarboxylic acids

Ethanedioic acid is made by heating sodium methanoate at 400°C to give disodium ethanedioate,

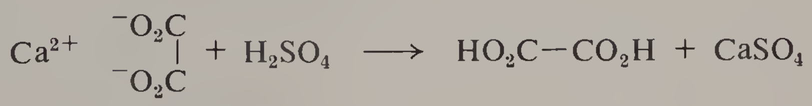
$$2H—CO_2^- \, Na^+ \rightarrow Na^+ \, ^-O_2C—CO_2^- \, Na^+ + H_2$$

dissolving this salt in water and adding calcium hydroxide to precipitate calcium ethanedioate,



$$Na^{+}\,^{-}O_2C—CO_2^{-}\,Na^{+} + Ca(OH)_2 \longrightarrow Ca^{2+}\begin{matrix}^{-}O_2C\\ | \\ ^{-}O_2C\end{matrix} + 2NaOH$$

and then adding to the dried calcium salt the exact quantity of dilute sulphuric acid needed to liberate the acid:



$$Ca^{2+}\begin{matrix}^{-}O_2C\\ | \\ ^{-}O_2C\end{matrix} + H_2SO_4 \longrightarrow HO_2C—CO_2H + CaSO_4$$

Calcium sulphate precipitates, and ethanedioic acid is crystallised from the filtrate as the hydrate, $(CO_2H)_2.2H_2O$.

Propanedioic acid is made by the reaction of sodium cyanide in water with the sodium salt of chloroethanoic acid, followed by hydrolysis of the nitrile with concentrated hydrochloric acid:

$$Cl—CH_2—CO_2^- \ Na^+ + NaCN \rightarrow N{\equiv}C—CH_2—CO_2^- \ Na^+ + NaCl$$

$$N{\equiv}C—CH_2—CO_2^- \ Na^+ + 2H_2O + 2HCl \rightarrow HO_2C—CH_2—CO_2H + NH_4Cl + NaCl$$

Butanedioic acid is prepared from 1,2-dibromoethane:

$$Br—CH_2—CH_2—Br + 2NaCN \rightarrow N{\equiv}C—CH_2—CH_2—C{\equiv}N + 2NaBr$$

$$N{\equiv}C—CH_2—CH_2—C{\equiv}N + 4H_2O + 2HCl \rightarrow HO_2C—CH_2—CH_2—CO_2H + 2NH_4Cl$$

Manufacture of dicarboxylic acids

Ethanedioic acid is manufactured by the oxidation of carbohydrates (e.g. corn starch) with nitric acid in the liquid phase.

Hexanedioic acid, required for the production of nylon-6.6 (21.3), is manufactured from cyclohexane (20.6), and **benzene-1,4-dicarboxylic acid**, required for the production of Terylene, is made from 1,4-dimethylbenzene (20.5).

Chemical properties of dicarboxylic acids

In most respects dicarboxylic acids resemble monocarboxylic acids. They react with bases to form two series of salts, for example:

$$HO_2C—CO_2H + NaOH \rightarrow HO_2C—CO_2^- \ Na^+ + H_2O$$

Sodium hydrogen-ethanedioate

$$HO_2C—CO_2^- \ Na^+ + NaOH \rightarrow Na^+ \ ^-O_2C—CO_2^- \ Na^+ + H_2O$$

Disodium ethanedioate

and with phosphorus halides and sulphur dichloride oxide to form acid halides, for example:

$$HO_2C—CO_2H + 2PCl_5 \rightarrow Cl—CO—CO—Cl + 2POCl_3 + 2HCl$$

Ethanedioyl chloride

The lower members of the series have certain special properties:

1. Ethanedioic acid and propanedioic acid are decarboxylated on being heated strongly:

$$HO_2C—CO_2H \xrightarrow{150°C} H—CO_2H + CO_2$$

$$HO_2C—CH_2—CO_2H \xrightarrow{150°C} CH_3—CO_2H + CO_2$$

2. Ethanedioic acid is a reducing agent, being readily oxidised to carbon dioxide and water, for example with a *warm* solution of acidified potassium manganate(VII):

$$HO_2C—CO_2H \xrightarrow{\text{‘O’}} 2CO_2 + H_2O$$

3. Ethanedioic acid is dehydrated by concentrated sulphuric acid:

$$HO_2C{-}CO_2H \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$$

This is a convenient method for the preparation of carbon monoxide in the laboratory.

4. Propanedioic acid is dehydrated to form tricarbon dioxide when heated with phosphorus pentoxide:

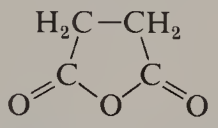
$$HO_2C{-}CH_2{-}CO_2H \xrightarrow{P_4O_{10}} O{=}C{=}C{=}C{=}O + 2H_2O$$

Tricarbon dioxide

5. Butanedioic acid forms a cyclic anhydride when heated with ethanoic anhydride:

$$HO_2C{-}CH_2{-}CH_2{-}CO_2H + CH_3{-}CO{-}O{-}CO{-}CH_3$$

$\longrightarrow$



$+ 2CH_3CO_2H$

Butanedioic anhydride

13.8
Substituted carboxylic acids

Chloroethanoic acid

Chloroethanoic acid is prepared by passing chlorine into hot ethanoic acid in the presence of ultraviolet light:

$$CH_3{-}CO_2H + Cl_2 \xrightarrow[\text{heat}]{\text{u.v. light}} CH_2Cl{-}CO_2H + HCl$$

Further chlorination can occur, giving dichloroethanoic acid and then trichloroethanoic acid (p. 193), and in order to optimise the yield of the monochloro compound the reaction is stopped when there has been the appropriate increase in weight.

Chloroethanoic acid is a deliquescent solid (m.p. 61 °C) which is soluble in water. It is a stronger acid than ethanoic acid (4.8).

The chlorine atom behaves as in alkyl halides. Thus, it is readily displaced, as chloride ion, by nucleophilic reagents, for example:

1. With dilute sodium hydroxide, the sodium salt of hydroxyethanoic acid is formed:

$$Cl{-}CH_2{-}CO_2H + 2NaOH \rightarrow HO{-}CH_2{-}CO_2^-\,Na^+ + NaCl + H_2O$$

Sodium hydroxyethanoate

2. With sodium cyanide, the sodium salt of cyanoethanoic acid is formed:

$$Cl{-}CH_2{-}CO_2H + 2NaCN \rightarrow N{\equiv}C{-}CH_2{-}CO_2^-\,Na^+ + NaCl + HCN$$

Sodium cyanoethanoate

3. With ammonia, aminoethanoic acid (glycine) is formed:

$$Cl{-}CH_2{-}CO_2H + 2NH_3 \rightarrow H_2N{-}CH_2{-}CO_2H + NH_4Cl$$

Glycine

Hydroxyethanoic acid

Hydroxyethanoic acid is prepared by the hydrolysis of chloroethanoic acid with sodium hydroxide, followed by acidification:

$$\mathrm{Cl{-}CH_2{-}CO_2H + 2NaOH \rightarrow HO{-}CH_2{-}CO_2^-\,Na^+ + NaCl + H_2O}$$

$$\mathrm{HO{-}CH_2{-}CO_2^-\,Na^+ + HCl \rightarrow \underset{\text{Hydroxyethanoic acid}}{HO{-}CH_2{-}CO_2H} + NaCl}$$

It is a white solid, readily soluble in water, and is a stronger acid than ethanoic acid though weaker than chloroethanoic acid.

It exhibits the properties of both a monocarboxylic acid and a primary alcohol:

1. As an acid, it can be converted into an ester, for example:

$$\mathrm{HO{-}CH_2{-}CO_2H + CH_3{-}OH \overset{H^+}{\rightleftharpoons} \underset{\text{Methyl hydroxyethanoate}}{HO{-}CH_2{-}CO{-}O{-}CH_3} + H_2O}$$

2. As a primary alcohol, it can be oxidised to an aldehyde by, for example, acidified sodium dichromate solution; further oxidation occurs readily:

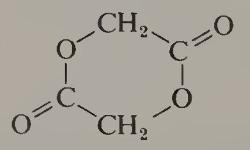
$$\mathrm{HO{-}CH_2{-}CO_2H \xrightarrow{Na_2Cr_2O_7} \underset{\text{Oxoethanoic acid}}{O{=}CH{-}CO_2H} \xrightarrow{Na_2Cr_2O_7}}$$

$$\mathrm{\underset{\text{Ethanedioic acid}}{HO_2C{-}CO_2H} \xrightarrow{Na_2Cr_2O_7} 2CO_2 + H_2O}$$

In addition, it undergoes two reactions which neither a carboxylic acid nor a primary alcohol can undergo:

3. On being heated, it forms a cyclic ester (an example of a **lactide**):

$$\mathrm{2HO{-}CH_2{-}CO_2H \longrightarrow}$$



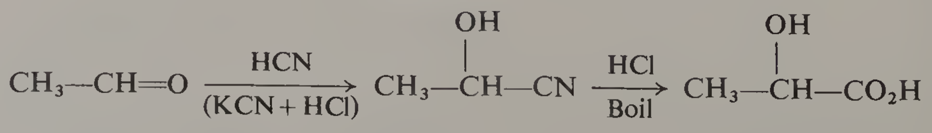
$$\mathrm{+\ 2H_2O}$$

4. When warmed with concentrated sulphuric acid, it forms methanal and carbon monoxide:

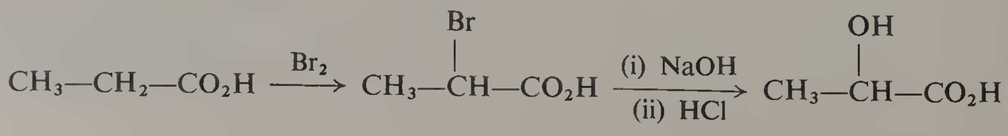
$$\mathrm{HO{-}CH_2{-}CO_2H \xrightarrow{conc.\ H_2SO_4} H{-}CH{=}O + CO + H_2O}$$

2-Hydroxypropanoic acid

2-Hydroxypropanoic acid (lactic acid) is prepared from ethanal or from propanoic acid:



$$\mathrm{CH_3{-}CH{=}O \xrightarrow[(KCN+HCl)]{HCN} CH_3{-}\overset{\overset{OH}{|}}{C}H{-}CN \xrightarrow[Boil]{HCl} CH_3{-}\overset{\overset{OH}{|}}{C}H{-}CO_2H}$$

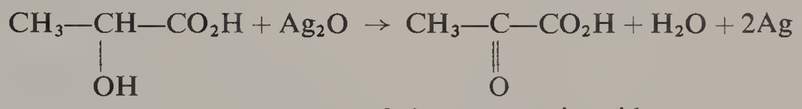


$$\mathrm{CH_3{-}CH_2{-}CO_2H \xrightarrow{Br_2} CH_3{-}\overset{\overset{Br}{|}}{C}H{-}CO_2H \xrightarrow[(ii)\ HCl]{(i)\ NaOH} CH_3{-}\overset{\overset{OH}{|}}{C}H{-}CO_2H}$$

2-Hydroxypropanoic acid exists as two optically active isomers (p. 238), each of which has m.p. 26°C. When prepared in the laboratory as above, it is obtained as a racemic mixture of the two isomers which is optically inactive and has m.p. 18°C; the individual isomers can be obtained by resolution of this mixture (p. 244).

The chemical properties of 2-hydroxypropanoic acid are similar to those of hydroxyethanoic acid:

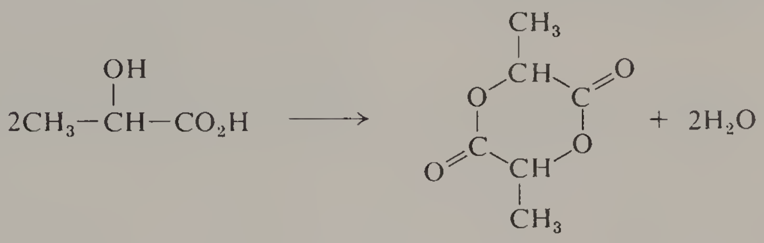
1. It has approximately the same acid dissociation constant as hydroxyethanoic acid.
2. As an acid, it forms esters and acid halides.
3. As an alcohol, the secondary alcohol group is oxidised to a keto group. To prevent oxidation of the product, 2-oxopropanoic acid, a weak oxidising agent such as silver oxide must be used:



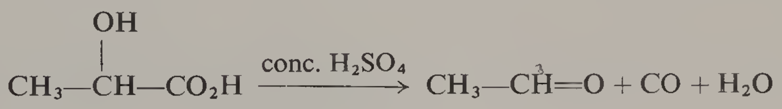
$$\mathrm{CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CO_2H + Ag_2O \rightarrow CH_3{-}\underset{\substack{\|\\ O}}{C}{-}CO_2H + H_2O + 2Ag}$$

2-Oxopropanoic acid

4. As a 2-hydroxy-acid, it forms a cyclic ester (lactide) on being heated:



5. As a 2-hydroxy-acid, it yields carbon monoxide when warmed with concentrated sulphuric acid:



$$\mathrm{CH_3{-}\overset{\substack{OH\\ |}}{CH}{-}CO_2H \xrightarrow{conc.\ H_2SO_4} CH_3{-}CH{=}O + CO + H_2O}$$

13.9
Salts of carboxylic acids

Carboxylic acids react with inorganic bases to form salts, for example:

$$\mathrm{CH_3{-}CO_2H + NaOH \rightarrow CH_3{-}CO_2{}^-\ Na^+ + H_2O}$$

Physical properties of salts

Sodium and potassium salts are white, crystalline solids which are soluble in water but practically insoluble in ether and most other organic solvents. The calcium salts are much less soluble in water, and the silver salts are practically insoluble. All the salts have relatively high melting points (200°–400°C).

The solutions in water have a pH above 7 as the result of hydrolysis:

$$\mathrm{R{-}CO_2{}^-\ Na^+ + H_2O \rightleftharpoons R{-}CO_2H + Na^+ + OH^-}$$

Chemical properties of salts

1. When the *anhydrous* sodium salt is heated with soda-lime, an **alkane** is formed:

$$\mathrm{R{-}CO_2{}^-\ Na^+ + NaOH \rightarrow R{-}H + Na_2CO_3}$$

This is an example of **decarboxylation**, the term used when the elements of carbon dioxide are removed from a molecule.

A well-known example of this reaction is the formation of methane from sodium ethanoate:

$$CH_3CO_2^- \, Na^+ + NaOH \xrightarrow{\text{soda-lime}} CH_4 + Na_2CO_3$$

These reactions also occur with the acid itself, the sodium salt of the acid being formed during the reaction, for example when benzoic acid is heated with soda-lime:

$$C_6H_5CO_2H + NaOH \rightarrow C_6H_5CO_2^- \, Na^+ + H_2O$$

$$C_6H_5CO_2^- \, Na^+ + NaOH \rightarrow C_6H_6 + Na_2CO_3$$

2. *Kolbe's reaction.* When a strong aqueous solution of a salt is electrolysed, an **alkane** is formed:

$$2R\text{—}CO_2^- \, Na^+ + 2H_2O \rightarrow R\text{—}R + 2CO_2 + 2NaOH + H_2$$

At the *anode*, the carboxylate ion releases one electron to give a radical, R—CO—O·. This fragments with formation of an alkyl radical and carbon dioxide, and two alkyl radicals combine to form the alkane:

$$R\text{—}CO_2^- \rightarrow R\text{—}CO\text{—}O\cdot + e$$

$$R\text{—}CO\text{—}O\cdot \rightarrow R\cdot + CO_2$$

$$2R\cdot \rightarrow R\text{—}R$$

At the *cathode*, there is competition between sodium ions and hydrogen ions (from water) for discharge. Although the concentration of hydrogen ions is very low, the discharge potential for hydrogen favours the formation of hydrogen gas:

$$H^+ + e \rightarrow H; \;\; 2H \rightarrow H_2$$

3. When the *anhydrous* sodium salt is heated with an acid chloride, an **acid anhydride** is formed:

$$R\text{—}CO_2^- \, Na^+ + R\text{—}CO\text{—}Cl \rightarrow R\text{—}CO\text{—}O\text{—}CO\text{—}R + NaCl$$

4. The sodium salts of monocarboxylic acids are stable when heated alone, except for sodium methanoate which decomposes at 400°C, yielding **disodium ethanedioate** and hydrogen:

$$2H\text{—}CO_2^- \, Na^+ \rightarrow Na^+ \, {}^-O_2C\text{—}CO_2^- \, Na^+ + H_2$$

5. The silver salts of carboxylic acids react on heating with alkyl halides to give **esters**:

$$R\text{—}CO_2^- \, Ag^+ + R'\text{—}Cl \rightarrow R\text{—}CO\text{—}O\text{—}R' + AgCl$$

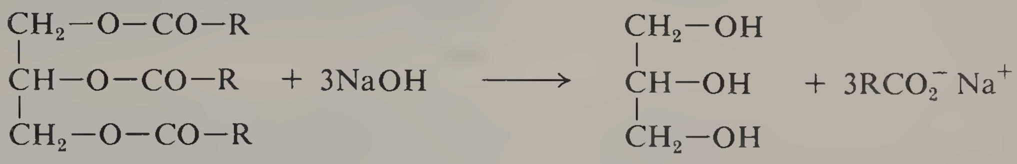
6. When the calcium salt of a carboxylic acid is heated strongly, a **ketone**

is formed, but the yield is usually very low.

$$(\mathrm{R{-}CO_2^-})_2\mathrm{Ca^{2+}} \rightarrow \mathrm{R{-}CO{-}R} + \mathrm{CaCO_3}$$

13.10 Soaps and detergents

Soaps are obtained from natural fats, known as **glycerides** because they are esters formed by the trihydric alcohol, propane-1,2,3-triol, which was formerly known as glycerol, with long-chain carboxylic acids. The glycerides are hydrolysed by heating with caustic soda (**saponification**) to form soaps—the sodium salts of the acids—and propane-1,2,3-triol:



$$\begin{array}{l} \mathrm{CH_2{-}O{-}CO{-}R} \\ | \\ \mathrm{CH{-}O{-}CO{-}R} \\ | \\ \mathrm{CH_2{-}O{-}CO{-}R} \end{array} + 3\mathrm{NaOH} \longrightarrow \begin{array}{l} \mathrm{CH_2{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2{-}OH} \end{array} + 3\mathrm{RCO_2^-\,Na^+}$$

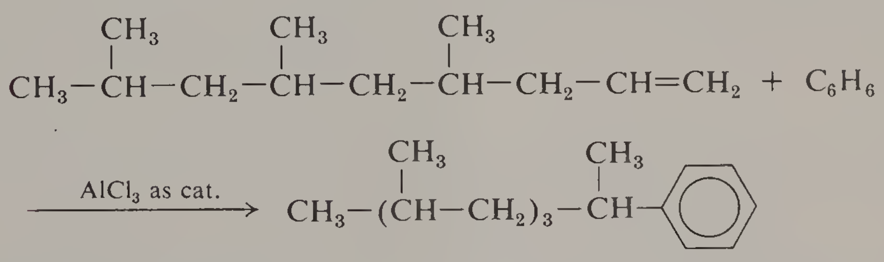
A glyceride Propane-1,2,3-triol A soap

Sodium chloride is added to precipitate the soap, and this is then processed into bars or soap powder. Glycerides contain saturated carboxylic acids which have an even number of carbon atoms, generally within the range 12–20, for example, octadecanoic acid (stearic acid), $\mathrm{CH_3{-}(CH_2)_{16}{-}CO_2H}$.

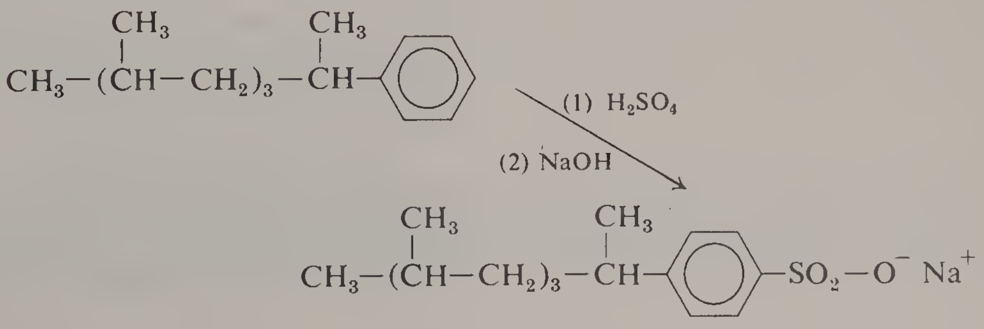
Soaps act by lowering the surface tension between water and an oil or other insoluble material. They do so by virtue of containing both a hydrophilic ('water-loving') group ($\mathrm{{-}CO_2^-}$) and a hydrophobic ('water-hating') group (the alkyl chain); molecules of water tend to congregate near the former and molecules of the water-insoluble material congregate around the latter.

One disadvantage of soaps is that they form insoluble calcium salts with the calcium ions in hard water and in the clays which are present in dirt; a good deal of the soap is wasted in this way. This problem is avoided by the use of synthetic detergents in which a sulphonate group, $\mathrm{{-}SO_2{-}O^-}$, or sulphate group, $\mathrm{{-}O{-}SO_2{-}O^-}$, replaces the carboxylate group as the hydrophilic component, since the corresponding calcium salts are more soluble in water than the calcium salts of carboxylic acids.

Until about 1965, the commonest detergents contained alkylbenzenesulphonates made from a polymer of propene by a Friedel-Crafts reaction:

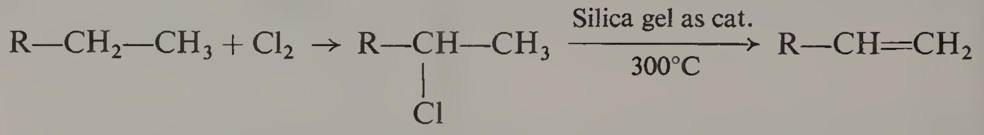


followed by sulphonation (p. 105) and neutralisation of the sulphonic acid with sodium hydroxide:



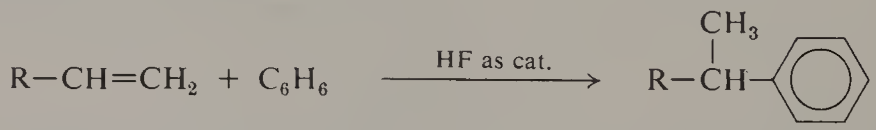
However, these detergents suffer from the disadvantage that they are not degraded by bacteria in sewage plants, which meant that many rivers suffered from the foam and there was also the danger that detergents could be ‘recycled’ into the drinking-water supplies. The failure of bacteria to attack the materials results from the presence of the large number of branches in their alkyl groups, and the use of such detergents has been abandoned in the United Kingdom. Reduction in the number of branches increases their capacity for biodegradation and so most detergents now contain linear or only singly branched alkyl groups. There are three important types; the first two are **anionic** detergents while the third is **non-ionic**.

All three types are obtained from non-branched alkenes, which themselves are derived partly from the cracking of waxes (19.8), partly from the polymerisation of ethene with a Ziegler catalyst (20.4) and partly from alkanes by free-radical chlorination followed by catalytic dehydrochlorination:



$$R{-}CH_2{-}CH_3 + Cl_2 \rightarrow R{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow[300°C]{\text{Silica gel as cat.}} R{-}CH{=}CH_2$$

1. *Alkylbenzenesulphonates,* which are made from non-branched alkenes (C_{10}–C_{14}):

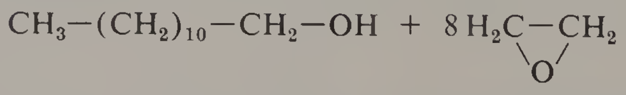


The alkylbenzene is sulphonated and neutralised. These are used in powder detergents (e.g. Omo, Surf, Tide), and are slowly biodegradable. The formation of an alkylbenzenesulphonate is described on p. 205.

2. *Alkyl sulphates,* which are made from straight-chain alcohols (C_{10}–C_{14}) derived from alkenes by the OXO process (p. 322) or with a Ziegler catalyst (p. 316):

$$R{-}CH_2OH \xrightarrow{H_2SO_4} R{-}CH_2{-}O{-}SO_2OH \xrightarrow{NaOH} R{-}CH_2{-}O{-}SO_2{-}O^- Na^+$$

3. *Ethoxylates* (which are non-ionic detergents) are made from long-chain alcohols and epoxyethane, for example:



$$\longrightarrow \quad CH_3{-}(CH_2)_{10}{-}CH_2{-}(OCH_2CH_2)_8{-}OH$$

An ethoxylate

These do not contain an ionic group as their hydrophilic component, but hydrophilic properties are conferred on them by the presence of a number of oxygen atoms in one part of the molecule which are capable of forming hydrogen-bonds with molecules of water.

A packet of detergent contains about 20 per cent of active detergent and an equal amount of sodium sulphate, which increases the bulk of the powder. A further 30 per cent is made up of inorganic phosphates, which are added to remove soluble, complex calcium salts by reaction with the calcium ions in the dirt. Other ingredients include sodium peroxoborate (about 5 per cent), which is a bleaching agent, and fluorescers, which are organic compounds which absorb ultraviolet light and re-emit the energy in the blue part of the visible spectrum, thereby making 'yellow' clothes appear white.

The inorganic phosphates which enter lakes and rivers *via* sewage are nutrients for algae and are responsible for the proliferation of these plants, as a green surface sludge, in seas and lakes in various parts of the world. It is likely that legislation will be introduced to remove, or at least reduce, the phosphate content of detergents so as to eliminate this source of pollution.

13.11 Practical work

Preparation of a carboxylic acid from an ester

The example given is the preparation of benzoic acid from ethyl benzoate.

Reflux a mixture of 5 cm^3 of ethyl benzoate and 25 cm^3 of sodium hydroxide solution (made by dissolving 10 g of sodium hydroxide in 25 cm^3 of water) for 30 minutes (cf. Fig. 2.1).

Distil the mixture and collect the first 2 cm^3 of distillate (cf. Fig. 2.2). Carry out some of the tests for ethanol (for example, No. 3, p. 161, and No. 7, p. 161).

Pour the residue from the flask into a beaker and add M sulphuric acid until the solution is acid to litmus. Filter the crystals, using a Buchner funnel (cf. Fig. 2.8). Dissolve the crystals in a minimum of boiling water. Allow the solution to cool and filter the crystals, dry them between pads of filter paper and determine their melting point.

Small-scale preparation of phenylmagnesium bromide and benzoic acid

1. *Preparation of phenylmagnesium bromide solution*

All apparatus and materials used in the preparation of a Grignard reagent must be thoroughly dry since traces of moisture not only react with the reagent but also inhibit its formation. Make sure that the apparatus is clean and that it has been dried in an oven before the experiment.

Diethyl ether must stand over clean sodium wire or pellets and the bromobenzene over anhydrous calcium chloride in carefully stoppered tubes or flasks, if possible, overnight before the experiment is to be carried out.

Place 0·5 g of magnesium turnings in a flask and add one or two crystals of iodine, followed by 10 cm^3 of dry ether. Stand the flask in a cold water-bath, add 2 cm^3 of dry bromobenzene, then fit a dry reflux condenser which is attached to a calcium chloride drying tube at its open end.

Raise the temperature of the water-bath to 40–45°C, turn out the bunsen and allow the contents of the flask to reflux for 20–25 minutes. The disappearance of the colour of the iodine and the formation of a cloudiness in the reaction mixture are indications that the reaction is proceeding satisfactorily. Remove the warm water-bath and replace it with a freezing mixture of ice and salt.

2. *Preparation of benzoic acid*

Arrange for the carbon dioxide, generated in the Kipp's apparatus, to be washed in water to remove traces of hydrochloric acid and to be dried by passing through *concentrated* sulphuric acid. A more satisfactory method is to place a few pieces of solid carbon dioxide in a conical flask and lead the carbon dioxide straight into the flask containing the solution, which should be immersed in ice.

Pass a gentle stream of dry carbon dioxide through the solution of phenylmagnesium bromide for 5–10 minutes. Decant the contents of the flask into a small beaker and place the latter in the freezing mixture. Dilute 3 cm^3 of *concentrated* hydrochloric acid by adding 3 cm^3 of water. Introduce the acid slowly into the beaker, with stirring, in order to liberate the benzoic acid.

Remove the beaker from the freezing mixture, add 15 cm^3 of ether and stir. Decant the liquid into a separating funnel and return the lower aqueous layer to the beaker. Repeat the ether extraction twice, using 5 cm^3 of ether each time.

Combine the ether extracts and shake with 10 cm^3 of 2M sodium hydroxide solution in a separating funnel. Remove the stopper from the funnel occasionally to release the pressure. Most of the benzoic acid enters the lower aqueous layer as the sodium salt. Transfer the aqueous layer to a beaker. (If a precipitate of magnesium hydroxide should appear, remove it by filtration through a Buchner funnel.) Acidify the filtrate with 2M hydrochloric acid (testing the solution with litmus paper). A white precipitate of benzoic acid is obtained. Precipitation is hastened by cooling in the freezing mixture and scratching with a glass rod. Filter off the precipitate; wash *in situ* with distilled water. Dry the solid and take its melting point. If time, purify by recrystallisation from hot water. Dry the crystals in the oven at about 100°C and redetermine the melting point.

Reduction of a carboxylic acid to an alcohol with lithium tetrahydridoaluminate

Lithium tetrahydridoaluminate is a specific reagent; for example, it does not reduce unsaturated carbon–carbon bonds (as in alkenes and alkynes).

The acid chosen for this reaction is 2-chlorobenzoic acid as the product, 2-chlorophenylmethanol, is a solid.

Lithium tetrahydridoaluminate is a dangerous chemical. It reacts violently with water and only dry solvents and dry apparatus must be used. Experiments should be done in a fume cupboard with a satisfacotry exhaust for the hydrogen formed during reactions to be led away. There should be no naked flames nearby.

Place 30 cm^3 of diethyl ether, previously dried over sodium, in a round-bottom flask, which has been carefully dried, and fit a reflux condenser. Weigh out 0·5 g of lithium tetrahydridoaluminate on a watch glass and add it, in *very small* quantities, to the ether. If there is any effervescence, it means that the ether is not dry.

Add, in very small quantities at a time, 1·5 g of 2-chlorobenzoic acid to the solution of lithium tetrahydridoaluminate in ether. After all the acid has been added, reflux the mixture, using a beaker of hot water, for about 30 minutes.

Then add, dropwise, 5 cm^3 of ethyl ethanoate which will be reduced by the excess of lithium tetrahydridoaluminate and thus decompose it. Allow the mixture to reflux for a further 10 minutes.

Cool the mixture and then add 20 cm^3 of M sulphuric acid. 2-Chlorophenylmethanol is liberated from the complex aluminium compound formed and dissolves in the ether layer.

Place the mixture in a separating funnel and run the ether layer into a conical flask. Add some anhydrous sodium sulphate, fit a stopper to the flask and swirl the mixture for about 5 minutes.

Decant the solution into a flask and distil off the ether using a beaker of hot water.

Detach the flask and place it in a beaker of ice. Filter off the crystals of 2-chlorophenylmethanol and dry them between filter papers. Take the melting point of the crystals, which, before further purification, will be about 70°C.

If time permits, recrystallise the product from a dilute aqueous solution of ethanol.

Preparation of detergents

1. To 5 g of dodecanol in a flask, add 2 cm^3 of chlorosulphonic acid dropwise (**CARE**), with stirring. Keep the mixture below 35°C by immersing the flask in a large beaker of cold water. Stir the mixture for a further 10 minutes and then divide into two parts.

$$C_{12}H_{25}\text{—OH} + \text{Cl—SO}_2\text{—OH} \rightarrow \underset{\text{Dodecyl sulphate}}{C_{12}H_{25}\text{—O—SO}_2\text{—OH}} + \text{HCl}$$

(a) To one part, add a dilute solution of sodium hydroxide, until the mixture is neutral. Transfer the solution to an evaporating basin and evaporate it until the solid detergent is formed. The detergent can be recrystallised from ethanol.

$$C_{12}H_{25}\text{—O—SO}_2\text{—OH} + \text{NaOH} \rightarrow C_{12}H_{25}\text{—O—SO}_2\text{—O}^-\ \text{Na}^+ + H_2O$$

(b) To the second part, add a solution of tris-(2-hydroxyethyl)amine (2 cm^3 in 20 cm^3 of water):

$$C_{12}H_{25}\text{—O—SO}_2\text{—OH} + \text{N(CH}_2\text{CH}_2\text{OH)}_3 \rightarrow$$

$$C_{12}H_{25}\text{—O—SO}_2\text{—O}^-\ \text{H}\overset{+}{\text{N}}\text{(CH}_2\text{CH}_2\text{OH)}_3$$

Finally, make the mixture neutral to litmus by adding dropwise a solution of sodium hydrogencarbonate.

(c) Examine the lathering properties of the two detergents in both hard and soft water.

2. *Great care must be taken when using oleum. Wear safety glasses and carry out the experiment in a fume cupboard.*

Place 11·5 cm^3 of an alkylbenzene in a flask fitted with a thermometer, and cool the hydrocarbon to about 5°C in an ice-bath. Add 5 cm^3 of oleum (sulphuric acid containing about 20 per cent free sulphur trioxide) using a dropping-pipette, shaking between each addition. The temperature rises slowly but must not be allowed to rise above 56°C. The temperature should be about 55 ± 1°C at the end of the addition.

Replace the ice-bath with a beaker of hot water to keep the mixture at 55 ± 1°C for a further 30 minutes. Cool the mixture.

Place 4 g of crushed ice in a beaker and then surround it with a larger beaker containing an ice-water mixture. Stir in a solution of 1·5 g of sodium hydroxide dissolved in 6 cm^3 of water.

Transfer the reaction mixture containing the alkylbenzenesulphonic acid to a tap-funnel and add it to the alkali solution, with stirring, making sure that the temperature of the mixture does not rise above 50°C. Add the sulphonic acid until the pH of the mixture in the beaker is between 6·5 and 7·5 (using narrow-range Universal Indicator papers). If the pH becomes too low, add 2M sodium hydroxide solution to adjust it to 6·5–7·5.

A solid will precipitate out, and the mixture is then heated in an evaporating basin over a beaker of boiling water until most of the liquid is removed.

Although it is difficult to purify the detergent any further, its detergent properties can be studied by transferring a small amount of the mixture in the evaporating basin to a test-tube and dissolving it in water.

The detergent may be discoloured owing to the formation of 'hot-spots' on adding oleum to the hydrocarbon.

Reactions of methanoic acid and sodium methanoate

1. To some solid sodium hydrogencarbonate in a test-tube, add some methanoic acid.

2. Make up neutral iron(III) chloride solution by adding dilute ammonia solution to 2 cm^3 of iron(III) chloride solution until a precipitate appears. Add the original iron(III) chloride solution until the precipitate just disappears.

Place 5 drops of methanoic acid in a test-tube. Add dilute ammonia solution until just alkaline and boil off excess of ammonia. To this neutral solution, add 5 drops of neutral iron(III) chloride solution.

3. To 1 cm^3 of methanoic acid in a test-tube, add 1 cm^3 of *concentrated* sulphuric acid and warm. Test the gas evolved with (a) a lighted splint, (b) lime-water.

4. Place sodium methanoate crystals in a test-tube to a depth of about 1 cm. Heat vigorously and test the gas evolved with a lighted splint.

Cool the residue and add 1 cm^3 of concentrated sulphuric acid. Test the gas evolved with (a) a lighted splint, (b) lime-water.

The reducing properties of methanoic acid are illustrated by the reactions 5–7.

5. To 0·5 cm^3 of methanoic acid in a test-tube, add 1 cm^3 of dilute sulphuric acid and warm gently. Add a 1 per cent solution of potassium manganate(VII) drop by drop, and note whether the permanganate is decolorised.

6. To 1 cm^3 of ammoniacal silver nitrate solution (p. 185), add 2 or 3 drops of methanoic acid. A white precipitate of silver methanoate is formed. If the test-tube is immersed in hot water, a deposit of silver is formed.

7. Add methanoic acid dropwise to 1 cm^3 of a solution of mercury(II) chloride. A white precipitate of mercury(I) chloride is slowly formed. On warming, the precipitate darkens owing to reduction to mercury.

Reactions of ethanoic acid and sodium ethanoate

8. Repeat experiment 1, using ethanoic acid.

9. Repeat experiment 2, using ethanoic acid.

10. Repeat experiment 5, using ethanoic acid.

11. Mix together some *anhydrous* sodium ethanoate and soda-lime in a test-tube. Heat the mixture strongly. Test the gas evolved with a lighted splint.

12. Warm a mixture of 5 drops of ethanol, 5 drops of ethanoic acid and 1 drop of *concentrated* sulphuric acid. Note the characteristic odour of the product.

Reactions of benzoic acid

13. Repeat experiment 1 using a hot solution of benzoic acid, and compare the result with that obtained when a solution of phenol is added to sodium hydrogencarbonate.

14. Repeat experiment 5 using a hot solution of benzoic acid.

15. Repeat experiment 11 using benzoic acid in place of sodium ethanoate.

16. Repeat experiment 12 using benzoic acid in place of ethanoic acid.

Reactions of ethanedioic acid and disodium ethanedioate

17. Repeat experiment 1 using a solution of ethanedioic acid.

18. Repeat experiment 3 using solid ethanedioic acid.

19. Repeat experiment 4 using solid disodium ethanedioate.

20. Repeat experiment 5 using solid ethanedioic acid. Shake until ethanedioic acid has dissolved. Note whether any reaction occurs (a) in the cold, (b) when the mixture is warmed.

21. Repeat experiment 11 using disodium ethanedioate instead of sodium ethanoate.

13.12 Further reading

Detergents. Elaine Moore (reprinted 1970). Unilever Educational Booklet. Revised Ordinary Series.

Theory of Detergency. R. J. Taylor (1969). Unilever Educational Booklet. Advanced Series.

13.13 Film

Outline of Detergency (F) Unilever.

13.14 Questions

1 Outline by means of balanced equations and essential reaction conditions (a) **two** general methods for the synthesis of aliphatic carboxylic acids from alkyl iodides, (b) **one** method for the synthesis of benzoic acid from benzene.

Give **two** reactions of methanoic acid which are not shown by other aliphatic carboxylic acids.

Describe with practical details how you would detect the presence of a hydroxyl group in benzoic acid. (AEB)

2 Describe, with equations, a chemical test you would employ to distinguish between the following compounds:

(a) Methanoic acid and ethanoic acid
(b) Methanoic acid and ethanedioic acid
(c) Ethanoic acid and ethanedioic acid
(d) Phenol and benzoic acid.

3 Outline practical reaction schemes to obtain as many compounds as possible from ethanoic acid. Give the names and formulae of the products and intermediates, and indicate the reagents which are used.

4 Starting with ethanoic acid, by what reactions can the following be prepared: (a) ethanoic anhydride, (b) ethanamide, (c) methane, (d) chloroethanoic acid, (e) ethane?

5 Give three general reactions by which an aliphatic carboxylic acid may be prepared.

Describe how you would carry out a practical test to show that alcohols and acids both contain hydroxyl groups.

State briefly how, starting from ethanoic acid, you would prepare (a) methane, (b) ethanoic anhydride.

6 Describe in outline two methods by which benzoic acid could be made in the laboratory from benzene, giving the equations for the reactions and conditions required.

Describe the reactions by which the following could be obtained from benzoic acid: (a) benzoyl chloride, (b) benzoic anhydride, (c) benzamide.

7 What reactions are characteristic of carboxylic acids? To what extent may methanoic acid, ethanoic acid and ethanedioic acid be regarded as typical of this class of compounds?

8 Name five organic substances which can be obtained *directly* from salts of ethanoic acid. State what other reagents, if any, would be required. Give the conditions and equations for the reactions.

9 Starting with carbon monoxide, outline in each case **one** method by which (a) methanoic acid and (b) sodium ethanedioate are obtained. What products are obtained when methanoic acid is treated with mercury(II) chloride solution?

10 The molecular weight of a weak, monobasic, organic acid *A* was calculated from (a) the osmotic pressure of its aqueous solution, (b) the depression of the freezing point of benzene observed when *A* was dissolved in this solvent. The two methods gave different values for the molecular weight of *A*. Suggest an explanation for this difference.

11 Most of the reactions of carboxylic acids can be classified as belonging to one of four types: (a) reactions involving cleavage of the O—H bond; (b) reactions at the carbonyl carbon; (c) reactions at the 2-carbon atom; (d) decarboxylation. Discuss the chemistry of carboxylic acids under these headings. (W(S))

12 Compare: (a) the properties of the CO group in ethanal, propanone and ethanoic acid; (b) the properties of the hydroxyl group in phenol and ethanol. What explanations have been suggested for these differences? How do you account for the fact that phenylamine is a weaker base than ethylamine? (O(S))

13 A substance *A* ($C_4H_6O_2$) rapidly decolourised a solution of potassium permanganate in the cold. On treatment with trioxygen and hydrolysis of the products, *A* gave a neutral substance *B* (C_2H_4O) and an acidic substance *C* ($C_2H_2O_3$), both of which gave silver mirrors with ammoniacal silver solutions, and orange precipitates with 2,4-dinitrophenylhydrazine sulphate in aqueous methanol (DNPH). *B*, on oxidation, gave an acid *D*, whose calcium salt, on heating, gave *E*, C_3H_6O, which gave an orange precipitate with DNPH, but did not react with the ammoniacal silver solution. Oxidation of *C* gave an acid *F*, which decolourised acidified potassium permanganate on warming, and which, on heating with concentrated sulphuric acid gave off some gas. This gas was passed through lime water, which turned cloudy, and the effluent gas was found to burn in air.

Deduce the structures of *A*, *B*, *C*, *D*, *E* and *F*, and outline the course of the above reactions. (L)

14 The following table gives the values of the dissociation constants of ethanoic acid and some of its related acids:

Acid	*Dissociation constant* (K_a)
Chloroethanoic	$1{\cdot}4 \times 10^{-3}$
Ethanoic	$1{\cdot}86 \times 10^{-5}$
Phenylethanoic	$5{\cdot}2 \times 10^{-5}$
Aminoethanoic	$1{\cdot}67 \times 10^{-10}$

(a) Discuss the theoretical reasons for the differences between the values for CH_3CO_2H, CH_2ClCO_2H and $CH_2NH_2CO_2H$.

(b) Calculate the pH of:

(i) 0·1M phenylethanoic acid;

(ii) a mixture of equal volumes of 0·2M phenylethanoic acid and 0·2M sodium phenylethanoate;

(iii) a mixture of equal volumes of 0·2M phenylethanoic acid and 0·2M ethanoic acid.

(c) Which of the solutions in (b) would change least in pH on dilution ten times? Explain your answer. (L(XS))

15 On combustion 0·1575 g of a hydroxy-monocarboxylic acid gave 0·2310 g of carbon dioxide and 0·0945 g of water. The vapour density of its ethyl ester is 59.

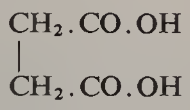
Calculate (a) the percentage composition, (b) the empirical formula, (c) the molecular weight, (d) molecular formula, of the acid.

Give the names and structural formula of all the hydroxy-acids having this molecular formula and account for their existence. (AEB)

16 Outline how pure ethanedioic acid crystals can be made, starting from carbon monoxide. How, and under what conditions, does ethanedioic acid react with

(a) potassium permanganate,
(b) methanol,
(c) sulphuric acid? (C(N))

17 Outline a synthesis of butanedioic acid,



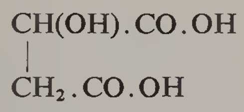
$$\begin{array}{l} CH_2.CO.OH \\ | \\ CH_2.CO.OH \end{array}$$

from ethene indicating the reagents and conditions for each reaction you mention.

By means of equations and brief notes on reaction conditions show how the following compounds could be prepared from butanedioic acid:

(a) butanedioic anhydride,

(b) 2-hydroxybutanedioic acid,



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

(c) 4-phenyl-4-oxobutanoic acid, $C_6H_5.CO.CH_2.CH_2.CO.OH$,

(d) a mixture of *cis*- and *trans*-butenedioic acids.

How could you convert *trans*-butenedioic acid into its *cis*-isomer? (JMB(S))

18 A substance, *A*, of molecular formula $C_3H_4OCl_2$ reacted with cold water to give a compound, *B*, $C_3H_5O_2Cl$. *A* on treatment with ethanol gave a liquid *C*, $C_5H_9O_2Cl$. When *A* was boiled with water, a compound *D*, $C_3H_6O_3$ was obtained. *D* was optically active and could be ethanoylated.

Deduce the nature of the compounds *A*, *B*, *C* and *D*, and account for the above reactions. (C Entrance)

19 Treatment of an aromatic compound *A*, C_8H_{10}, with ethanoyl chloride in the presence of aluminium chloride gives *B*, $C_{10}H_{12}O$. On being warmed with iodine and sodium hydroxide, *B* forms the sodium salt of *C*, $C_9H_{10}O_2$. Both *B* and *C* are converted to *D*, $C_9H_6O_6$, by vigorous oxidation with chromic acid. When heated, *D* readily forms *E*, $C_9H_4O_5$.

Deduce structures for the compounds *A* to *E* and elucidate the above reactions. (O Schol.)

20 Three isomeric organic acids have the following composition:

H = 2·09 per cent; C = 43·98 per cent; O = 16·75 per cent; Cl = 37·17 per cent.

When heated with soda-lime, all three isomers are converted to the same dichlorobenzene.

Give the structural formulae of the dichlorobenzene and each of the three acids from which it is obtained. (O Schol.)

21 A solid *A*, m.p. 32·5° and formula $C_5H_8O_3$, can be isolated from the mixture formed when starch is boiled with hydrochloric acid. The following reactions can be carried out with *A*:

(i) $A \xrightarrow{Na_2CO_3} B\,(C_5H_7O_3Na) + CO_2$

(ii) $A \xrightarrow[HCl]{CH_3OH} C_6H_{10}O_3$

(iii) $A \xrightarrow{\text{hydroxylamine}} C_5H_9O_3N$

(iv) $A \xrightarrow{NaOH + I_2}$ A yellow precipitate $C + (C_4H_4O_4Na_2)$

(v) $A \xrightarrow[\text{with } HNO_3]{\text{oxidation}}$ Ethanoic acid + an acid $D\ (C_3H_4O_4)$

(vi) $A \xrightarrow[\text{Na/Hg and water}]{\text{reduction with}} F\,(C_5H_9O_3Na)$.

Elucidate the structure of *A*, giving your reasoning.

Acidification of *F* gives a neutral substance $C_5H_8O_2$, instead of the expected acid, and electrolysis of *B* affords octane-2,7-dione. Can you write formulae to explain these reactions? (O Schol.)

22 (a) (i) Outline the general structure of a detergent molecule.
(ii) What are the properties of the two parts?
(b) In what way do soaps and sulphonates differ in chemical structure?
(c) By means of equations show how a sulphonate is made from petrochemical raw materials.
(d) With the aid of diagrams explain how a detergent removes grease from a fabric.
(e) Why do soaps not cause a nuisance in rivers by foaming?

(JMB Syllabus A)

Chapter 14

Derivatives of carboxylic acids

14.1 Introduction

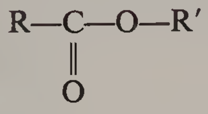
The hydroxyl group, —OH, in a carboxylic acid can be replaced by other functional groups, so that there is a series of compounds which contain the **acyl** group, RCO—, which form a parallel series to the derivatives of the alkanes:

Functional group	*Acyl derivatives*		*Alkyl derivatives*	
—OH	RCO—OH	Acid	R—OH	Alcohol
—OR′	RCO—OR′	Ester	R—OR′	Ether
—X (—F, —Cl, —Br, —I)	RCO—X	Acid halide	R—X	Alkyl halide
—OCOR′	RCO—OCOR′	Acid anhydride	R—OCOR′	Ester
$—NH_2$	$RCO—NH_2$	Acid amide	$R—NH_2$	Amine

In addition, carboxylic acids can be converted into **acid nitriles,** R—CN.

14.2 Esters

General formula



$$R-\underset{\underset{O}{\|}}{C}-O-R'$$

Physical properties

Esters are neutral liquids with pleasant, fruity smells. They are usually insoluble in water but are soluble in organic solvents.

Their melting points and boiling points are below those of the corresponding acids because ester molecules, unlike acid molecules, are not associated by hydrogen-bonding.

Table 14.1. Some esters

NAME	FORMULA	B.P./°C
Methyl methanoate	$H—CO_2—CH_3$	32
Ethyl methanoate	$H—CO_2—C_2H_5$	53
Methyl ethanoate	$CH_3—CO_2—CH_3$	56
Ethyl ethanoate	$CH_3—CO_2—C_2H_5$	77
Methyl propanoate	$C_2H_5—CO_2—CH_3$	79
Ethyl propanoate	$C_2H_5—CO_2—C_2H_5$	98
Methyl benzoate	$C_6H_5—CO_2—CH_3$	200

Preparation

1. By the reaction between an acid and an alcohol in the presence of a small amount of a strong acid such as sulphuric acid as catalyst

(**esterification**), for example:

$$CH_3—CO_2H + C_2H_5—OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl ethanoate}}{CH_3—CO—O—C_2H_5} + H_2O$$

The equilibrium constants for esterification are usually close to 1. In order to obtain a good yield of an ester from a given amount of an acid, it is necessary to use an excess of the alcohol. Suppose the equilibrium constant in the above reaction is 1·0. Then, if 1 mol of both ethanol and ethanoic acid are used, and if the total volume is V cm^3 and the amounts of ester and water at equilibrium are x mol,

$$\frac{x^2/V^2}{(1-x)^2/V^2} = 1$$

Thus, $x = 0{\cdot}5$ mol, so that the yield of ester, based on ethanoic acid or ethanol, is 50 per cent. However, if 10 mol of ethanol are used per mol of ethanoic acid, then

$$\frac{x^2/V^2}{(1-x)(10-x)/V^2} = 1$$

so that $x \simeq 0{\cdot}9$ mol; that is, the yield of ethyl ethanoate based on ethanoic acid is about 90 per cent.

2. By the reaction between an alcohol and either an acid chloride (14.3) or an acid anhydride (14.4), for example:

$$\underset{\text{Ethanoyl chloride}}{CH_3—CO—Cl} + C_2H_5—OH \rightarrow CH_3—CO—O—C_2H_5 + HCl$$

$$\underset{\text{Ethanoic anhydride}}{CH_3—CO—O—CO—CH_3} + CH_3—OH \rightarrow CH_3—CO—O—CH_3 + CH_3CO_2H$$

3. By the reaction between the silver salt of an acid and an alkyl halide (13.9):

$$R—CO_2^- \, Ag^+ + R'—X \rightarrow R—CO—O—R' + AgX$$

Chemical properties

1. Esters are hydrolysed by heating with mineral acids or alkalis. The catalysed reaction is reversible, and is the exact opposite of esterification, for example:

$$CH_3—CO—O—C_2H_5 + H_2O \overset{H^+}{\rightleftharpoons} CH_3—CO—OH + C_2H_5—OH$$

Consequently, because the equilibrium constant is usually close to 1, some ester always remains at the end of the reaction.

The alkali-catalysed reaction is also reversible:

$$R—CO—O—R' + H_2O \overset{OH^-}{\rightleftharpoons} R—CO—OH + R'—OH$$

However, in this case the carboxylic acid formed reacts with hydroxide ion to give the acid anion:

$$R{-}CO_2H + OH^- \rightleftharpoons R{-}CO_2^- + H_2O$$

Equilibrium in this step lies almost completely to the right-hand side. Consequently, as the acid is formed in the first reaction it is removed by the second, so that eventually practically all the ester is converted into its hydrolysis products. This makes the alkali-catalysed reaction more efficient than the acid-catalysed one, and it is normally the process chosen. It is often referred to as **saponification**; naturally occurring esters are converted into soaps in this way (13.10).

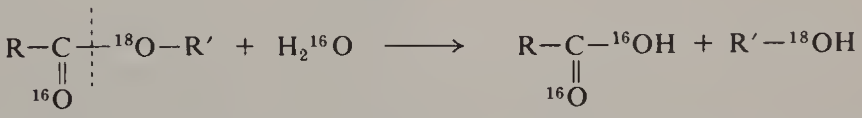
In the hydrolysis of an ester, either the bond between the carbonyl group and the oxygen atom, or the bond between the alkyl group and the oxygen atom, might be broken.

$$R{-}CO{-}O{-}R' + HO{-}H \longrightarrow R{-}CO{-}OH + H{-}O{-}R'$$

or

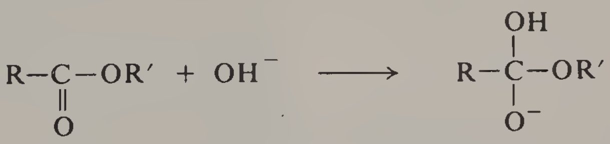
$$R{-}CO{-}O{-}R' + H{-}OH \longrightarrow R{-}CO{-}O{-}H + R'{-}OH$$

A study of the hydrolysis of esters which are labelled with an ^{18}O isotope has shown that it is the former bond that is broken. Thus, when the ester $R{-}C^{16}O{-}^{18}O{-}R'$ is hydrolysed, the ^{18}O isotope is found in the resulting alcohol and not in the carboxylic acid:



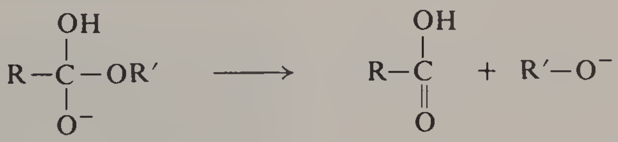
$$R{-}C({=}^{16}O){-}^{18}O{-}R' + H_2{}^{16}O \longrightarrow R{-}C({=}^{16}O){-}^{16}OH + R'{-}^{18}OH$$

The mechanism of alkali-catalysed ester hydrolysis is as follows. The nucleophilic hydroxide ion adds to the carbonyl group of the ester to give an intermediate like that formed in addition to an aldehyde or ketone (12.5):



$$R{-}C({=}O){-}OR' + OH^- \longrightarrow R{-}C(OH)(O^-){-}OR'$$

This intermediate then fragments into the acid and an alkoxide ion:



$$R{-}C(OH)(O^-){-}OR' \longrightarrow R{-}C(OH){=}O + R'{-}O^-$$

The alkoxide ion reacts with the solvent, for example water, to give the alcohol, and the carboxylic acid dissociates:

$$R'{-}O^- + H_2O \rightleftharpoons R'{-}OH + OH^-$$

$$R{-}CO_2H + OH^- \rightleftharpoons R{-}CO_2^- + H_2O$$

2. Esters, like acids, can be reduced with lithium tetrahydridoaluminate to form alcohols:

$$R\text{—}CO\text{—}OR' \xrightarrow{LiAlH_4} R\text{—}CH_2\text{—}OH + R'\text{—}OH$$

e.g.

$$CH_3\text{—}CO\text{—}OCH_3 \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3OH$$

Esters cannot be reduced with sodium tetrahydridoborate (p. 177).

Unlike acids, esters can be reduced with sodium in ethanol to form alcohols:

$$R\text{—}CO\text{—}OR' \xrightarrow{Na/C_2H_5OH} R\text{—}CH_2\text{—}OH + R'\text{—}OH$$

3. Esters react with ammonia, in either concentrated aqueous or alcoholic solution, to form acid amides:

$$R\text{—}CO\text{—}OR' + NH_3 \rightarrow R\text{—}CO\text{—}NH_2 + R'\text{—}OH$$

e.g.

$$CH_3\text{—}CO\text{—}OC_2H_5 + NH_3 \rightarrow \underset{\text{Ethanamide}}{CH_3\text{—}CO\text{—}NH_2} + C_2H_5OH$$

However, the reaction is much slower than with acid chlorides or anhydrides, and amides are therefore more easily made from these acid derivatives.

Uses

Esters are used extensively as solvents and plasticisers (p. 327), and some long-chain esters are used as special lubricants.

Esters are responsible for the smell and flavour of many fruits and flowers. Hence, artificial flavouring essences are prepared from esters. Ethyl methanoate is used in raspberry essence and 3-methylbutyl ethanoate in pear essence. Esters are also used in artificial scents.

Waxes are esters of higher carboxylic acids and higher alcohols. For example, a constituent of beeswax is $C_{15}H_{31}CO_2C_{31}H_{63}$.

Fats and oils are esters of higher carboxylic acids and propane-1,2,3-triol. These esters are known as **glycerides**, and some are used to make soaps (13.10).

Diethyl propanedioate

Diethyl propanedioate (often called malonic ester) is made from the sodium salt of chloroethanoic acid by nucleophilic displacement of chloride by cyanide ion (by heating with potassium cyanide) followed by heating with ethanol in the presence of sulphuric acid:

$$Cl\text{—}CH_2\text{—}CO_2^-\,Na^+ \xrightarrow{CN^-} N{\equiv}C\text{—}CH_2\text{—}CO_2^-\,Na^+ \xrightarrow[H_2SO_4]{2C_2H_5OH}$$

$$\underset{\text{Diethyl propanedioate}}{C_2H_5O_2C\text{—}CH_2\text{—}CO_2C_2H_5}$$

Diethyl propanedioate (a liquid, b.p. 198°C) is a valuable reagent in organic synthesis. Its usefulness stems from the fact that it forms a sodium salt when treated with sodium ethoxide in ethanol,

$$CH_2(CO_2C_2H_5)_2 + C_2H_5O^- Na^+ \rightleftharpoons Na^+ \bar{C}H(CO_2C_2H_5)_2 + C_2H_5OH$$

the anion of which is a nucleophilic reagent. For example, its reaction with an alkyl halide gives an alkylpropanedioic ester which, after hydrolysis and decarboxylation, gives a carboxylic acid:

$$Na^+ \bar{C}H(CO_2C_2H_5)_2 + R{-}X \rightarrow R{-}CH(CO_2C_2H_5)_2 + NaX$$

$$R{-}CH(CO_2C_2H_5)_2 \xrightarrow{2NaOH} R{-}CH(CO_2^- Na^+)_2 \xrightarrow{2HCl}$$

$$R{-}CH(CO_2H)_2 \xrightarrow{heat} R{-}CH_2{-}CO_2H + CO_2$$

Ethyl 3-oxobutanoate

Ethyl 3-oxobutanoate (often called acetoacetic ester) is made by refluxing ethyl ethanoate in the presence of a little ethanol over sodium wire. Sodium ethoxide is formed,

$$Na + C_2H_5OH \rightarrow C_2H_5O^- Na^+ + \tfrac{1}{2}H_2$$

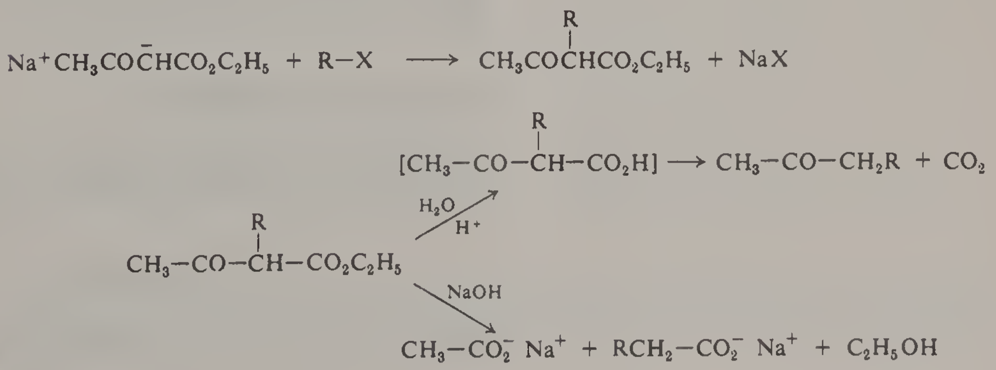
and catalyses the reaction:

$$2CH_3{-}CO_2C_2H_5 \rightarrow CH_3{-}CO{-}CH_2{-}CO_2C_2H_5 + C_2H_5OH$$

Ethyl 3-oxobutanoate is a colourless liquid (b.p. 181°C) which exists as a mixture of two tautomers (15.2). Like diethyl propanedioate, it is useful in organic synthesis as a result of its forming a sodium salt,

$$CH_3COCH_2CO_2C_2H_5 + C_2H_5O^- Na^+ \rightleftharpoons Na^+ CH_3CO\bar{C}HCO_2C_2H_5 + C_2H_5OH$$

whose anion is a nucleophilic reagent. For example, its reaction with an alkyl halide gives a derivative which, after hydrolysis with aqueous acid, yields a ketone and, after hydrolysis with concentrated alkali, yields a carboxylic acid:



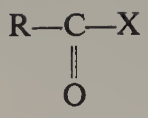
$$Na^+CH_3CO\bar{C}HCO_2C_2H_5 + R{-}X \longrightarrow CH_3CO\overset{R}{\overset{|}{C}}HCO_2C_2H_5 + NaX$$

$$CH_3{-}CO{-}\overset{R}{\overset{|}{C}}H{-}CO_2C_2H_5 \xrightarrow[H^+]{H_2O} [CH_3{-}CO{-}\overset{R}{\overset{|}{C}}H{-}CO_2H] \longrightarrow CH_3{-}CO{-}CH_2R + CO_2$$

$$CH_3{-}CO{-}\overset{R}{\overset{|}{C}}H{-}CO_2C_2H_5 \xrightarrow{NaOH} CH_3{-}CO_2^- Na^+ + RCH_2{-}CO_2^- Na^+ + C_2H_5OH$$

14.3
Acid halides

General formula



$$R{-}\underset{\underset{O}{\|}}{C}{-}X \quad \text{(X is F, Cl, Br or I)}$$

Physical properties

The lower acid halides are mobile, colourless liquids with pungent odours. They fume in moist air owing to their ready hydrolysis to the corresponding halogen acid. Some typical members are in Table 14.2.

Table 14.2. Some acid halides

NAME	FORMULA	B.P./°C
Ethanoyl chloride	$CH_3{-}CO{-}Cl$	52
Ethanoyl bromide	$CH_3{-}CO{-}Br$	77
Ethanoyl iodide	$CH_3{-}CO{-}I$	108
Propanoyl chloride	$CH_3CH_2{-}CO{-}Cl$	80
Benzoyl chloride	$C_6H_5{-}CO{-}Cl$	197

(Methanoyl chloride has not been isolated.)

Preparation

Acid chlorides are prepared by the reaction between a carboxylic acid and phosphorus trichloride, phosphorus pentachloride, or sulphur dichloride oxide:

$$3R{-}CO{-}OH + PCl_3 \rightarrow 3R{-}CO{-}Cl + H_3PO_3$$

$$R{-}CO{-}OH + PCl_5 \rightarrow R{-}CO{-}Cl + POCl_3 + HCl$$

$$R{-}CO{-}OH + SOCl_2 \rightarrow R{-}CO{-}Cl + SO_2 + HCl$$

The choice of reagent is governed by the boiling points of the products. If the acid halide has a very low boiling point (e.g. ethanoyl chloride), PCl_3 is used and the halide is easily separated by distillation from phosphorous acid (which decomposes at 200°C). If the acid halide has a very high boiling point (e.g. benzoyl chloride), PCl_5 can be used; fractional distillation gives first $POCl_3$ (b.p. 107°C) and then the acid chloride. If it has an intermediate boiling point (e.g. propanoyl chloride), $SOCl_2$ is suitable; the gaseous SO_2 and HCl pass off first.

Acid bromides and iodides are made from carboxylic acids and phosphorus tribromide and phosphorus tri-iodide respectively. These phosphorus halides are prepared *in situ* (p. 117).

Chemical properties

The principal reactions of acid halides are with water, ammonia and amines, in which the overall reaction can be described by the equation:

$$R{-}CO{-}X + H{-}Y \rightarrow R{-}CO{-}Y + H{-}X$$

The process is known as **acylation**. **Ethanoylation** is the name reserved for the

substitution of the **ethanoyl** group, $CH_3CO—$, for example by ethanoyl chloride or ethanoic anhydride. The introduction of the **benzoyl** group, $C_6H_5CO—$, by, for example, benzoyl chloride, is known as **benzoylation**.
Benzoylation generally takes place more slowly than ethanoylation.

1. Aliphatic acid halides are readily hydrolysed:

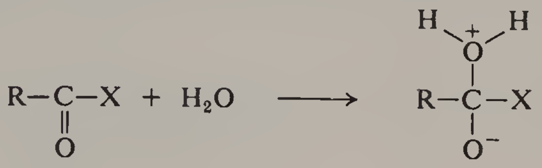
$$R—CO—X + H_2O \rightarrow R—CO—OH + HX$$

e.g.

$$CH_3—CO—Cl + H_2O \rightarrow CH_3—CO—OH + HCl$$

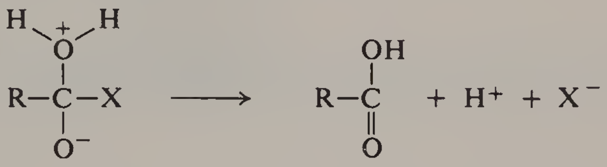
Thus, when the stopper is removed from a bottle of ethanoyl chloride, white fumes are seen, owing to the interaction of hydrogen chloride with the moist air.

Reaction occurs by addition of water to the carbonyl group:



$$R-\underset{\underset{O}{\|}}{C}-X + H_2O \longrightarrow R-\overset{\overset{H\diagdown\overset{+}{O}\diagup H}{|}}{\underset{\underset{O^-}{|}}{C}}-X$$

followed by loss of a proton and the halide ion, X^-:



$$R-\overset{\overset{H\diagdown\overset{+}{O}\diagup H}{|}}{\underset{\underset{O^-}{|}}{C}}-X \longrightarrow R-\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{C}} + H^+ + X^-$$

Hydrolysis is far easier than with esters, which are unaffected by water alone although they react with hydroxide ion. The reason is that a halogen substituent —X is more strongly electron-attracting than an alkoxide substituent —OR′; the carbon atom of the carbonyl group is therefore more electron-deficient in an acid halide than in an ester and reacts with water, H_2O, a weak nucleophilic reagent, whereas for an ester a much stronger nucleophilic reagent, the hydroxide ion, OH^-, is necessary.

2. Acid halides react with alcohols and phenols to form esters, for example:

$$CH_3—CO—Cl + CH_3—OH \rightarrow \underset{\text{Methyl ethanoate}}{CH_3—CO—O—CH_3} + HCl$$

$$CH_3—CO—Cl + C_6H_5—OH \rightarrow \underset{\text{Phenyl ethanoate}}{CH_3—CO—O—C_6H_5} + HCl$$

$$C_6H_5—CO—Cl + C_6H_5—OH \rightarrow \underset{\text{Phenyl benzoate}}{C_6H_5—CO—O—C_6H_5} + HCl$$

The mechanisms of these reactions are similar to those between acid halides and water, with the oxygen atom of the alcohol, R—O—H, or the phenol, $C_6H_5—O—H$, acting as the nucleophile.

3. Acid halides react with ammonia to form acid amides, for example:

$$CH_3{-}CO{-}Cl + NH_3 \rightarrow \underset{\text{Ethanamide}}{CH_3{-}CO{-}NH_2} + HCl$$

$$NH_3 + HCl \rightarrow \overset{+}{N}H_4\ Cl^-$$

Acid halides react with primary amines in a similar way:

$$CH_3{-}CO{-}Cl + CH_3{-}NH_2 \rightarrow \underset{N\text{-Methylethanamide}}{CH_3{-}CO{-}NH{-}CH_3} + HCl$$

$$CH_3{-}NH_2 + HCl \rightarrow CH_3{-}\overset{+}{N}H_3\ Cl^-$$

The reactions have mechanisms similar to that in hydrolysis, with the nitrogen atom acting as the nucleophile.

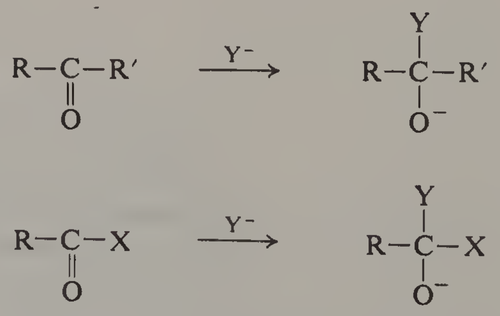
4. Acid halides react with *anhydrous* sodium salts of carboxylic acids to form acid anhydrides (14.4), for example:

$$CH_3{-}CO{-}Cl + CH_3{-}CO_2^-\ Na^+ \rightarrow \underset{\text{Ethanoic anhydride}}{CH_3{-}CO{-}O{-}CO{-}CH_3} + NaCl$$

The carboxylate ion acts as the nucleophile and the mechanism of the reaction is as described above.

The reactions of acid halides with nucleophilic reagents, such as reactions 1-4, can be compared with those of aldehydes and ketones with nucleophilic reagents on the one hand and with those of primary alkyl halides with nucleophilic reagents on the other.

Like aldehydes and ketones, acid halides react by addition of a nucleophile (symbolised as Y^-):



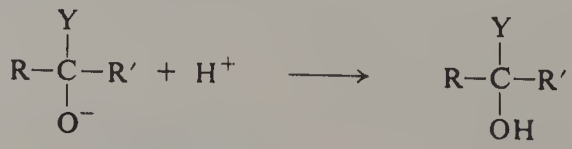
$$R{-}\underset{\underset{O}{\|}}{C}{-}R' \xrightarrow{Y^-} R{-}\overset{\overset{Y}{|}}{\underset{\underset{O^-}{|}}{C}}{-}R'$$

$$R{-}\underset{\underset{O}{\|}}{C}{-}X \xrightarrow{Y^-} R{-}\overset{\overset{Y}{|}}{\underset{\underset{O^-}{|}}{C}}{-}X$$

In the case of the acid halide, the halide ion then breaks off:

$$R{-}\overset{\overset{Y}{|}}{\underset{\underset{O^-}{|}}{C}}{-}X \longrightarrow R{-}\overset{\overset{Y}{|}}{\underset{\underset{O}{\|}}{C}} + X^-$$

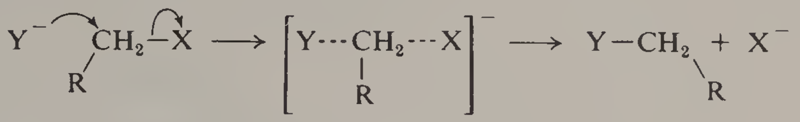
and the overall process is a *substitution reaction*. In contrast, in the case of aldehydes and ketones, the group —H or —alkyl does not form a stable anion, so that instead of one of these groups breaking off, a proton is transferred to the intermediate adduct from the solvent:



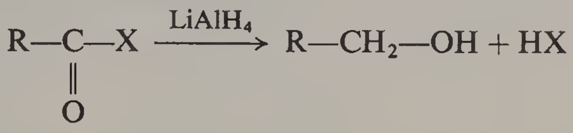
$$R{-}\overset{\overset{Y}{|}}{\underset{\underset{O^-}{|}}{C}}{-}R' + H^+ \longrightarrow R{-}\overset{\overset{Y}{|}}{\underset{\underset{OH}{|}}{C}}{-}R'$$

and the overall process is an *addition reaction.*

Primary alkyl halides, like acid halides, undergo substitution with nucleophiles, but in this case an intermediate adduct cannot be formed since carbon cannot form 5 bonds; instead, the approach of the nucleophile to the alkyl group is concerted with the departure of halide ion:

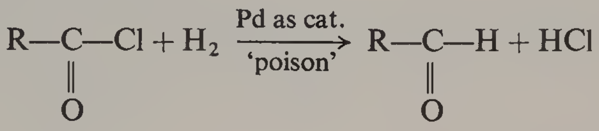


5. Acid halides are reduced by lithium tetrahydridoaluminate to alcohols:



$$R\text{—}\overset{}{\underset{\underset{O}{\|}}{C}}\text{—}X \xrightarrow{LiAlH_4} R\text{—}CH_2\text{—}OH + HX$$

This reduction occurs by way of the aldehyde, RCHO, and in another method of reduction, due to Rosenmund, it is possible to obtain the aldehyde as the product. The method is to pass hydrogen into a solution of the acid chloride in the presence of palladium as catalyst suspended on barium sulphate; a mixture of sulphur and quinoline is added as a 'poison' to prevent further reduction:



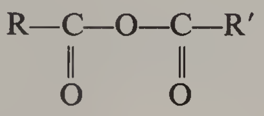
$$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}Cl + H_2 \xrightarrow[\text{'poison'}]{\text{Pd as cat.}} R\text{—}\underset{\underset{O}{\|}}{C}\text{—}H + HCl$$

Uses

Acid halides (normally the chlorides) are used mainly as acylating agents (i.e. to introduce the group RCO—) for the preparation of esters and acid amides.

14.4
Acid anhydrides

General formula



$$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}O\text{—}\underset{\underset{O}{\|}}{C}\text{—}R'$$

Physical properties

The lower aliphatic members are mobile, colourless liquids with pungent smells. The simplest aromatic member, benzoic anhydride, is a white solid, m.p. 42°C. Some typical acid anhydrides are in Table 14.3.

Table 14.3. Some acid anhydrides

NAME	FORMULA	B.P./°C
Ethanoic anhydride	$(CH_3CO)_2O$	136
Propanoic anhydride	$(CH_3CH_2CO)_2O$	168
Benzoic anhydride	$(C_6H_5CO)_2O$	360

Preparation

By the reaction between an acid chloride and the anhydrous sodium salt of a carboxylic acid, for example:

$$\underset{\qquad}{CH_3{-}CO{-}Cl + CH_3{-}CO_2^-\ Na^+} \rightarrow \underset{\text{Ethanoic anhydride}}{CH_3{-}CO{-}O{-}CO{-}CH_3} + NaCl$$

'Mixed' acid anhydrides can be formed, using an acid chloride and a sodium salt with different groups, R and R′:

$$R{-}CO{-}Cl + R'{-}CO_2^-\ Na^+ \rightarrow R{-}CO{-}O{-}CO{-}R' + NaCl$$

Manufacture of ethanoic anhydride

Ethanoic anhydride is manufactured by passing ethenone through ethanoic acid:

$$CH_2{=}C{=}O + CH_3CO_2H \rightarrow CH_3{-}CO{-}O{-}CO{-}CH_3$$

Ethenone is manufactured by the cracking of propanone vapour at 700°C:

$$CH_3{-}CO{-}CH_3 \rightarrow CH_2{=}C{=}O + CH_4$$

Chemical properties

Acid anhydrides react with nucleophilic reagents in the same way as acid halides except that, because the group R′CO—O— in an anhydride RCO—OCOR′ is less strongly electron-attracting than the halogen X in an acid halide RCO—X, reaction is slower. Typical examples are:

1. With water, to give the corresponding acid, for example:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3CO_2H$$

2. With alcohols or phenols, to give esters, for example:

$$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3CO_2C_2H_5 + CH_3CO_2H$$

3. With concentrated aqueous ammonia, to give acid amides, for example:

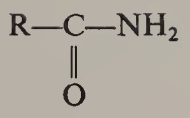
$$(CH_3CO)_2O + NH_3 \rightarrow \underset{\text{Ethanamide}}{CH_3CONH_2} + CH_3CO_2H$$

Uses of ethanoic anhydride

The principal use of ethanoic anhydride is in the manufacture of cellulose ethanoate (p. 297). In the laboratory, it is used to make esters (ethanoates) (p. 212) and acid amides (p. 221).

14.5
Acid amides

General formula



$$R{-}\underset{\underset{O}{\|}}{C}{-}NH_2$$

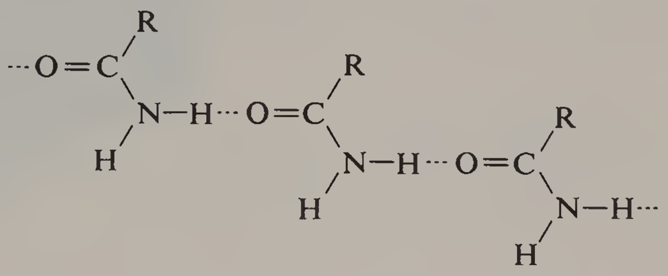
Physical properties

Table 14.4. Some acid amides

NAME	FORMULA	M.P./°C	B.P./°C
Methanamide	$H{-}CO{-}NH_2$	2	193
Ethanamide	$CH_3{-}CO{-}NH_2$	82	222
Propanamide	$CH_3CH_2{-}CO{-}NH_2$	79	222

With the exception of methanamide, amides are white crystalline solids. The lower members are soluble in water; all amides are soluble in organic solvents. As ordinarily prepared, ethanamide has the characteristic smell of mice, owing to the presence of the methyl derivative $CH_3{-}CO{-}NH{-}CH_3$; pure ethanamide has no smell.

The high melting points and boiling points of amides are due to the formation of hydrogen-bonds between the oxygen atom of one molecule and the amino-hydrogen atom of another:



Preparation

1. By the dehydration of the ammonium salt of a carboxylic acid. For example, ethanamide is generally prepared by refluxing a solution of ammonium carbonate in an excess of ethanoic acid for about 4 hours; ammonium ethanoate is first formed and then dehydrated:

$$CH_3CO_2H \xrightarrow{(NH_4)_2CO_3} CH_3CO_2^-\ NH_4^+ \rightarrow CH_3CONH_2 + H_2O$$

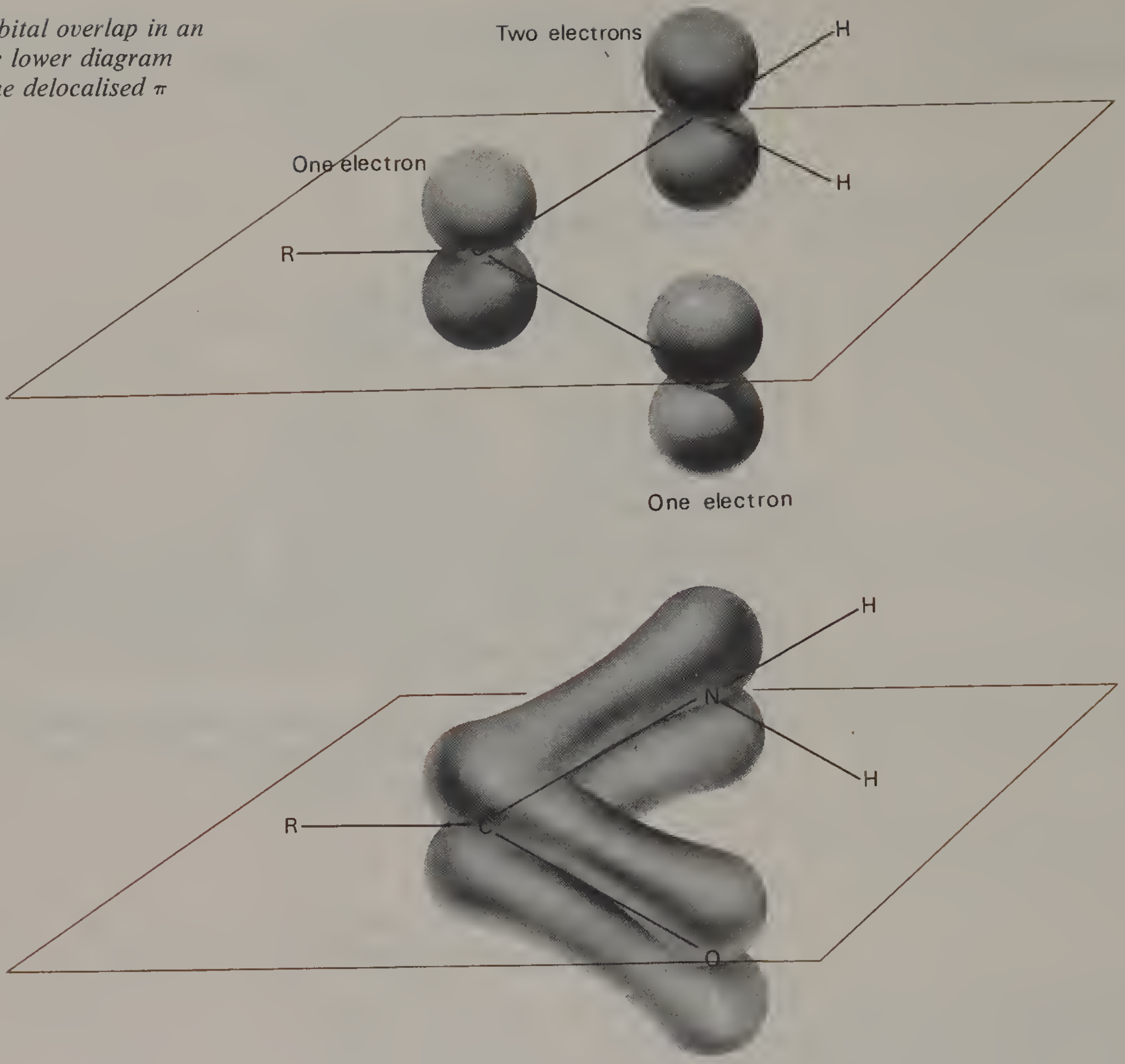
2. By the action of ammonia on esters (14.2), acid halides (14.3) or acid anhydrides (14.4).

Chemical properties

1. Amides are much weaker bases than amines, even though both contain the group $-NH_2$; thus, amides are neutral to litmus and do not dissolve in hydrochloric acid to form salts.

This is because the orbital on the nitrogen atom which contains the unshared pair of electrons interacts with the *p* orbital of the adjacent carbon atom (Fig. 14.1), giving increased delocalisation in an amide as compared with an amine.

FIG. 14.1. p-*Orbital overlap in an acid amide; the lower diagram shows one of the delocalised π orbitals*



Therefore, relative to an amine, an amide resists reaction with a proton since this process requires the use of the unshared pair of electrons on nitrogen in the formation of the new N—H bond and so results in the loss of the extra bonding.

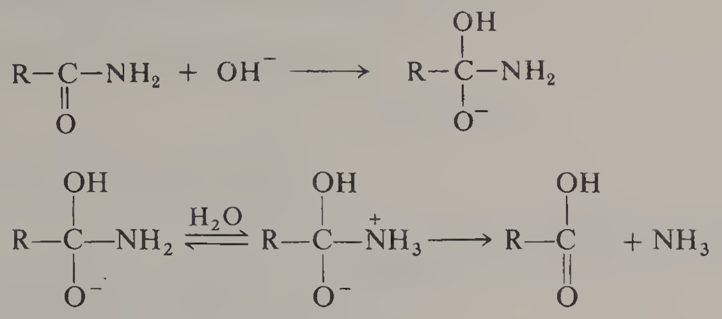
2. Amides are hydrolysed by heating with a mineral acid (usually hydrochloric acid), for example:

$$CH_3\text{—}CO\text{—}NH_2 \xrightarrow[H^+]{H_2O} CH_3\text{—}CO_2H + NH_4^+$$

They are also hydrolysed by heating with an alkali such as caustic soda, for example:

$$CH_3\text{—}CO\text{—}NH_2 \xrightarrow[OH^-]{H_2O} CH_3\text{—}CO_2^- + NH_3$$

The alkali-catalysed reaction occurs by a similar mechanism to that of the hydrolysis of esters and acid halides. The hydroxide ion adds to the carbonyl group of the amide to give an adduct which takes up a proton from the solvent and then eliminates ammonia:



$$R{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + OH^- \longrightarrow R{-}\overset{\overset{OH}{|}}{\underset{\underset{O^-}{|}}{C}}{-}NH_2$$

$$R{-}\overset{\overset{OH}{|}}{\underset{\underset{O^-}{|}}{C}}{-}NH_2 \xrightleftharpoons{H_2O} R{-}\overset{\overset{OH}{|}}{\underset{\underset{O^-}{|}}{C}}{-}\overset{+}{N}H_3 \longrightarrow R{-}\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{C}} + NH_3$$

$$R{-}CO_2H + OH^- \longrightarrow R{-}CO_2^- + H_2O$$

The group —NH_2 is less strongly electron-attracting than —OR′, so that amides are less easily hydrolysed by alkali than esters, RCO_2R', and much less easily than acid chlorides.

The fact that heating an amide with caustic soda liberates ammonia while an amine does not react enables the two types of compound to be readily distinguished. Amides can also be distinguished from ammonium salts in this way, for the latter liberate ammonia in the cold,

$$R{-}CO_2^-\,NH_4^+ + NaOH \rightarrow R{-}CO_2^-\,Na^+ + NH_3 + H_2O$$

whereas the former do so only on heating.

3. When amides are distilled over phosphorus pentoxide, acid nitriles are formed, for example:

$$CH_3{-}CO{-}NH_2 \xrightarrow{P_4O_{10}} \underset{\text{Ethanenitrile}}{CH_3{-}C{\equiv}N} + H_2O$$

4. Like amines, amides react with nitrous acid to liberate nitrogen, for example:

$$CH_3{-}CO{-}NH_2 + HNO_2 \rightarrow CH_3{-}CO_2H + N_2 + H_2O$$

5. Amides react with bromine in a solution of sodium hydroxide to give amines (**Hofmann reaction**), for example:

$$CH_3{-}CO{-}NH_2 \xrightarrow{Br_2/NaOH} \underset{\text{Methylamine}}{CH_3{-}NH_2} + CO_2$$

Carbamide

Although carbamic acid, $H_2N{-}CO_2H$, has never been isolated, its acid amide, carbamide (urea) ($H_2N{-}CO{-}NH_2$), is stable. It can be made by heating ammonium cyanate to dryness (1.1) or by the action of ammonia on carbonyl chloride:

$$Cl{-}CO{-}Cl + 4NH_3 \rightarrow H_2N{-}CO{-}NH_2 + 2NH_4Cl$$

Physical properties of carbamide

Carbamide is a white, crystalline solid (m.p. 133°C) which is soluble in water and alcohol but insoluble in most organic solvents.

Manufacture of carbamide

By heating excess of ammonia with carbon dioxide at 200°C and 200 atmospheres pressure:

$$CO_2 + 2NH_3 \rightarrow H_2N{-}CO_2^-\ NH_4^+ \rightarrow H_2N{-}CO{-}NH_2 + H_2O$$

Chemical properties of carbamide

1. Carbamide is a monoacidic base; it is a stronger base than simple acid amides like ethanamide but a weaker base than amines. For example, it forms an insoluble nitrate, $H_2N{-}CO{-}NH_3^+\ NO_3^-$.

2. Carbamide is hydrolysed when heated with a solution of alkali:

$$H_2N{-}CO{-}NH_2 + 2NaOH \rightarrow Na_2CO_3 + 2NH_3$$

3. Carbamide reacts with nitrous acid to form nitrogen:

$$H_2N{-}CO{-}NH_2 + 2HNO_2 \rightarrow CO_2 + 3H_2O + 2N_2$$

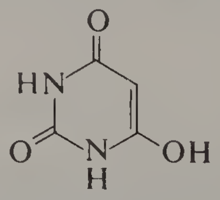
4. When carbamide is heated above its melting point, a compound known as **biuret** is formed:

$$2H_2N{-}CO{-}NH_2 \rightarrow \underset{\text{Biuret}}{H_2N{-}CO{-}NH{-}CO{-}NH_2} + NH_3$$

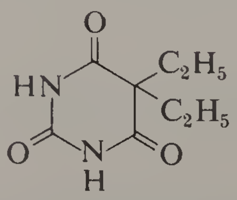
If an alkaline solution of biuret is treated with a drop of copper(II) sulphate solution, a violet colour appears. This is known as the **biuret test**, and is a test for all compounds containing the **peptide** linkage, —CO—NH—, such as proteins (18.2).

Uses of carbamide

1. As a fertilizer. Carbamide (sold under its older name, urea) contains 46% nitrogen and is (except for ammonia) the most concentrated nitrogeneous fertilizer available. It is very satisfactory for feeding quick-growing crops in hot climates.
2. In the manufacture of carbamide-methanal plastics (p. 333).
3. In the manufacture of melamine, used to make melamine-methanal plastics (p. 333).
4. In the manufacture of a range of fine chemicals including the barbiturates, a group of drugs with sedative properties of which the parent is barbituric acid; for example:



Barbituric acid



Veronal

14.6
Acid nitriles

The compounds are also known as cyanides.

General formula

$$R—C\equiv N$$

Physical properties

The lowest members (except for hydrogen cyanide) are colourless liquids with pleasant smells. They are fairly soluble in water and very soluble in organic compounds.

Some typical members are in Table 14.5.

Table 14.5. Some acid nitriles

NAME	FORMULA	B.P./°C
Methanenitrile (Hydrogen cyanide)	$H—CN$	26
Ethanenitrile (Methyl cyanide)	$CH_3—CN$	81
Propanenitrile (Ethyl cyanide)	$C_2H_5—CN$	97
Benzonitrile (Phenyl cyanide)	$C_6H_5—CN$	190

Preparation

1. By refluxing an alcoholic solution of an alkyl halide and potassium cyanide, for example:

$$CH_3—I + KCN \rightarrow \underset{\text{Ethanenitrile}}{CH_3—CN} + KI$$

Reaction takes place by nucleophilic displacement of halide ion by cyanide ion (S_N2 reaction; 9.3).

2. By dehydration of the ammonium salt of a carboxylic acid or an amide with phosphorus pentoxide, for example:

$$CH_3—CO_2^- NH_4^+ \xrightarrow{P_4O_{10}} CH_3—CO—NH_2 \xrightarrow{P_4O_{10}} CH_3—C\equiv N$$

Chemical properties

1. Nitriles are hydrolysed, *via* the amide, by refluxing with either mineral acid:

$$CH_3—C\equiv N \xrightarrow[H^+]{H_2O} CH_3—CO—NH_2 \xrightarrow[H^+]{H_2O} CH_3—CO_2H + NH_4^+$$

or alkali:

$$CH_3—C\equiv N \xrightarrow[OH^-]{H_2O} CH_3—CO—NH_2 \xrightarrow[OH^-]{H_2O} CH_3—CO_2^- + NH_3$$

2. Nitriles are reduced to primary amines by sodium and an alcohol, and by lithium tetrahydridoaluminate, for example:

$$CH_3—C\equiv N \rightarrow \underset{\text{Ethylamine}}{CH_3—CH_2—NH_2}$$

$$C_6H_5—C\equiv N \rightarrow \underset{\text{(Phenylmethyl)amine}}{C_6H_5—CH_2—NH_2}$$

14.7 Isocyano-compounds

Isocyano-compounds (isonitriles) have the structure

$$R{-}\overset{+}{N}{\equiv}\overset{-}{C}$$

and are isomers of the nitriles, $R{-}C{\equiv}N$. The lower members are unpleasant-smelling liquids.

The compounds are made by refluxing an alcoholic solution of an alkyl halide and silver cyanide:

$$R{-}X + AgCN \rightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C} + AgX$$

or by heating a primary amine and trichloromethane with an ethanolic solution of alkali (the carbylamine reaction; 9.4):

$$R{-}NH_2 + CHCl_3 + 3KOH \rightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C} + 3KCl + 3H_2O$$

They are stable to alkali (unlike nitriles) but are readily hydrolysed by mineral acid to primary amines:

$$R{-}\overset{+}{N}{\equiv}\overset{-}{C} + 2H_2O \xrightarrow{H^+} R{-}NH_2 + HCO_2H$$

They can thus be distinguished from their isomers, the nitriles, which are hydrolysed to the ammonium salt of the corresponding carboxylic acid.

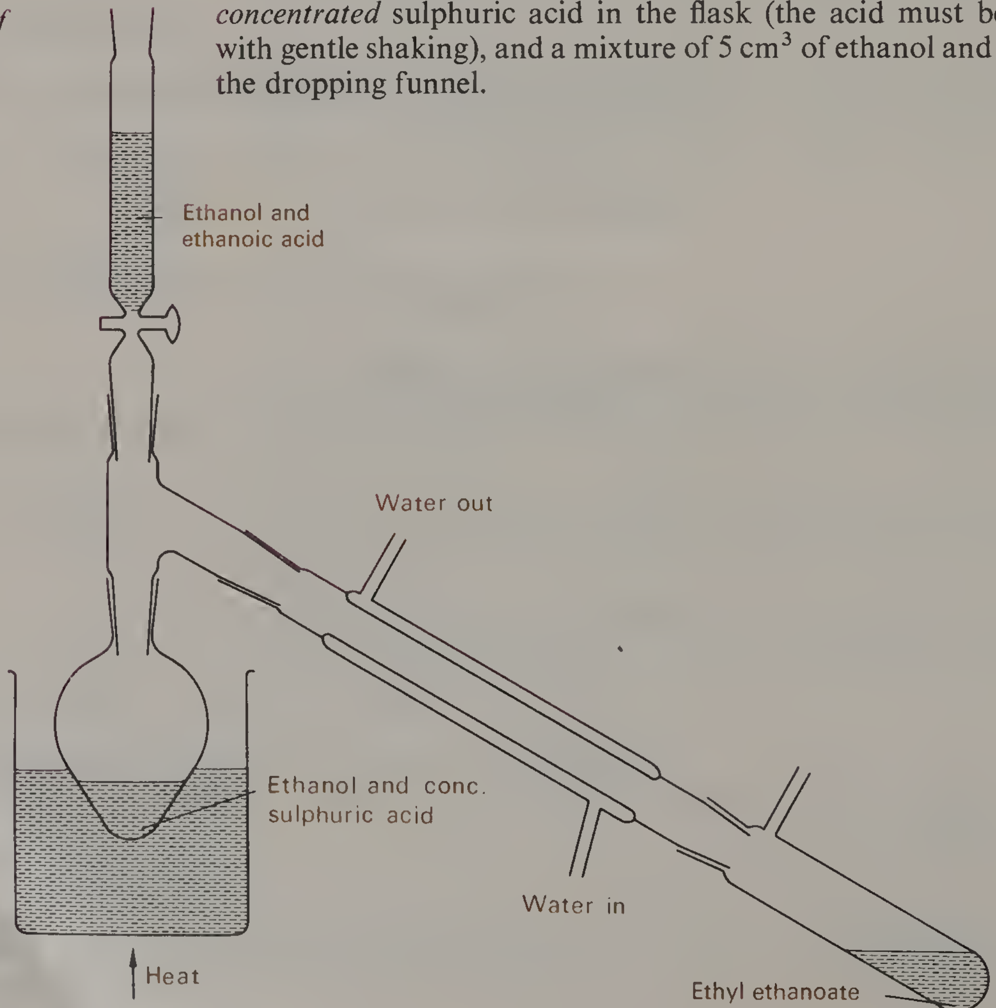
14.8 Practical work

Small-scale preparation of an ester

In this example, ethyl ethanoate is prepared from ethanoic acid and ethanol.

Set up the apparatus (Fig. 14.2), with 5 cm^3 of ethanol and 5 cm^3 of *concentrated* sulphuric acid in the flask (the acid must be added slowly, with gentle shaking), and a mixture of 5 cm^3 of ethanol and ethanoic acid in the dropping funnel.

FIG. 14.2. *Preparation of ethyl ethanoate*



Heat the oil-bath to 140°C and add the mixture from the funnel at the same rate as the ester distils over.

When distillation stops, transfer the distillate to a separating funnel and add 5 cm^3 of a 30 per cent solution of sodium carbonate. Shake, removing the stopper from time to time to relieve the pressure due to carbon dioxide.

Remove the lower (aqueous) layer and add a solution of 5 g of calcium chloride in 5 cm^3 of water to the separating funnel and shake the mixture (to remove excess of ethanol). Remove the lower layer again.

Pour the ester into a test-tube and add 2 or 3 pieces of anhydrous calcium chloride. Stopper the tube and shake it. Decant the clear liquid into a flask and distil it (cf. Fig. 2.2), collecting the fraction boiling between 75 and 79°C.

Preparation of phenyl benzoate

Details of the preparation of phenyl benzoate are given on p. 161.

Reactions of esters

1. *Saponification of an ester.* Details of the saponification of an ester, ethyl benzoate, are given on p. 203.

2. *Saponification of a fat.* Boil for 20 minutes under reflux about 1 g of lard or olive oil (or any fat), 1 g of potassium hydroxide and 10 cm^3 of ethanol, until no more oil is observed when a few drops of the mixture are added to water. Distil the reaction mixture to remove the ethanol, and dissolve the residue in 15 cm^3 of hot water.

(a) To 5 cm^3 of the solution of the residue, add slowly a saturated solution of sodium chloride. Filter the precipitate and test the soap for its lathering properties.

(b) To another 5 cm^3 of the solution, add 5 cm^3 of water. Shake well.

Reactions of ethanoyl chloride and benzoyl chloride

Take great care when handling these compounds.

1. Carry out the following reactions with both ethanoyl chloride and benzoyl chloride and compare their reactivities:
   - (a) To 5 drops of the acid chloride in a test-tube, add 5 drops of water. Test the gas evolved.
   - (b) To 5 drops of ethanol, add 2 drops of the acid chloride. Warm the mixture *if necessary.* Dilute the solution with 5 drops of water and note the smell of the organic product.

2. (a) To 5 drops of phenylamine, add 2 drops of ethanoyl chloride (**CARE**). A vigorous reaction takes place, and a white precipitate of *N*-phenylethanamide is formed.

(b) *Schotten-Baumann reaction.* To 3 drops of phenylamine in a test-tube, add 5 cm^3 of dilute sodium hydroxide solution. Shake to form a fine oily suspension and add 5 drops of benzoyl chloride. Fit a cork to the tube and shake for a minute. Cool the tube and contents under the tap, removing the cork periodically to release the pressure. Filter the residue of *N*-phenylbenzamide, using a small Buchner funnel and flask.

Transfer the residue to another test-tube and dissolve it in the smallest possible quantity of hot ethanol. Filter if necessary and allow the solution to cool. (If the crystals do not appear within 5 minutes, add a few drops of water, and 'scratch' the sides of the test-tube with a glass rod to 'seed'.) Filter the crystals, and dry them between pads of filter papers. M.p. 163°C.

Reactions of ethanoic anhydride

1. To 5 drops of ethanoic anhydride in a test-tube, add 5 drops of water. Shake the mixture and note the rate of reaction compared with that between ethanoyl chloride and water.

2. *Preparation of* N-*phenylethanamide.* See p. 266.

3. *Preparation of cellulose ethanoate.* See p. 299.

Reactions of ethanamide

1. To about 0·1 g of ethanamide in a test-tube, add 2 cm^3 of dilute sodium hydroxide solution. Boil, and test the vapour evolved with moist red litmus paper.

2. To about 0·1 g of ethanamide in a test-tube, add 3 drops of bromine (**CARE**). Add 1–2 cm^3 of dilute sodium hydroxide solution; cork the test-tube and shake for about a minute.

Remove the cork, add one pellet of sodium hydroxide and boil the solution gently. Test the gas by (a) its smell, (b) its action on moist red litmus paper.

Reactions of ethanenitrile

1. To 5 drops of ethanenitrile in a test-tube, add 5 drops of dilute sodium hydroxide solution. Warm gently and test the gas evolved with moist red litmus paper.

2. To 5 drops of ethanenitrile in a test-tube, add about 0·1 g of zinc dust followed by 10 drops of *concentrated* hydrochloric acid. When the effervescence due to the evolution of hydrogen has more or less stopped, add sodium hydroxide solution until the mixture is alkaline. Warm the mixture and test the gas evolved with moist red litmus paper.

Reactions of carbamide

1. Carbamide is a monoacidic base. To 1 cm^3 of hot water in a test-tube, add some crystals of carbamide until the solution is saturated. Decant this solution into a clean test-tube and add *concentrated* nitric acid dropwise. A white precipitate of the nitrate is formed.

2. *Hydrolysis of carbamide.* (a) To 0·1 g of carbamide in a test-tube, add 1 cm^3 of 2M sodium hydroxide solution and boil the mixture. Test the vapour evolved with moist red litmus paper and note the smell of the gas evolved.

This reaction shows that the amide group, —CONH_2, is present.

(b) Action of the enzyme, urease. Experiment 3(a) in Section 18.4.

3. Dissolve a few crystals of sodium nitrite in water in a test-tube and cool the solution in a beaker of ice. Add 1 cm^3 of dilute hydrochloric acid. (There may be some effervescence due to reaction between sodium nitrite and the acid.) Add a few crystals of carbamide. Observe whether any gas is evolved.

4. Heat about 0·1 g of carbamide in a test-tube until it melts. Test gases evolved with moist red litmus paper.

Continue to heat the residue gently for a further 3 minutes. Cool it and add 10 drops of water followed by 2 drops of a dilute solution of copper(II) sulphate followed by dilute sodium hydroxide solution until the mixture is alkaline.

A violet coloration confirms that the residue contains a compound which has a peptide link, —CO—NH—. This compound is called biuret and the test is named after it, the **biuret test**.

14.9 Questions

1 Name and give the structural formulae of the aliphatic acids and esters which have an empirical formula C_2H_4O and a molecular weight of 88.

Outline the chemical tests that you would apply to enable you to distinguish between each isomer. (L)

2 Give **three** general methods for the preparation of esters. State which of them you would select for the preparation of phenyl benzoate and outline the procedure you would adopt.

How would you prepare a pure water-free specimen of ethanol from ethyl benzoate? Briefly indicate the necessary conditions for each step.

Give a brief account of the constitution of naturally occurring fats, and show what useful products may be derived from them. (JMB)

3 Describe the preparation from ethanol of pure samples of ethanoic acid and of ethyl ethanoate.

How, and under what conditions, does ethanoic acid react with (a) thionyl chloride, (b) methylamine, and (c) soda lime? (C(T))

4 0·6 g of ethanoic acid were mixed with an equimolecular amount of ethanol and the mixture was sealed in a small glass tube which was immersed in a bath of boiling water. When equilibrium had been reached the glass tube was removed from the water bath and broken open under the surface of about 30 cm^3 of water in a conical flask. The resulting mixture was titrated with 0·1 M sodium hydroxide using phenolphthalein as indicator and required 33·30 cm^3 of the alkali.

Calculate the equilibrium constant for the esterification of ethanol by ethanoic acid.

Describe in outline how you would modify the above reaction conditions for the preparation of a pure sample of ethyl ethanoate. (AEB)

5 What do you understand by the equilibrium constant of a reversible reaction? What do you need to know if you are to predict correctly the qualitative effect of temperature on this constant? State and explain the principle involved.

When one gram-mole each of ethanoic acid and ethanol are mixed together at 20°C, two-thirds of a gram-mole of ethyl ethanoate is formed. How many gram-moles of ethyl ethanoate would be present eventually if one gram-mole of water was added to the above mixture? (O)

6 Give the structural formulae of the functional groups characteristic of (a) carboxylic acids, (b) acid chlorides, (c) acid anhydrides, (d) primary amines, (e) amides.

Suggest a scheme whereby ethanoic acid might be obtained from methane as starting material. Indicate by equations how ethanoic acid might be converted into the corresponding acid chloride, acid anhydride, acid amide and ethyl ester respectively. (AEB)

7 How would you prepare ethanoyl chloride from ethanoic acid?

Name the products and write the equations for the reactions of ethanoyl chloride with: (a) sodium hydroxide, (b) ammonia, (c) ethanol, (d) phenol, (e) anhydrous sodium ethanoate. (C(N, T))

8 Describe, with essential practical details, the preparation of ethanamide from ammonium ethanoate.

Describe the reactions which occur between ethanamide and (a) phosphorus pentoxide, (b) nitrous acid, and (c) bromine and sodium hydroxide solution.

9 An organic compound **W**, on analysis, gave $C = 40\%$, $H = 8{\cdot}5\%$, $N = 23{\cdot}7\%$, $O = 27{\cdot}1\%$ by mass. Refluxing **W** with dilute hydrochloric acid produced a compound **X** which contained 40% carbon by mass and had the general formula $C_nH_{2n}O_2$.

X was also prepared by the oxidation of a compound **Y** which had the general formula $C_nH_{2n}O$.

- (a) Calculate the empirical formula of **W**.
- (b) Determine the molecular formula of **X** and hence deduce the molecular formula of **W**.
- (c) Write a balanced equation to represent the reaction which occurred when **W** was refluxed with dilute hydrochloric acid.
- (d) Identify **Y** giving reasons for your answer.
- (e) Give **two** chemical tests to distinguish between **Y** and butanone ($CH_3CH_2COCH_3$). (AEB)

10 For each of the following pairs of substances describe **one** simple chemical test which would serve to distinguish between them:

- (a) ethanoyl chloride and ethanoic anhydride;
- (b) ethanal and propanone;
- (c) methanoic acid and ethanoic acid;
- (d) ethanamide and phenylamine.

In each case state the conditions under which the reaction occurs and give the equation for it. (L)

11 Compare the hydrolysis of (a) ethyl benzoate, (b) benzoyl chloride, (c) benzamide. Describe how you would isolate a pure specimen of the common product of hydrolysis and explain how it may be reconverted into (a), (b) and (c). (W)

12 By means of equations, supplemented by brief notes on relative speeds of reaction, indicate what reactions occur between ammonia and the following compounds: (a) chloromethane, (b) ethanoyl chloride, (c) chlorobenzene, (d) ethanal, (e) ethanoic acid, (f) methyl propanoate.

By what *simple* chemical means could you quickly distinguish between the product formed from (b) and that formed from (e)? (JMB)

13 In this problem the molecular formula of some of the compounds is given in brackets.

- (i) A substance X (C_4H_8ONBr) yielded ammonia when boiled under reflux with an aqueous solution of sodium hydroxide.
- (ii) A portion of the resulting solution was acidified, treated with chlorine, and then shaken with trichloromethane. Two layers were formed, the lower of which was orange in colour.
- (iii) The remainder of the solution from (i) was evaporated to a solid substance which on acidification and distillation yielded an acidic substance Y ($C_4H_8O_3$).
- (iv) On oxidation Y yielded Z ($C_4H_6O_3$). Z gave a precipitate with 2,4-dinitrophenylhydrazine, but not with Fehling's solution.

Suggest a possible structure for X, Y and Z, and describe what happens in the reactions outlined above. (L(Nuffield)(S))

14 On analysis a compound X of molecular weight 59 was found to contain 40·67 per cent carbon, 8·5 per cent hydrogen, 23·72 per cent nitrogen, the remainder being oxygen. Derive the formula of X, write a structural formula and name the compound.

Stating essential conditions of reaction, describe how the compound you name for X reacts with (a) phosphorus pentoxide, (b) sodium hydroxide, (c) nitrous acid, (d) bromine and potassium hydroxide. (AEB)

15 The reaction between ethanoic acid and ethanol is catalysed by hydrogen ions. Describe how you would attempt to prove this.

16 The percentage composition of an aliphatic compound was found to be C = 20·0, H = 6·7, O = 26·7, N = 46·6. A solution of 0·25 g of the compound in 20 g of water froze at −0·39°C. What was the compound and what would be the action of heat on it?

(Molecular depression constant for water is 18·6° per 100 g.)

17 How, and under what conditions, does ethanamide react with (i) dilute hydrochloric acid, (ii) bromine and sodium hydroxide, (iii) phosphorus pentoxide, (iv) nitrous acid (acidified sodium nitrite solution)?

Give balanced equations and essential conditions for the reactions by which ethylammonium chloride (ethylamine hydrochloride) could be prepared from ethanamide.

What volume of 0·50M (0·50N) hydrochloric acid would be required to react completely with the gas evolved when 1·00 g of ethanamide is boiled with an excess of sodium hydroxide? (C(T))

18 What general methods are available for the preparation of (a) ethers, (b) acid anhydrides, (c) esters?

Compare the structures of diethyl ether, ethyl ethanoate, and ethanoic anhydride, and their reactions and methods of preparation, so as to bring out the similarities in structure and the effect of the modifications in structure.

19 What is the importance in organic chemistry of derivatives of hydrogen cyanide?

20 A compound has the structural formula $CH_3COCH_2CH{=}CHCH_2CN$. How would you expect this compound to react with (a) sodium and ethanol, (b) bromine, (c) sodium hydroxide, and (d) phosphorus pentachloride?

21 A colourless liquid, *A*, contains 58·54 per cent of carbon, 7·32 per cent of hydrogen and 34·14 per cent of nitrogen. When boiled with hydrochloric acid, *A* produced a compound *B*. When a pure sample of *B* was fused with soda-lime, a colourless inflammable gas was formed. When *A* was treated with dilute sulphuric acid and zinc, a colourless liquid, *C*, was formed, which reacted with iron(III) chloride to give a brown precipitate.

Identify *A*, *B*, and *C* and explain, giving equations, the reactions which occurred above.

Describe two reactions by which *A* could be made.

22 An organic acid *P*, on treatment with phosphorus pentachloride yielded a substance *Q*, which contained 78·0 per cent of chlorine and had a molecular weight of 182. *Q* when heated with dilute sodium carbonate solution yielded a substance *R*, which when crystallised and heated with soda lime produced a volatile liquid *S*. The product when heated with phenylamine and sodium hydroxide yielded a substance possessing a highly offensive smell. Derive a formula for *P* and explain the course of the reactions described. (L(X,S))

23 2·000 g of a neutral aliphatic compound *X*, containing carbon, hydrogen and oxygen only, gave on combustion 3·617 g of carbon dioxide and 1·233 g of water. If the vapour density of *X* is 73, calculate its molecular formula.

When *X* was refluxed with aqueous sodium hydroxide and then distilled, the distillate contained only one organic compound and this gave a positive response to the iodoform test. The solution left in the flask was evaporated to give a solid, which reacted with hot concentrated sulphuric acid to give a mixture of two gases, one of which turned lime-water milky whilst the other burnt with a blue flame.

Identify *X*, give its structural formula and explain fully the reactions which have been used to find out what it is. (O)

24 Describe briefly the preparation of ethanonitrile starting from (a) methanol, and (b) ethanol.

Ethanonitrile (*x* g) was boiled under reflux with sodium hydroxide solution and the ammonia which was evolved was passed into molar hydrochloric acid solution (50 cm^3). The excess of acid required 26 cm^3 of molar sodium hydroxide solution for neutralisation. Calculate x. (O and C)

25 Outline **two** methods of preparing carbamide. What is the historical importance of its first synthesis?

How does carbamide react with (a) nitrous acid solution (sodium nitrite and hydrochloric acid), (b) concentrated nitric acid, (c) sodium hydroxide solution, (d) a dilute alkaline solution of bromine? (O and C)

26 When 0·357 g of a colourless liquid, *A*, which was almost insoluble in water, was burnt, 0·616 g of carbon dioxide and 0·189 g of water were obtained. When *A* was warmed with an excess of aqueous sodium hydroxide and the resulting solid obtained on evaporation was strongly heated, a gas *B* was evolved. When 10 cm^3 of *B* was exploded with 30 cm^3 of oxygen (an excess) and the resulting gas, after cooling, was shaken with caustic potash solution there was a diminution in the volume of the gas by 10 cm^3.

When *A* was warmed with aqueous ammonia, under suitable conditions a crystalline solid, *C*, was obtained, which contained 23·75 per cent of nitrogen.

Identify *A*, *B* and *C* and explain the reactions that take place.

What would happen if *A* was heated with calcium hydroxide in equimolecular proportions? (L)

27 A compound *A* has the molecular formula $C_6H_{10}O_4$. It is a sweet-smelling liquid, sparingly soluble in water.

(a) When *A* is boiled under reflux with aqueous sodium hydroxide, a clear solution, *B*, is obtained.

(b) When solution *B* is distilled, the distillate, *C*, turns warm acidified sodium dichromate solution green.

(c) When a portion of the residual liquid from (b) is neutralised with hydrochloric acid, and calcium chloride solution added, a white precipitate, *D*, is observed.

(d) When the remaining liquid from (b) is acidified and then warmed with potassium permanganate solution carbon dioxide is evolved and a colourless solution results.

(e) When *A* is shaken with 0·880 ammonia solution, a white solid, *E*, is formed.

Suggest the most probable structures for *A* and explain the reactions described.

How would the result of the reaction of iodine and alkali on distillate *C* affect the decision on the structure assigned to *A*? (SUJB(S))

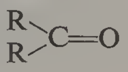
28 A neutral compound, *A*, has an empirical formula $C_8H_7O_2$. When 0·4824 g of *A* is dissolved in 40·20 g of benzene, the boiling point is raised by 0·119°C (the boiling point constant, *K*, for benzene = 2·67°C per 1000 g of benzene). Treatment of *A* with an excess of boiling aqueous potash gives a clear solution which when saturated with carbon dioxide affords a liquid turning to a low-melting solid, *B*, molecular formula C_6H_6O. *B* gives a purple colour with iron(III) chloride [ferric chloride] solution, and a white precipitate when treated with bromine water.

Acidification (with mineral acid) of the aqueous solution after removal of *B* yields a solid acid, *C*, empirical formula $C_2H_3O_2$, and this gives a neutral compound, *D*, when it is boiled with methanol in the presence of a trace of acid. The empirical formula of *D* is $C_3H_5O_2$ and the vapour density, 73. Also when *C* is heated it loses water to give *E*, a neutral substance with molecular formula $C_4H_4O_3$.

Deduce the structure of *A* and explain the formation of the substances *B*, *C*, *D* and *E*. (JMB(S))

29 Give an account of the general properties associated with the unsaturated groups present in each of the following aliphatic types:

(a) $R{-}CH{=}CH{-}R$

(b) 
$R_2C{=}O$

(c) $R{-}C{\equiv}C{-}H$

(d) $R{-}C{\equiv}N$

Call attention to any points of comparison or contrast which you consider of special interest.

30 When a compound *P* was heated with concentrated aqueous sodium hydroxide solution and the reaction product acidified, equimolar amounts of *Q*, containing C, 77·8 per cent; H, 7·4 per cent; and *R*, containing C, 68·8 per cent; H, 4·9 per cent were obtained. Mild oxidation of *Q* gave *P*, but more vigorous oxidation gave *R*. When 25 cm^3 of a solution of *R*, containing 11·0 g/dm^3, were titrated with 0·10N sodium hydroxide, 22·6 cm^3 were required for neutralisation (phenolphthalein). When *R* was heated with soda-lime it gave a hydrocarbon *S*, containing C, 92·4 per cent; H, 7·6 per cent.

Identify *P*, *Q*, *R* and *S* and give equations for the reactions involved in the above sequence.

Describe how you would make a pure crystalline derivative from *P*. (C(S))

31 Three isomeric compounds, *A*, *B* and *C*, have the molecular formula $C_8H_8O_2$.

(a) When heated for a long time with soda-lime *A* gave benzene, while both *B* and *C* gave methylbenzene.

(b) *A* was a neutral compound, whereas both *B* and *C* were monobasic acids.

(c) *B* and *C* were both readily chlorinated in sunlight; *B* gave a compound containing three chlorine atoms per molecule which was easily hydrolysed to a dibasic acid *D* which in turn gave an anhydride on heating. When *D* was heated with soda-lime it gave benzene. The chlorinated product from *C* contained two chlorine atoms per molecule and was a strong monobasic acid.

Identify *A*, *B*, *C* and *D*, write equations for the reactions, and indicate how you would prepare *A* from benzoic acid. (C(S))

32 Give examples of (a) addition reactions, and (b) condensation reactions, of the carbonyl group $>C{=}O$. Account for the difference in reactivity of the carbonyl group in (a) acids, (b) aldehydes, (c) ketones, (d) esters. (L(S))

33 A neutral white solid, *P* (C, 40·6 per cent; H, 5·1 per cent), was refluxed with an excess of aqueous sodium hydroxide and the reaction mixture was then distilled to give a distillate, *Q*, and a residue, *R*.

No reaction was observed when *Q* was treated with iodine and alkali, but *Q* was oxidised by acid dichromate solution to give a compound *S* (C, 40·0 per cent; H, 6·67 per cent) which reduced silver nitrate to silver and mercury(II) chloride to mercury(I) chloride and mercury.

Careful acidification of *R*, followed by suitable treatment, gave an anhydrous crystalline compound, *T*, 0·90 g of which required 20·0 cm^3 of 1M (1N) sodium hydroxide for neutralisation or 40·0 cm^3 of 0·1M (0·5N) acidified potassium permanganate for oxidation.

Compound *P* reacted with ethanolic ammonia to give *U*, empirical formula CH_2NO, and *Q*.

Identify compounds *P* to *U*, and write equations for all the reactions. (C(S))

34 Describe in outline the preparation of diethyl propanedioate from ethanoic acid.

Starting from diethyl propanedioate how would you prepare:

(a) butanoic acid;

(b) 2-methylpropanoic acid.

35 A neutral solid *A*, $C_2H_3O_2$, slowly dissolved in water to give a solution which became progressively more acidic as the substance went into solution. After boiling *A* with two molecular proportions of sodium hydroxide, evaporation of the solution gave *B*, CO_2Na, which on heating with soda-lime evolved hydrogen. On treatment with ammonia, *A* gave a white infusible solid *C*, CH_2ON, which gave the biuret reaction. All the formulae given above are empirical.

Elucidate the above reactions.

36 Discuss from a practical point of view the synthesis and hydrolysis of esters.

What explanation can you offer for the following observations:

(a) Esterification and hydrolysis are equilibrium processes,

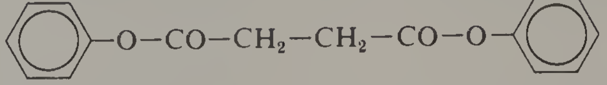
$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O,$$

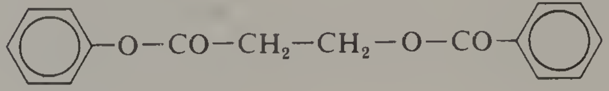
yet in some reactions, nearly quantitative yields of ester may be obtained.

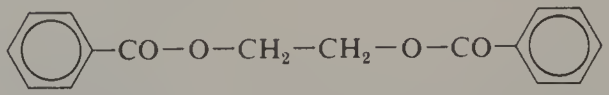
(b) Most esters show a molar freezing point depression of two when dissolved in concentrated sulphuric acid.

(c) The methyl ester of 2,4,6-trimethylbenzoic acid gives a fourfold freezing point depression in sulphuric acid? (C Schol.)

37 Three alternative structures were proposed for a compound *A*, $C_{16}H_{14}O_4$, namely

(i)


(ii)


(iii)


A dissolved completely when it was boiled with aqueous sodium hydroxide and it was found possible to isolate the organic products liberated when the solution was acidified, in almost quantitative yields.

Given bromine water and either standard acid or alkali, describe the investigations you might make to assign the correct structure to *A*. (O Schol.)

38 A neutral oil *A* ($C_{15}H_{26}O_6$) can be extracted from butter. It is immiscible with water but it dissolves on boiling with aqueous sodium hydroxide. From the resulting solution a syrupy liquid *B* ($C_3H_8O_3$) and a salt *C* ($C_4H_7O_2Na$) can be isolated. Phosphorus pentachloride converts *B* into a liquid which contains 24·41 per cent carbon, 3·39 per cent hydrogen and 72·20 per cent chlorine.

Suggest formulae for the compounds *A*, *B* and *C* and if alternatives are possible state whether it is easy to choose between them in assigning a structure to *A*. Give your reasons. (O Schol.)

39 A neutral compound *A*, $C_{10}H_{18}O_4$, dissolved slowly in boiling sodium hydroxide solution to give ethanol and, after acidification, a solid *B*, $C_6H_{10}O_4$. The solid *B* decomposed smoothly at its melting point (118°) to give a liquid acid *C*, $C_5H_{10}O_2$. The acid *C* was optically inactive, but could be resolved with an optically active base. Compound *B* could not be resolved.

Suggest structures for *A*, *B* and *C* and explain the reactions involved. (O Schol.)

40 Distinguish between the terms *order* and *molecularity* as referred to a chemical reaction.

During the saponification of ethyl propanoate in alkaline aqueous solution at 295 K, the initial concentrations of ester and sodium hydroxide were each 0·025 mol dm^{-3}. The concentration of the ester after various time intervals is given in the table below.

Time (minutes)	0	5	10	20	40	60	80	100
Ester concentration (1000 × mol dm^{-3})	25	15·5	11·3	7·3	4·3	3·0	2·3	1·9

(a) Show that the reaction is second order.
(b) Calculate the reaction velocity constant, stating the units.
(c) Determine the time for 50% of the reaction to be completed.
(d) Suggest an analytical technique for following the reaction.

(O and C (S))

Chapter 15

Isomerism

15.1 Introduction

Isomerism is said to occur when two or more compounds have the same molecular formula, but have different physical or chemical properties. The compounds that exhibit isomerism are said to be **isomers**. There are two principal subdivisions of isomerism—**structural isomerism** and **stereoisomerism.**

Structural isomerism occurs when two or more compounds have the same molecular formula but different structural formulae; that is, at least one atom is bonded to a different atom in one isomer as compared with another.

Stereoisomerism occurs when two or more compounds have the same molecular formula and the same structural formula, corresponding atoms being linked to the same atoms, but different spatial arrangements of their bonds.

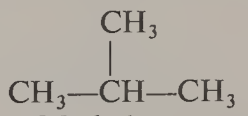
15.2 Structural isomerism

An outline of structural isomerism was given earlier (1.7) and many examples of isomerism have been met in the previous chapters. We shall here describe briefly the convenient sub-divisions of the subject.

(a) **Chain isomerism**, concerned with the arrangement of the carbon atoms in the molecule. For example, butane and 2-methylpropane are chain isomers:

$CH_3{-}CH_2{-}CH_2{-}CH_3$

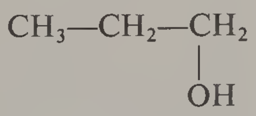
Butane



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

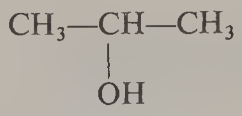
2-Methylpropane

(b) **Position isomerism**, exhibited by isomers in the same homologous series which have the same carbon skeleton but differ in the position of the functional group, for example:



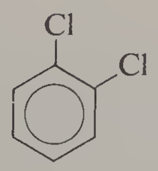
$$\begin{array}{r} CH_3{-}CH_2{-}CH_2 \\ | \\ OH \end{array}$$

Propan-1-ol

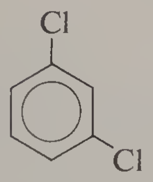


$$\begin{array}{c} CH_3{-}CH{-}CH_3 \\ | \\ OH \end{array}$$

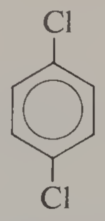
Propan-2-ol



1,2-Dichlorobenzene



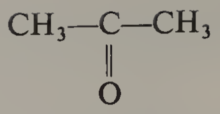
1,3-Dichlorobenzene



1,4-Dichlorobenzene

(c) **Functional group isomerism**, exhibited by isomers which have the same molecular formula but contain different functional groups, for example:

$CH_3—CH_2—CH{=}O$

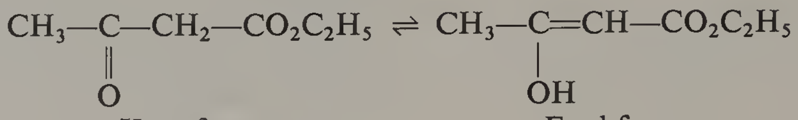


$CH_3—\underset{\overset{\|}{O}}{C}—CH_3$

Propanal

Propanone

(d) **Tautomerism**, exhibited by isomers which are in dynamic equilibrium. An example is ethyl 3-oxobutanoate; the two isomers rapidly interconvert, the equilibrium constant being about 0.11 (i.e. 90 per cent keto form and 10 per cent enol form):

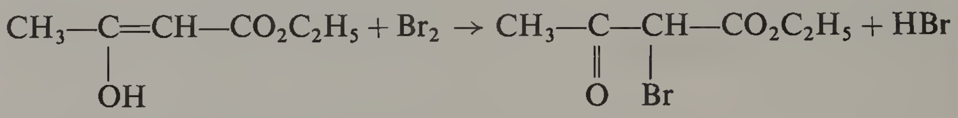


$$CH_3—\underset{\overset{\|}{O}}{C}—CH_2—CO_2C_2H_5 \rightleftharpoons CH_3—\underset{\overset{|}{OH}}{C}{=}CH—CO_2C_2H_5$$

Keto form

Enol form

If a reagent is added which reacts with the carbonyl group (e.g. hydroxylamine), it removes the keto isomer and more of the enol form is then converted into the keto form to re-establish the equilibrium; eventually the entire mixture reacts with the reagent. The opposite occurs if a reagent is added which reacts with the enol form, such as bromine:



$$CH_3—\underset{\overset{|}{OH}}{C}{=}CH—CO_2C_2H_5 + Br_2 \rightarrow CH_3—\underset{\overset{\|}{O}}{C}—\underset{\overset{|}{Br}}{CH}—CO_2C_2H_5 + HBr$$

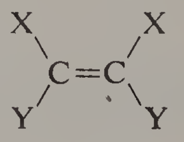
Eventually the entire mixture is converted into the bromo-compound.

15.3 Introduction to stereoisomerism

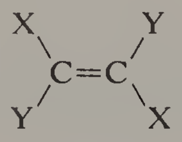
Stereoisomerism occurs when two or more compounds have both the same molecular formula and the same structural formula but differ in the spatial arrangement of the atoms. There are two subdivisions: **geometrical isomerism** and **optical isomerism**.

15.4 Geometrical isomerism

The essential requirement for the existence of geometrical isomers is the prevention of rotation around at least one bond in the compound. The commonest situation of this sort is when a carbon-carbon double bond is present; there can then be two geometrical isomers:



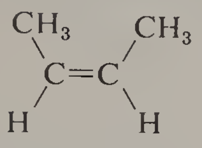
cis isomer



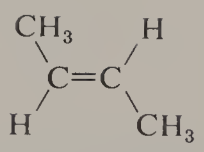
trans isomer

Note that these isomers have the same structural formula, for in both isomers each carbon atom is attached to one group X and one group Y; however, the relative positions in space of these groups are different for the two isomers. The nomenclature *cis* is often used when identical substituents are on the *same* side of the double bond, and *trans* when they are on *opposite* sides.

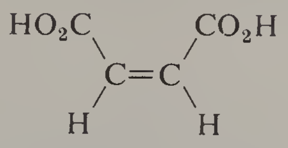
Typical examples of geometrical isomers are:



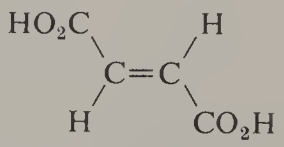
cis-But-2-ene



trans-But-2-ene

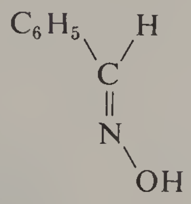


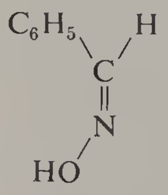
cis-Butene-dioic acid



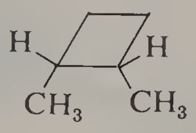
trans-Butene-dioic acid

Oximes, which have a C=N bond, also exhibit geometrical isomerism, for example:

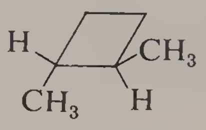




Rotation is also prevented by the presence of a ring of atoms; for example, 1,2-dimethylcyclobutane exists in *cis* and *trans* forms:

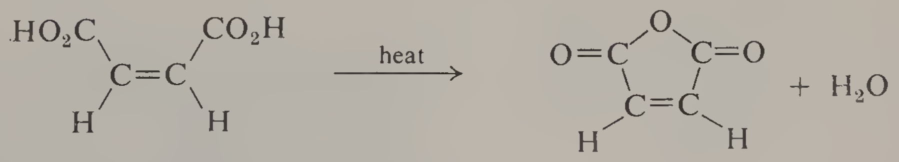


cis isomer



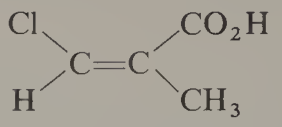
trans isomer

Geometrical isomers have different physical and chemical properties. For example, *cis*-butenedioic acid readily forms a cyclic anhydride on being heated:



but the *trans*-isomer is unable to do so.

The nomenclature *cis* and *trans* is now being replaced by the more general nomenclature *Z* (German: *zusammen*, together) and *E* (German: *entgegen*, across), according to whether the substituents of *the higher priority* on each carbon atom are on the same or opposite sides of the double bond. Priority is decided by the relative atomic mass of the atom attached to the unsaturated carbon atom: the higher the relative atomic mass, the higher the priority (e.g. $-OH > -CH_3$). If these atoms are the same, the atoms to which they are attached are considered (e.g. $-CH_2Cl > -CH_3$); and if the atom forms a double or triple bond to another atom, X, it is regarded as being attached to two or three atoms of X (e.g. $-CHO > -CH_2OH$). Thus,



is the *Z*-isomer, since Cl is of higher priority than H, and CO_2H is of higher priority than CH_3.

15.5
Optical isomerism

When two compounds have the same molecular and structural formulae but one is not superimposable upon the other, they are described as **optical isomers**. The reason is that they differ in their optical properties.

For example, if a compound contains a carbon atom bonded to four different atoms or groups (e.g. 2-hydroxypropanoic acid, $CH_3CH(OH)CO_2H$; p. 198), the construction of models shows that it can exist in two forms which are not superimposable (Plate 15.1). The two forms are related as object and mirror image; if a mirror were placed between the models in the photograph, perpendicular to the page, then the reflection of the right-hand form in the mirror would be seen as identical with the left-hand form, and *vice-versa*. The two forms differ in their behaviour towards polarised light.

Plate 15.1. Molecular models of stereoisomers. The carbon atom is surrounded by four different groups of atoms. Each group is represented, for clarity, by a single coloured ball. The two stereoisomers are mirror images of one another which cannot be superimposed

Introduction to polarised light

Light is a form of electromagnetic radiation, like radio waves and *X*-rays. It is a wave-motion, the wavelength of each wave being about 5×10^{-7} m, the exact value being characteristic of the colour of the light. In free space all these waves, irrespective of colour, travel with a velocity of 3×10^8 m s^{-1}. When they impinge upon a transparent homogeneous material, however, they are slowed down in a constant ratio, so that:

$$\frac{\text{Velocity in free space}}{\text{Velocity in medium}} = \text{a constant},$$

known as the 'refractive index', and usually denoted by the symbol μ; its value depends upon both the medium and the wavelength of the light.

Those who find difficulty in appreciating the properties of electromagnetic radiation may be helped by likening light waves to the material waves which can be made by regularly vibrating one end of a long string—which we shall assume to be stretched horizontally in what follows—although they must not push the analogy too far, nor expect an analogy to *prove* anything. Just as it is possible for the end of the string to oscillate vertically up and down, or horizontally to and fro, or even in a combination of these directions, so also the direction of oscillation of the light waves can be in any direction which lies at right angles to the direction of propagation of the light.

Many common media are not homogeneous, in either the optical or in any other sense; for example, the directional properties of wood are clearly recognisable in its 'grain'; the ease with which a paper-knife may be inserted between the pages of a closed book will depend upon whether its blade is parallel or perpendicular to the leaves of paper. In the optical analogues of such 'anisotropic' media, the velocity of light which is oscillating in one plane is not the same as that which is oscillating in the perpendicular plane, and therefore it will have two different refractive indices. Thus a ray of light which comprises oscillations in many planes in free space will travel on as two distinct rays when once it gets inside such a 'birefringent' medium. By subtle optical means it is possible to suppress one or other of these rays in such devices as Nicol Prisms (two crystals of calcite, $CaCO_3$, mounted together by Canada balsam) or Polaroids. The emergent ray then consists of vibrations in one plane only and it is said to be 'polarised' (Fig. 15.1).

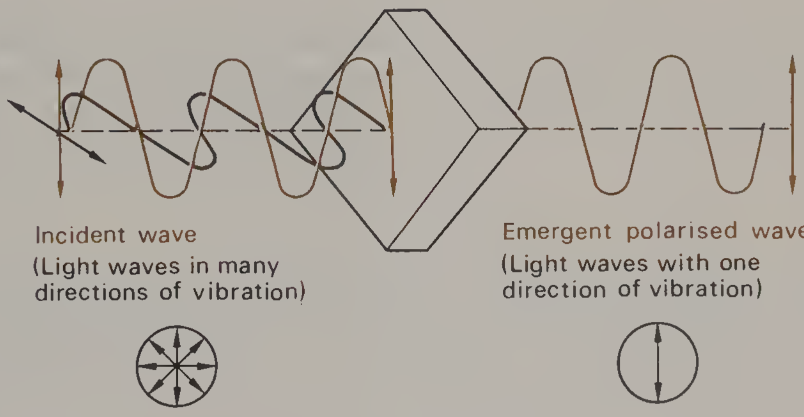
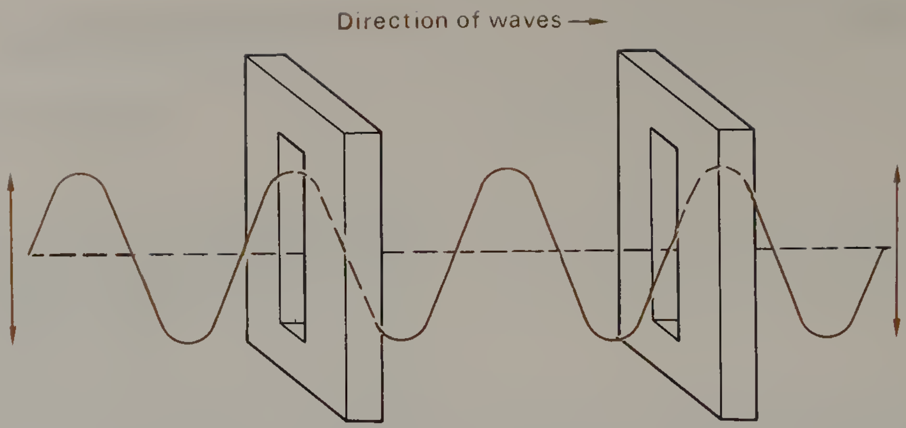


FIG. 15.1. *The passage of light through a Polariser to form plane polarised light*

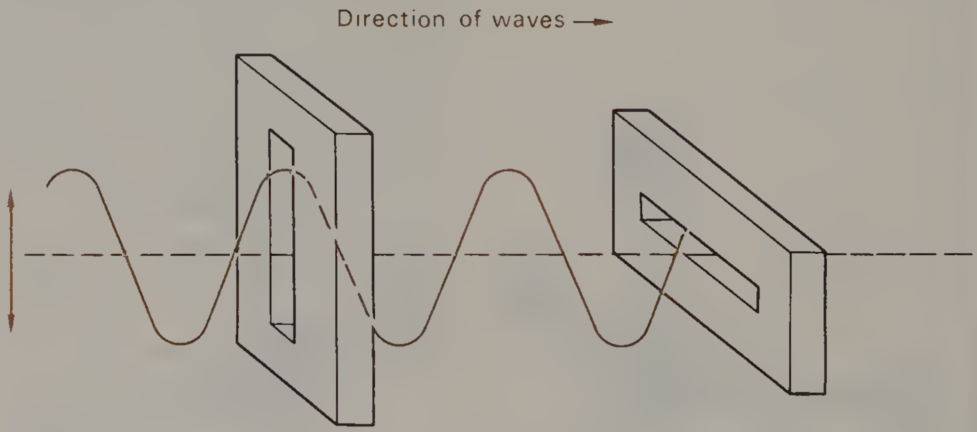
To the human eye this polarised ray will be indistinguishable from an ordinary, non-polarised ray vibrating in many planes. But suppose a plane polarised ray, produced by a 'Polarising Prism', impinges subsequently upon another, similar 'Analysing Prism', several possibilities arise. If the axes of the two prisms are parallel to one another, the light will pass through them both without diminution in intensity, just as plane polarised waves on a string would pass unimpeded through parallel slits in two obstructing screens (Fig. 15.2).

FIG. 15.2. *Transmission of plane polarised light when the axes of the Polariser and Analyser are parallel*



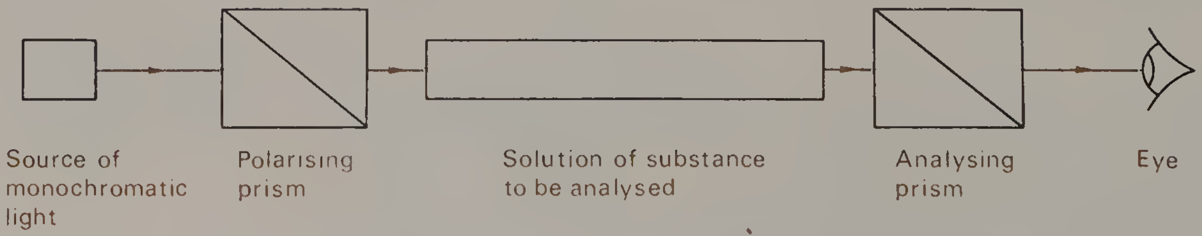
If, however, the second slit were turned through a right angle by rotating it about the direction of the plane of the waves in the string, the material waves would not be able to get through (Fig. 15.3). Light waves are similarly extinguished when the axes of the Polariser and the Analyser are perpendicular to one another, or 'crossed'. It can be shown that if the axes are at some intermediate angle, θ, then the intensity of the emergent ray is proportional to $\cos^2 \theta$.

FIG. 15.3. *The extinction of plane polarised light when the axes of the Polariser and Analyser are at right angles to one another*



A Polarimeter is an instrument for carrying out precise measurements of this effect. It consists of a fixed Polarising Prism adjacent to the source of monochromatic light, followed by a container for the substance under investigation, and finally an Analysing Prism carried on a circular scale which can be rotated about the axis of the whole apparatus (Fig. 15.4).

FIG. 15.4. *A Polarimeter*



When an optically inactive solution is placed in the containing tube, light emerges at full intensity from the Analyser when its axis is parallel to that of the Polariser, and is completely extinguished when these two axes are perpendicular to one another; the latter situation can be more easily detected in practice, but even so it is subject to some uncertainty because the $\cos^2 \theta$ function changes only slowly as it reaches its minimum value.

If, however, a solution of an 'optically active' substance is used (this is explained in detail later), it will be found that the axis of the Analyser is no longer perpendicular to that of the Polariser when extinction occurs, but differs from that position by an angle through which the plane of polarised light has been rotated while the light has passed through the solution. Experiment shows that the angle of rotation is directly proportional to the length of the tube and to the concentration of the solution, for a given wavelength and at a fixed temperature.

The **molar optical rotatory power** of a compound, at a given temperature and for a given wavelength, is the rotation produced by a column of solution 1 m long and of concentration 1 mol m^{-3}.

Introduction to optical activity

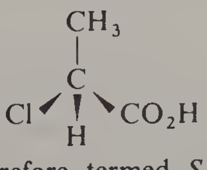
The ability to rotate the plane of polarised light is not confined to calcite crystals. Other inorganic crystals, such as sodium bromate and sodium iodate, have the same property. However, they lose the ability when they dissolve in water; it is the asymmetric arrangement of the atoms or ions in the crystal lattice which gives these crystals this property.

In contrast, any organic compound which contains a carbon atom attached to four different atoms or groups rotates the plane of polarised light both in the crystalline state and in solution; its mirror-image isomer likewise rotates the plane, but in the opposite direction. Such a carbon atom is described as an **asymmetric carbon atom** or **chiral carbon atom. Chirality** is the property of ‘handedness’ (Greek: *cheir*, a hand); the two isomers that can be formed by attaching four different atoms or groups to an asymmetric or chiral carbon atom are non-superimposable mirror images just as are a left and a right hand.

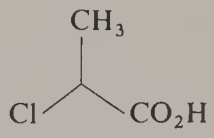
The molar optical rotatory powers of the two isomers are equal but of opposite sign: the one which rotates the plane of polarised light to the right is described as **dextrorotatory**, as giving a positive rotation and as the (+) form; the other isomer, rotating the plane to the left, is described as **laevorotatory**, as giving a negative rotation and as the (−) form. The two isomers are described as **enantiomers**. An equimolar mixture of the two does not rotate the plane of polarised light and is said to be optically inactive; it is also known as the **racemic form** ((±) form).

It is essential to realise that the phenomenon of optical activity can only be explained by assuming the tetrahedral arrangement for the molecule. Such an arrangement was proposed independently by van’t Hoff and Le Bel in 1874, and is supported by two particular pieces of evidence: (a) there is only one form of such substances as dichloromethane CH_2Cl_2 (1.2), and (b) the phenomenon of optical isomerism.

The sign of rotation associated with an optically active compound gives no information about its **absolute configuration**—the actual arrangement in space of the four atoms or groups attached to asymmetric carbon. However, it is possible to find out what the configuration is, and it is now described in a way related to that for geometrical isomers (p. 237): the chiral carbon is viewed from the side opposite the atom or group of lowest priority (often hydrogen). If the other three atoms or groups then appear in a clockwise order of decreasing priority, the compound is given the prefix *R* (Latin: *rectus*, right); if anticlockwise, the prefix *S* (Latin: *sinister*, left). For example, when viewed in this way,



would appear as



and is therefore termed *S*-2-chloropropanoic acid since the three groups in descending order of priority ($Cl > CO_2H > CH_3$) appear in the anticlockwise order.

Properties of enantiomers

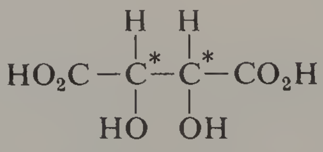
1. The physical properties of enantiomers, such as melting point, boiling point and solubility, are identical except for the direction of rotation of polarised light. Note, however, that it is not possible to predict from the structural formulae of the enantiomers which will be the (+) and which the (−) form; this can only be determined by experiment once the actual structure has been found.

2. Enantiomers give crystals of the same type as each other, but the crystals of one are the mirror images of those of the other (p. 244), and the two are described as **enantiomorphs**.

3. The chemical properties of enantiomers are identical for their reactions with compounds which are not optically active; for example, (+) and (−)2-hydroxypropanoic acid undergo esterification with methanol at exactly the same rate as each other. However, enantiomers can react at different rates with an optically active reagent. This has especially important consequences when biological materials are involved, because enzymes, which are the catalysts for reactions in living systems, occur in optically active forms (18.2). Thus enantiomers often behave differently towards bacteria; for example, (+)2-hydroxypropanoic acid is consumed by penicillium glaucum but (−)2-hydroxypropanoic acid is relatively unaffected. Again, enantiomers can have different physiological properties; for example, (−)adrenalin is more active in contracting the blood capillaries than (+)adrenalin, and (−)nicotine is more poisonous than (+)nicotine.

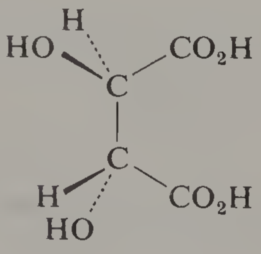
Optical isomerism of compounds containing two asymmetric carbon atoms

The 2,3-dihydroxybutanedioic acid molecule contains two asymmetric carbon atoms:

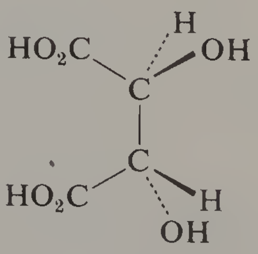


$$\mathrm{HO_2C-\underset{HO}{\overset{H}{C^*}}-\underset{OH}{\overset{H}{C^*}}-CO_2H}$$

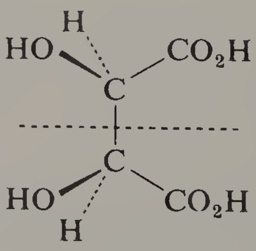
2,3-Dihydroxybutanedioic acid exists in three stereoisomeric forms, which can be represented in two dimensions as follows:



(1)



(2)



(3)

Structures (1) and (2) are mirror images of each other but they are not superimposable on each other. Therefore, each is optically active and the two constitute a pair of enantiomers; one is dextrorotatory ((+)2,3-dihydroxybutanedioic acid) and the other is laevorotatory ((−)2,3-dihydroxybutanedioic acid).

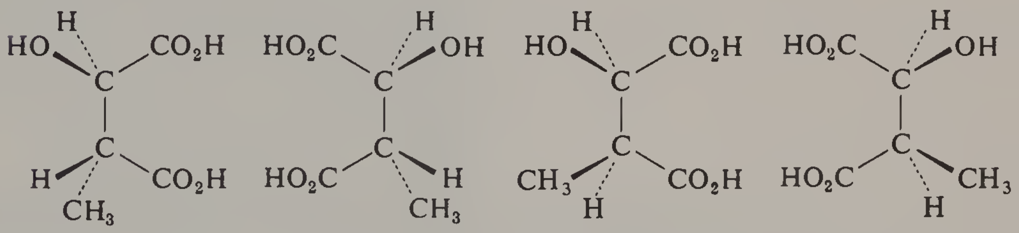
Structure (3) is not superimposable on either (1) or (2), nor is it the mirror image of either. It is found that it is optically inactive, for the optical activity due to one of the asymmetric carbon atoms is counterbalanced by the optical activity due to the other; the top half of structure (3) is the mirror image of the bottom half, the dotted line representing a plane of symmetry. [In a sense, (3) has the structure of the top half of (1) and the bottom half of (2).]

Compounds which contain two or more asymmetric carbon atoms but are optically inactive are described as **internally compensated** and defined by the prefix *meso*; thus structure (3) is (*meso*)2,3-dihydroxybutanedioic acid. An equimolar mixture of (+) and (−)2,3-dihydroxybutanedioic acid is also optically inactive since the specific rotations of the two are equal in magnitude but opposite in sign; it is described as a **racemic mixture**, or as the (±)form, and is said to be **externally compensated.**

The (+) and (−)isomers have identical physical and chemical properties except in the direction of rotation of polarised light and in their reactions with other optically active substances However, the (*meso*)isomer has different properties, for example:

Physical property	(+)	(−)	(*meso*)
M.p./°C	170	170	140
Density/g cm^{-3}	1·76	1·76	1·67
Solubility/g 100 cm^{-3} H_2O	139	139	125

When a compound contains two asymmetric carbon atoms of which one is not bonded to the same three groups as the other, four stereoisomers exist; for example, for the compound $HO_2C—CH(OH)—CH(CH_3)—CO_2H$:



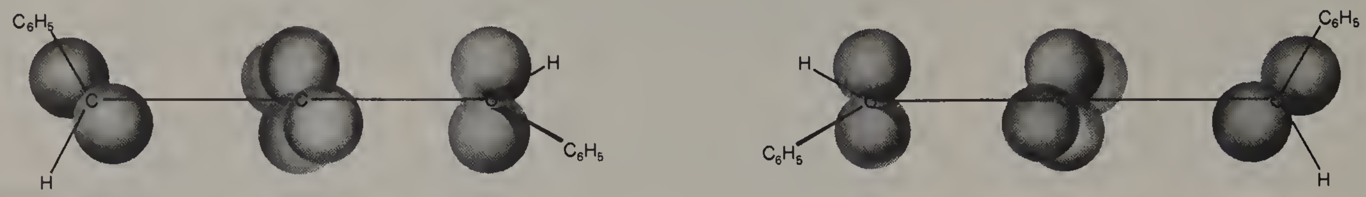
The first two are non-superimposable mirror-images of each other and so constitute one pair of enantiomers, and likewise the other two constitute a second pair of enantiomers, with different properties from the first pair.

In general, a compound with n asymmetric carbon atoms exists in 2^n optically active forms, although when one set of substituents in the compound mirrors another, internal compensation occurs to reduce this number, as we have seen for 2,3-dihydroxybutanedioic acid.

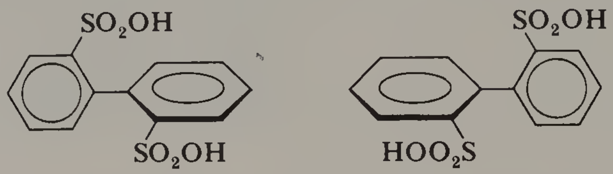
Other optically active compounds

As we have seen, compounds containing an asymmetric carbon atom can exist in optically active forms. However, compounds which do not possess an asymmetric carbon atom can also exist in optically active forms provided that the *molecule* is asymmetric. Examples occur with certain derivatives of propadiene ($CH_2{=}C{=}CH_2$), such as 1,3-diphenylpropadiene: the central atom forms *sp*-hybridised σ-bonds with the other carbon atoms and provides two *p* electrons, one in each of two *p* orbitals which are mutually perpendicular, for forming π-bonds with the other carbon atoms. As a result, the substituents at one end of the molecule are in a plane which is perpendicular to that of the substituents at the other end, so that the compound exists in two forms which are non-superimposable mirror-images and are optically active (Fig. 15.5).

FIG. 15.5. *The stereoisomers of 1,3-diphenylpropadiene*



Substituted biphenyls exhibit optical isomerism when substituents in the 2- positions are large enough to prevent rotation about the bond joining the two benzene rings. For example, biphenyl-2,2′-disulphonic acid exists in two forms



which are non-superimposable mirror-images but do not interconvert at room temperature because the energy required to twist one ring through 180° relative to the other is too high (about 80 kJ mol^{-1}). This in turn is because, during the twisting process, the two sulphonic acid groups must come into very close proximity when the two benzene rings become coplanar and strong repulsive forces are introduced.

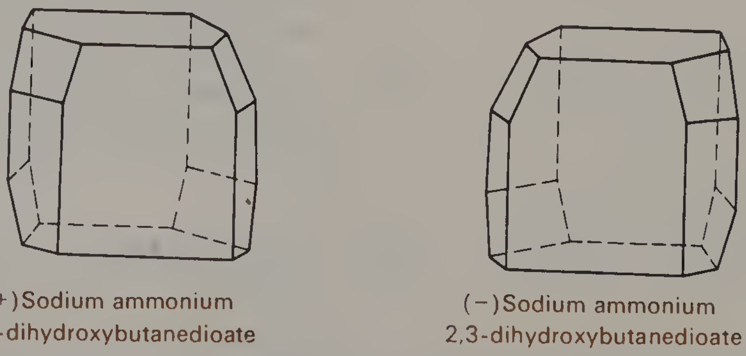
Resolution of enantiomers

The separation of a racemic mixture into the individual enantiomers is described as **resolution**. Three methods for resolving enantiomers are:

(a) **Crystal picking.** When sodium ammonium 2,3-dihydroxybutanedioate crystallises from solution below 28°C, the (+) and (−)isomers form crystals which are mirror images of each other (Fig. 15.6). The two types of crystals can be separated by hand.

This is a tedious method, and is in any case not always applicable (e.g. when the enantiomers are liquid). It is mentioned mainly for historical interest, for it was the first method to be employed, by Pasteur. In one sense Pasteur was fortunate, because if his solution of sodium ammonium 2,3-dihydroxybutanedioate had crystallised *above* 28°C, he would have obtained only one type of crystal, so that no separation would have been possible. In this crystal, there is an ordered arrangement of the (+) and (−)isomers, and the state is called a **racemic compound**.

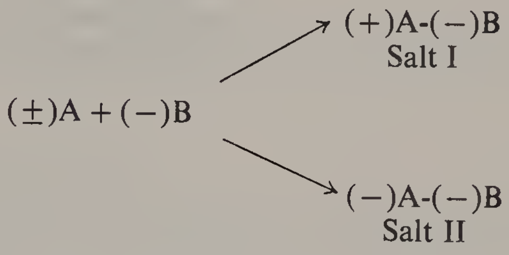
FIG. 15.6. *The crystal forms of (+) and (−)sodium ammonium 2,3-dihydroxybutanedioate*


(+)Sodium ammonium 2,3-dihydroxybutanedioate

(−)Sodium ammonium 2,3-dihydroxybutanedioate

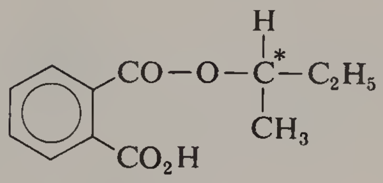
(b) **Chemical method.** This is the method of most general use. It is based on the principle that when each of the two enantiomers reacts with another compound which is optically active, the products are not mirror images and do not have identical properties. They are known as **diastereoisomers**. Usually one will be less soluble in a particular solvent than the other, and so the two can be separated by fractional crystallisation and then converted back into the individual enantiomers.

For example, a (±)acid ((±)A) can be resolved by making it into a mixture of two salts with an optically active base (say, (−)B),



separating them, and then treating each with mineral acid to release (+)A and (−)A. A number of optically active bases suitable for the purpose occur naturally as alkaloids (e.g. quinine) in plants. Similarly, a (±) base can be separated by the use of an optically active acid.

Racemic mixtures which are not acids or bases can often be resolved by first making them into derivatives with acid groups and resolving the resulting mixture as above. For example, the enantiomers of butan-2-ol, $CH_3—\overset{*}{C}H(OH)—C_2H_5$, can be resolved by esterification with a dibasic acid (e.g. benzene-1,2-dicarboxylic acid) to give enantiomeric esters such as the (±) form of



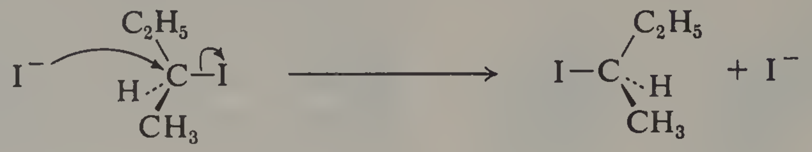
resolving with an optically active base, and then hydrolysing the individual (+) and (−)esters to give the (+) and (−)alcohols.

Diastereoisomers can sometimes be separated by chromatographic techniques. For example, it has been found that (±)amino-acids can be resolved by converting them into diastereoisomeric esters with an optically active secondary alcohol, separating these by gas-liquid chromatography, collecting the fractions and hydrolysing each separately to give the (+) and (−)amino-acids.

(c) **Biochemical method.** Bacteria will sometimes grow in solutions of racemates, and may feed on them by consuming one of the forms. Thus, (−)2-hydroxypropanoic acid can be prepared by allowing penicillium glaucum to feed on (±)2-hydroxypropanoic acid; it destroys the (+) acid.

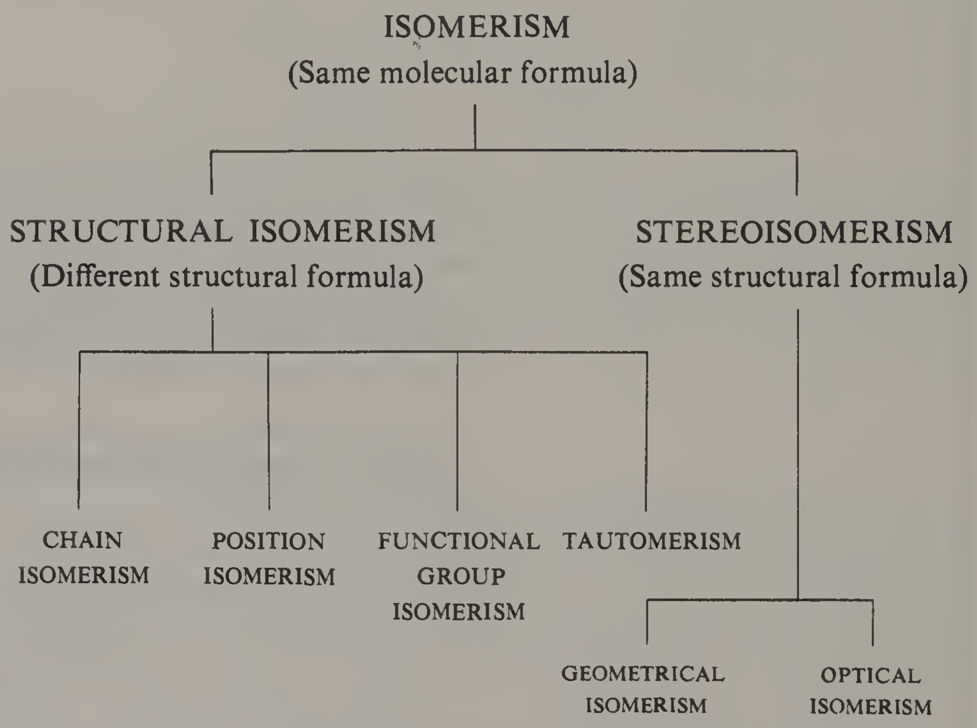
Racemisation

Racemisation is the opposite of resolution; that is, it consists of the formation of equal amounts of a pair of enantiomers from either of the two. It can occur when a reaction takes place which breaks one of the bonds to the asymmetric carbon atom. For example, if a solution of one of the enantiomers of 2-iodobutane, say the (−)isomer, is treated with a solution of sodium iodide, an iodide ion in the solution displaces an iodide ion from the organic compound by attacking from the opposite side:



Consequently, the (+)isomer is formed. However, this too can react, in the reverse manner, to regenerate the (−)isomer, and eventually a point is reached when equal amounts of the two isomers are in dynamic equilibrium.

15.6
Summary

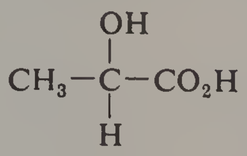


15.7
Practical work

Optical isomerism

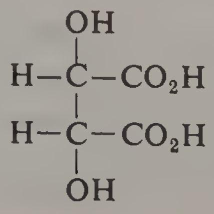
Make ball and stick models of the following compounds, using different coloured balls to represent different functional groups:

(a) The stereoisomers of 2-hydroxypropanoic acid:



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{CH_3-C-CO_2H} \\ | \\ \mathrm{H} \end{array}$$

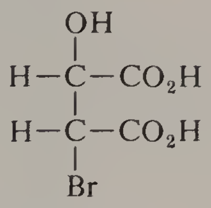
(b) The stereoisomers of 2,3-dihydroxybutanedioic acid:



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{H-C-CO_2H} \\ | \\ \mathrm{H-C-CO_2H} \\ | \\ \mathrm{OH} \end{array}$$

Make sure that you have constructed a model of (*meso*)2,3-dihydroxybutanedioic acid and that you can see why it is internally compensated.

(c) The stereoisomers of the acid:

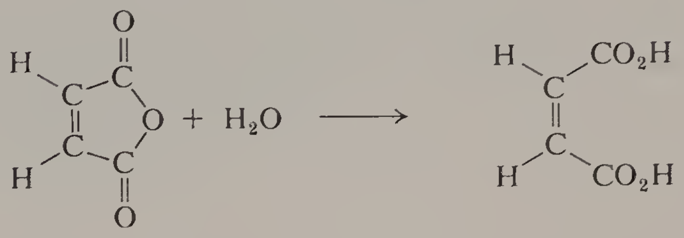


$$\begin{array}{l} \quad\;\;\text{OH} \\ \quad\;\;\,| \\ \text{H}-\text{C}-\text{CO}_2\text{H} \\ \quad\;\;\,| \\ \text{H}-\text{C}-\text{CO}_2\text{H} \\ \quad\;\;\,| \\ \quad\;\;\text{Br} \end{array}$$

Show whether or not it is possible for this compound to have a (*meso*) form.

Geometrical isomerism

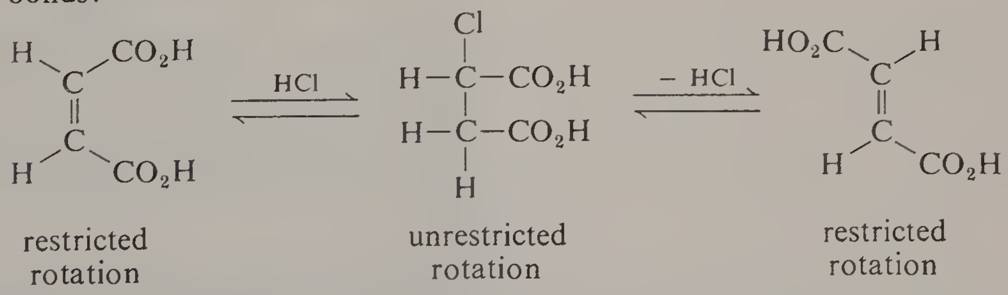
Dissolve 10 g of butenedioic anhydride in 12 cm^3 of boiling water in a test-tube to form a solution of *cis*-butenedioic acid:



Cool the solution by placing the test-tube in a beaker of cold water. Filter the solid acid using a Buchner funnel (Fig. 2.8), but do not attempt to wash the solid. Dry it between pads of filter papers and determine its melting point.

Collect the filtrate, add 20 cm^3 of *concentrated* hydrochloric acid and reflux the mixture for about 20 minutes. Crystals are formed which can be filtered, washed with water and dried between pads of filter paper. Determine the melting point. [M.p. of *cis*-butenedioic acid 130°C; m.p. of *trans*-butenedioic acid 287°C (sublimes).]

Hydrogen chloride adds on to the *cis*-butenedioic acid molecule to form an intermediate in which there is unrestricted rotation about the C—C bonds:



15.8 Questions

1 Explain the terms (a) Empirical formula, (b) Molecular formula, (c) Structural formula, (d) Isomerism.

Three unsaturated dichloroalkenes of molecular formula $C_2H_2Cl_2$ exist and also two unsaturated dicarboxylic acids of molecular formula $C_4H_4O_4$. Account for the existence of these isomers discussing the stereochemical principles.

Indicate one method by which you could assign to each its structure if you were given pure specimens of the two unsaturated acids. (SUJB)

2 (a) Distinguish between the terms empirical, molecular and structural formulae.

(b) Discuss the various types of isomerism which occur in organic chemistry, illustrating your answer by reference to the isomerism of the following compounds: (i) C_2H_6O, (ii) $C_2H_2Cl_2$, (iii) $C_3H_6O_3$ (only acids).

There are no isomers of compounds of the type CH_2X_2 where $X = Cl$, Br, etc.; what does this show? (O)

3 (a) What do you understand by (i) structural isomerism, (ii) optical isomerism and (iii) geometrical isomerism? Illustrate your answers with examples chosen from the chemistry of aldehydes and ketones and their derivatives.

(b) Three isomeric mononitrobenzoic acids are known to exist. Write down their structural formulae, and state, giving reasons, which of these would normally be formed on the nitration of benzoic acid. Suggest how you might attempt to prepare the other isomer(s). (L(X))

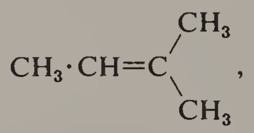
4 Discuss the various types of isomerism which occur in organic chemistry, illustrating your answer by reference to the isomerism that is shown by the following compounds: (a) $C_2H_2Br_2$; (b) CH_4N_2O; (c) $C_3H_6O_3$ (only acids); (d) C_3H_5N (no ring structures); (e) $C_6H_3Cl_3$ (only derivatives of benzene).

Describe **two** tests by which you would distinguish between two isomers in (d). (O(S))

5 Explain as fully as you can what is meant by the term 'isomerism', illustrating your answer by examples of your own choice.

How would you distinguish by not more than two chemical tests in each case between the substances in each of the following pairs?

(*a*) $(CH_3)_3C{\cdot}OH$ and $CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3$,

(*b*) $CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_3$ and  $CH_3{\cdot}CH{=}C(CH_3)_2$,

(*c*) $CH_3{\cdot}CO{\cdot}O{\cdot}C_2H_5$ and $C_2H_5{\cdot}CO{\cdot}O{\cdot}CH_3$. (L)

6 Describe, with diagrams, the type of isomerism shown by *cis*- and *trans*-butenedioic acids. Give examples of the differences in physical properties of these acids. How can these acids be distinguished by chemical methods?

The addition of hydrogen bromide to each of the two acids gives the same pair of isomers, while the addition of bromine to the two acids gives a total of three isomeric dibromo-acids. Draw the structures of the five brominated compounds and describe the type of isomerism involved. How might the two monobromodicarboxylic acids be separated?

7 An optically active compound *A* when oxidised with chromic acid yields a substance *B* which gives a condensation product with phenylhydrazine but no precipitate when warmed with a solution of potassium iodide in sodium hypochlorite. The empirical formulae of *A* and *B* are $C_6H_{14}O$ and $C_6H_{12}O$ respectively. When *A* is warmed with concentrated sulphuric acid it gives a hydrocarbon *C*, the percentage composition of which is C, 85·7; H, 14·3; and the vapour density, 42.

Treatment of a trichloromethane solution of *C* with trioxygen yields a compound which on decomposition with water yields two compounds, *D* and *E*, both having an empirical formula, C_3H_6O. Both *D* and *E* give precipitates with phenylhydrazine, but only *E* yields a yellow precipitate with a solution of iodine in sodium hydroxide. On the other hand the compound *D* is easily oxidised to an acid, $C_3H_6O_2$.

Deduce the structure of *A*, explaining briefly why it is optically active, and write equations for the formation of *B*, *C*, *D* and *E*.

8 What do you understand by the terms *structural isomerism*, *cis-trans* (*geometrical*) *isomerism* and *optical isomerism*? Illustrate your answer with examples of isomers drawn from as wide an area of organic chemistry as you can and explain how **each** type of isomerism arises.

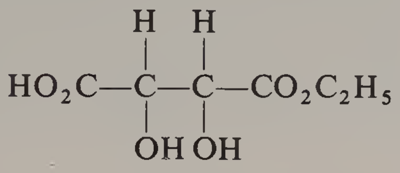
To what extent are the properties of corresponding isomers similar? (C)

9 Give an account of structural, geometrical and optical isomerism, illustrating your answer with two examples in each case.

(a) The physical and chemical properties of geometrical isomers often differ greatly. Choose suitable examples to illustrate this.

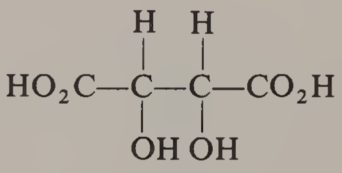
(b) Some compounds have several asymmetric carbon atoms. Discuss the relationship between the number of asymmetric carbon atoms and the number of isomers which result. Illustrate your answer by reference to

(i)



$HO_2C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CO_2C_2H_5$

(ii)



$HO_2C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CO_2H$

(L(S))

10 (a) Give **two** factors which may restrict rotation about carbon-carbon bonds, and indicate the consequences which this restriction may lead to in the field of isomerism. Illustrate your answer with specific compounds.

(b) What is meant by the term *chiral molecule* and to what extent is the term confined to organic chemistry? Illustrate your answer with diagrams of specific molecules.

(c) Illustrate the importance of stereochemistry as an approach to understanding organic reaction mechanisms. (O and C)

11 Describe the different types of isomerism which occur in carbon compounds. Illustrate your answer by reference to isomers of each of the following: C_4H_{10}, C_3H_7Cl, C_4H_8 and $CH_3CH(OH)COOH$. State what differences (if any) in chemical behaviour and in physical properties you would expect the various isomers of each formula to show.

A hydrocarbon C_5H_{10} reacts with sulphuric acid and the product is hydrolysed to give an alcohol $C_5H_{12}O$. This alcohol can be separated into two enantiomeric forms (optical isomers). Suggest one possible structure for the hydrocarbon. (JMB)

12 Define *isomerism*. What isomers exist for the following compounds:

$R_1R_2R_3SiCl$ (R_1, R_2, and R_3 represent different alkyl or aryl groups)
$HOOCCH{=}CHCOOH$
$Pt(NH_3)_2Cl_2$
$R_1R_2R_3R_4N^+I^-$ (R_1, R_2, R_3, and R_4 represent different alkyl or aryl groups)?

(C Schol.)

13 Show by means of examples what types of isomers are encountered in organic chemistry. Write the structures of the isomers of formula C_3H_5Cl. Indicate briefly how you might distinguish between them.

14 A compound is found to have the molecular formula $C_4H_8O_2$. Write down as many possible structures for this compound as you can *classifying* them according to the types of functional group present. Indicate briefly how you might distinguish between the various classes by chemical tests. (O Schol.)

15 Optically active 2-iodobutane

$$(CH_3.CH_2.CHI.CH_3)$$

racemises in acetone solution containing sodium iodide. When the experiment is carried out with labelled sodium iodide (prepared from ^{131}I, the radioactive isotope of iodine), the alkyl iodide is found to lose optical activity and to exchange its ordinary iodine for radioactive iodine. The rates of each of these reactions are proportional to

$$[\text{alkyl iodide}][\text{I}^-]$$

but racemisation is exactly *twice* as fast as isotopic exchange.

Discuss the stereochemical implications of these experiments.

What conclusions would you have drawn if the rates of racemisation and isotopic exchange had been independent of the concentration of iodide ion and exactly *equal*? (O Schol.)

16 Describe the different types of isomerism exhibited by organic compounds, illustrating your answer with specific examples.

Vigorous oxidation of a compound *X* $(C_2H_4)_n$ gives only ethanoic acid. With bromine *X* forms *Y* $(C_2H_4Br)_n$ and with hydriodic acid it forms *Z*, C_4H_9I.

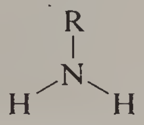
Draw possible structures for compounds, *X*, *Y* and *Z*, and indicate the stereoisomeric forms in which they could exist. (O Schol.)

Chapter 16

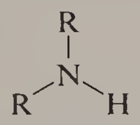
Amines

16.1 Introduction

Amines can be regarded as organic derivatives of ammonia. There are three classes of amines:



Primary amine



Secondary amine

Tertiary amine

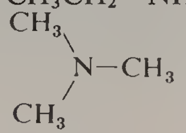
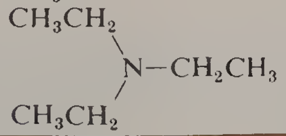
where R can be an alkyl group or an aromatic ring. The prefixes, primary, secondary and tertiary, define the number of carbon groups attached to the nitrogen atom and *not* (as with alkyl halides and alcohols) the number of such groups attached to the carbon atom which bears the functional group.

Aliphatic amines

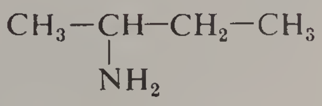
Simple amines are usually named by adding the word amine to the names of the groups to which the nitrogen atom is attached (Table 16.1).

16.2 Nomenclature

Table 16.1. Some aliphatic amines

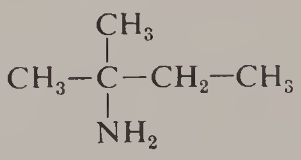
NAME	FORMULA	CLASS	B.P./°C
Methylamine	$CH_3—NH_2$	Primary	−7
Ethylamine	$CH_3CH_2—NH_2$	Primary	17
Dimethylamine	$CH_3—NH—CH_3$	Secondary	7
Methylethylamine	$CH_3CH_2—NH—CH_3$	Secondary	35
Diethylamine	$CH_3CH_2—NH—CH_2CH_3$	Secondary	56
Trimethylamine		Tertiary	3
Triethylamine		Tertiary	89

An alternative nomenclature employs the prefix **amino**; for example:



$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CH_2-CH_3$

2-Aminobutane

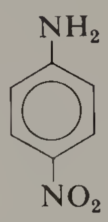


$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$

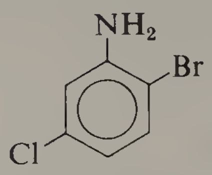
2-Amino-2-methylbutane

Aromatic amines

The simplest, phenylamine, $C_6H_5-NH_2$, is sometimes called by its original name, aniline. Examples of substituted phenylamines are:

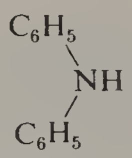


4-Nitrophenylamine

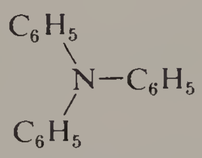


2-Bromo-5-chlorophenylamine

There are also amines which contain more than one aryl group, for example:



Diphenylamine



Triphenylamine

As will be seen, there are significant differences both in methods of preparation and in properties between aliphatic amines and those aromatic amines in which the nitrogen atom is attached to the benzene ring (aryl amines, e.g. phenylamine). (Phenylmethyl)amine, $C_6H_5CH_2NH_2$, although it contains the benzene ring, behaves like an aliphatic amine since the nitrogen atom is not attached directly to the ring.

16.3 Physical properties of amines

The lower aliphatic amines are gases or low-boiling liquids, their boiling points being lower than those of the corresponding alcohols. They have a smell rather like bad fish; indeed, decaying fish produce various amines. They are readily soluble in water and in organic solvents.

Aromatic amines are liquids or solids with high boiling points. They have a characteristic smell and are soluble in organic solvents but almost insoluble in water.

16.4 Methods of preparation of amines

Laboratory methods

1. Aliphatic amines can be prepared by the reaction between an alkyl halide and ammonia (9.3). However, the method is rarely used because a mixture of primary, secondary and tertiary amines and quaternary ammonium salts is obtained:

$$R{-}Br + NH_3 \rightarrow R{-}NH_2 + HBr$$

$$R{-}Br + R{-}NH_2 \rightarrow R_2NH + HBr$$

$$R{-}Br + R_2NH \rightarrow R_3N + HBr$$

$$R{-}Br + R_3N \rightarrow R_4N^+\ Br^-$$

(The hydrogen bromide evolved reacts with ammonia and amines to form salts.)

Aryl amines cannot be made in this way because aryl halides are unreactive towards ammonia.

2. By the reduction of a nitro compound, giving a primary amine. The reducing agent can be hydrogen, catalysed by nickel:

$$R\text{—}NO_2 + 3H_2 \xrightarrow{\text{Ni as cat.}} R\text{—}NH_2 + 2H_2O$$

or lithium tetrahydridoaluminate:

$$R\text{—}NO_2 \xrightarrow{LiAlH_4} R\text{—}NH_2$$

Tin and hydrochloric acid are used to reduce aromatic nitro compounds; the amine is produced as a complex salt from which it is liberated with alkali, for example:

$$2C_6H_5\text{—}NO_2 + Sn + 6HCl \rightarrow (C_6H_5\text{—}\overset{+}{N}H_3)_2SnCl_6{}^{2-} + 2H_2O$$

$$(C_6H_5\overset{+}{N}H_3)_2SnCl_6{}^{2-} + 8NaOH \rightarrow 2C_6H_5NH_2 + Na_2SnO_3 + 5H_2O + 6NaCl$$

3. Primary amines are also formed by the reduction of nitriles and amides with lithium tetrahydridoaluminate:

$$R\text{—}CN \xrightarrow{LiAlH_4} R\text{—}CH_2\text{—}NH_2$$

$$R\text{—}CO\text{—}NH_2 \xrightarrow{LiAlH_4} R\text{—}CH_2\text{—}NH_2$$

4. By the Hofmann degradation reaction, giving a primary amine (14.5). An amide is treated with bromine and alkali, and the resulting amine is distilled off:

$$R\text{—}CO\text{—}NH_2 + Br_2 + 4NaOH \rightarrow R\text{—}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

It should be noted that an amide, $RCONH_2$, is reduced to the amine with the same number of carbon atoms, RCH_2NH_2, with lithium tetrahydridoaluminate but gives the lower homologue RNH_2 in the Hofmann reaction.

Manufacture

Primary aliphatic amines are usually produced by heating the appropriate alcohol with ammonia under pressure, in presence of a catalyst.

Phenylamine is manufactured by the hydrogenation of nitrobenzene in the gas-phase over copper, or in the liquid phase with nickel as the catalyst.

16.5 Chemical properties of amines

Reactions at the nitrogen atom

1. Amines, like ammonia, give alkaline solutions in water as a result of the equilibrium:

$$R\text{—}NH_2 + H_2O \rightleftharpoons R\text{—}\overset{+}{N}H_3 + OH^-$$

The equilibrium constant for this reaction is given by

$$K = \frac{[\text{R—}\overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R—NH}_2][\text{H}_2\text{O}]}$$

As with carboxylic acids, it is customary to assume $[H_2O]$ is constant, and the base strength of an amine, K_b, is defined as:

$$K_b = \frac{[\text{R—}\overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R—NH}_2]}$$

Again, as with carboxylic acids, K_b is usually defined as a dimensionless quantity in advanced texts (p. 62). Moreover, base strength is often described in terms of the dissociation constant of the *conjugate acid* of the base; for example, RNH_3^+ is the conjugate acid of the base RNH_2:

$$\text{R—}\overset{+}{\text{N}}\text{H}_3 \rightleftharpoons \text{R—NH}_2 + \text{H}^+$$

$$\text{and } K_a = \frac{[\text{RNH}_2][\text{H}^+]}{[\text{R}\overset{+}{\text{N}}\text{H}_3]}$$

Since $[H^+][OH^-] = K_w$ (the ionic product of water), it follows that $K_b = K_w/K_a$.

Amines are weak bases; values of K_b are in Table 16.2.

Table 16.2. Dissociation constants of ammonia and some amines

COMPOUND	K_b AT 25°C
NH_3	$1{\cdot}8 \times 10^{-5}$
$CH_3—NH_2$	$4{\cdot}4 \times 10^{-4}$
$(CH_3)_2NH$	$5{\cdot}9 \times 10^{-4}$
$(CH_3)_3N$	$6{\cdot}3 \times 10^{-5}$
$C_6H_5—NH_2$	$4{\cdot}2 \times 10^{-10}$
$C_6H_5CH_2—NH_2$	$2{\cdot}2 \times 10^{-5}$

The aliphatic amines are approximately as basic as ammonia. However, the aryl amines such as phenylamine are much weaker bases.

This is because the unshared pair of electrons on the nitrogen atom in phenylamine is in an orbital which overlaps with the adjacent carbon *p* orbital, giving increased delocalisation in the aromatic, as compared with an aliphatic, amine. One of the delocalised π molecular orbitals is shown in Fig. 16.1.

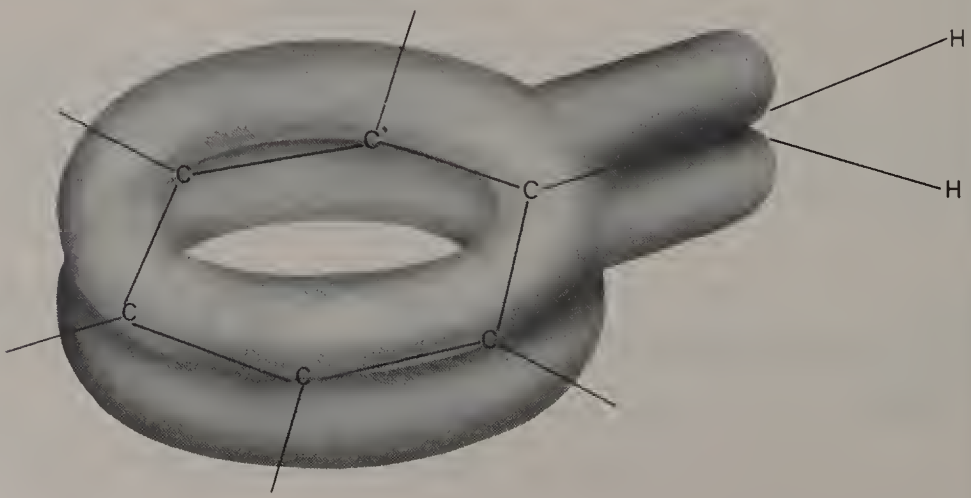


FIG. 16.1. *A π molecular orbital in phenylamine*

Therefore, relative to an aliphatic amine, phenylamine resists reaction with a proton since this process requires the use of the unshared pair of electrons on nitrogen in the formation of the new N—H bond and so results in the loss of the extra delocalisation (*cf.* the weaker basicity of an amide compared with an amine, p. 221).

On the other hand, an aromatic amine such as (phenylmethyl)amine does not contain a nitrogen atom adjacent to a carbon atom with a *p* orbital and is approximately as strong a base as an aliphatic amine.

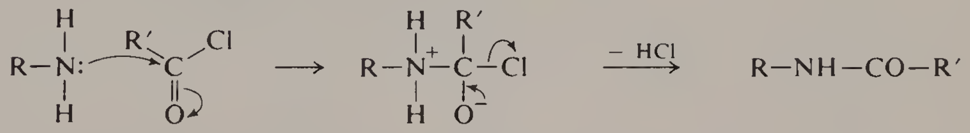
The salts formed by amines with acids are analogous to ammonium salts. For example, amine hydrochlorides, like methylammonium chloride, $CH_3\overset{+}{N}H_3\ Cl^-$, are white crystalline solids with high melting points (above about 200°C) which are soluble in water.

2. Primary and secondary amines react with acid chlorides and acid anhydrides to form substituted amides, for example:

$$CH_3{-}NH_2 + CH_3{-}CO{-}Cl \rightarrow \underset{\text{N-Methylethanamide}}{CH_3{-}NH{-}CO{-}CH_3} + HCl$$

$$C_6H_5{-}NH_2 + CH_3{-}CO{-}O{-}CO{-}CH_3 \rightarrow \underset{\text{N-Phenylethanamide}}{C_6H_5{-}NH{-}CO{-}CH_3} + CH_3CO_2H$$

In these reactions the amine acts as a nucleophile:



3. Amines react with nitrous acid in a way which depends on whether they are primary, secondary or tertiary amines.

Primary aliphatic amines react to yield gaseous nitrogen. The reaction is complex; for example, propylamine gives nitrogen almost quantitatively, but a mixture of other compounds is also formed, among them being propene, propan-2-ol and a trace of propan-1-ol.

Primary aryl amines react to give aromatic diazonium salts, providing that the temperature is below about 10°C. For example, when phenylamine is treated with hydrochloric acid and sodium nitrite, it reacts with the nitrous acid formed to give benzenediazonium chloride:

$$C_6H_5{-}NH_2 + HNO_2 + HCl \rightarrow \underset{\substack{\text{Benzenediazonium}\\ \text{chloride}}}{C_6H_5{-}\overset{+}{N}{\equiv}N\ Cl^-} + 2H_2O$$

Aromatic diazonium salts are of value in making other aromatic compounds and are discussed separately (16.8).

Secondary amines, both aliphatic and aromatic, react with nitrous acid to give nitroso compounds, which are yellow oils:

$$R_2NH + HNO_2 \rightarrow \underset{\text{A nitrosamine}}{R_2N{-}N{=}O} + H_2O$$

Tertiary amines react with nitrous acid to give solutions containing substituted ammonium nitrites. Since these are salts formed by a weak acid and a weak base, they are extensively hydrolysed; that is, the equilibrium

$$R_3N + HNO_2 \rightleftharpoons R_3\overset{+}{N}H\ NO_2^-$$

lies to the left-hand side.

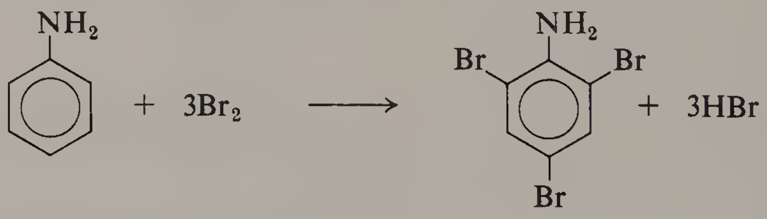
4. Primary amines react with trichloromethane and a solution of potassium hydroxide in ethanol to form isocyano-compounds (carbylamine reaction; 9.4);

$$R{-}NH_2 + CHCl_3 + 3KOH \rightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C} + 3KCl + 3H_2O$$

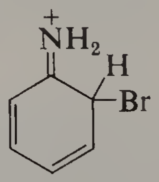
For example, phenylamine forms isocyanobenzene, C_6H_5NC.

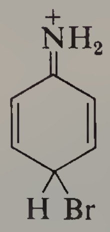
Substitution in the aromatic ring of aryl amines

The amino group in an aryl amine directs electrophilic reagents mainly to the 2- and 4-positions and renders the compound far more reactive than benzene towards these reagents. For example, whereas benzene requires a halogen carrier to react with bromine to form bromobenzene (8.3), phenylamine reacts rapidly with bromine water in the absence of a carrier at all three 2- and 4-positions:

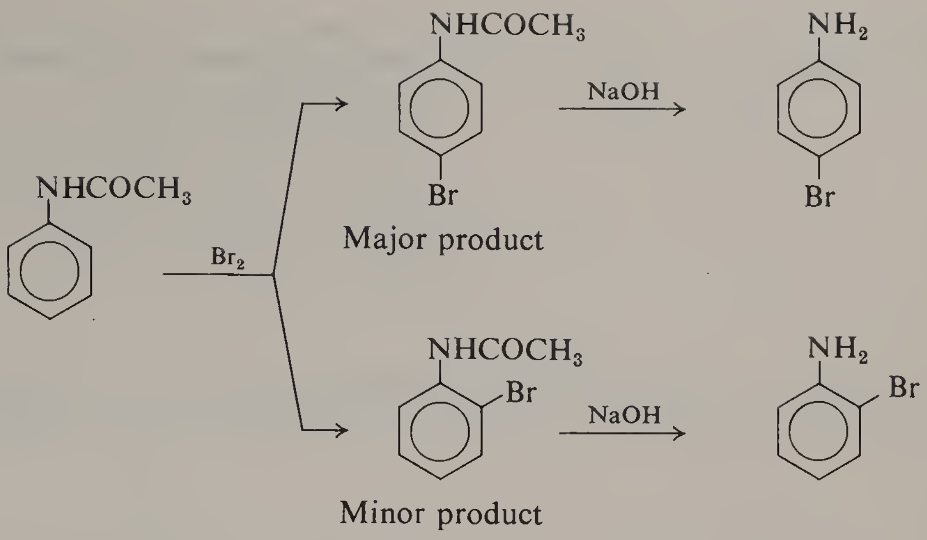


The reason is that the amino group stabilises the adducts formed by reaction at the 2- and 4-positions by sharing the positive charge (8.5). This can be represented by the structures:

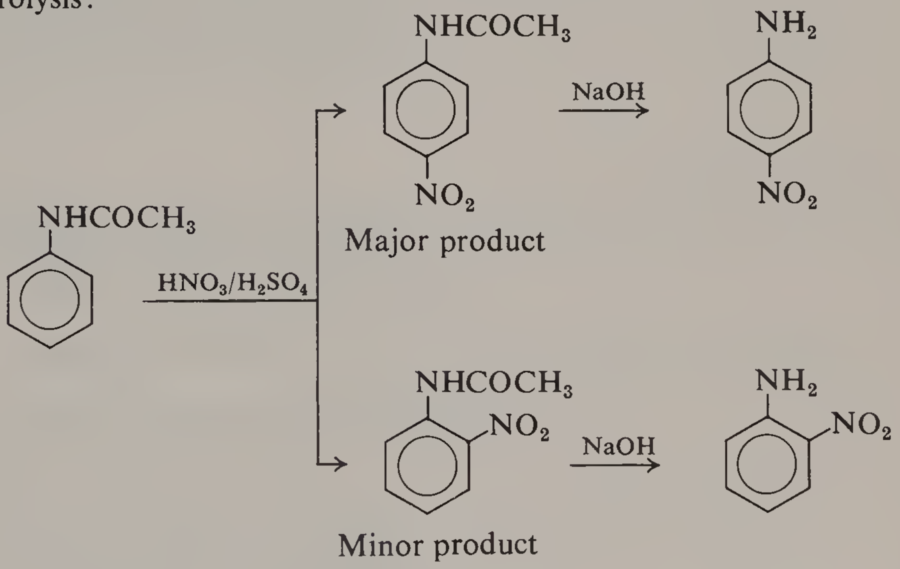




In order to obtain a monobromo derivative, it is necessary to reduce the reactivity of the aromatic ring. This can be achieved by ethanoylation of the amino group with ethanoic anhydride (p. 255); the substituent —NH—CO—CH_3 is 2-,4-directing, but much less strongly activating than —NH_2, and reaction with bromine gives *N*-2- and *N*-(4-bromophenyl) ethanamide. The ethanoyl group can then be removed by hydrolysis with a dilute solution of sodium hydroxide:



This use of the ethanoyl group is an example of **protection**: the aromatic ring is protected from the extensive reactions which occur with phenylamine itself. Protection is also required for the nitration of phenylamine, in this case not only because otherwise reaction would occur at all the 2- and 4-positions but also because the amino group is itself readily oxidised by nitric acid. Nitration of *N*-phenylethanamide gives the 2- and 4-nitro derivatives from which 2- and 4-nitrophenylamine can be obtained by hydrolysis:



16.6 Uses of amines

1. *Plastics*. 1,6-Diaminohexane, $H_2N—(CH_2)_6—NH_2$, is used in the manufacture of nylon-6.6 (p. 336). Other amines are used in the production of isocyanates for polyurethane plastics (p. 334).

2. *Inhibitors*. Amines are effective at preventing the deterioration of rubber through oxidation by atmospheric oxygen.

3. *Dye-stuffs*. Primary aromatic amines are used to make azo-dyes (16.8).

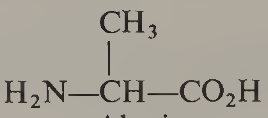
4. *Medicines*. Amines are used in the manufacture of many pharmaceuticals (e.g. Paludrine, an antimalarial drug).

16.7
Amino-acids

Amino-acids contain at least one amino and one carboxyl group. The most important are the 2-amino-acids, which are traditionally referred to as α-amino-acids and retain their original names, which will be used in this book; examples are aminoethanoic acid (glycine), 2-aminopropanoic acid (α-alanine) and 2,6-diaminohexanoic acid (lysine). Their importance stems from their being the constituents of the proteins (18.2). There are also 3-amino-acids (β-amino-acids), such as 3-aminopropanoic acid (β-alanine), 4-amino-acids (γ) and so on.

$H_2N{-}CH_2{-}CO_2H$

Glycine

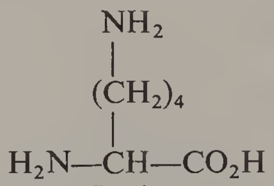


$$H_2N{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CO_2H$$

α-Alanine

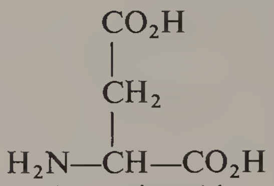
$H_2N{-}CH_2{-}CH_2{-}CO_2H$

β-Alanine



$$H_2N{-}\overset{\displaystyle NH_2}{\overset{|}{\overset{\displaystyle (CH_2)_4}{\overset{|}{C}}}}H{-}CO_2H$$

Lysine



$$H_2N{-}\overset{\displaystyle CO_2H}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{C}}}}H{-}CO_2H$$

Aspartic acid

Physical properties

Amino-acids are high-melting crystalline solids (e.g. glycine has m.p. 235°C) which are usually readily soluble in water but insoluble in organic solvents. In these respects, they resemble salts, and this is because they exist as internal salts, known as **zwitterions**, in which both cation and anion are held together in the same unit, for example:

$$H_3\overset{+}{N}{-}CH_2{-}CO_2^-$$

Amino-acids with an equal number of amino and carboxyl groups (e.g. glycine) are neutral in solution, but when the solution is acidified the carboxyl group is protonated,

$$H_3\overset{+}{N}{-}CH_2{-}CO_2^- + H^+ \rightarrow H_3\overset{+}{N}{-}CH_2{-}CO_2H$$

and when it is basified the amino group is freed:

$$H_3\overset{+}{N}{-}CH_2{-}CO_2^- + OH^- \rightarrow H_2N{-}CH_2{-}CO_2^- + H_2O$$

If the amino-acid contains more carboxyl groups than amino groups (e.g. aspartic acid), its solution in water is acidic. Conversely, if it contains an excess of amino groups (e.g. lysine), its solution in water is basic.

Most α-amino-acids have at least one asymmetric carbon atom and exist in optically active forms (e.g. α-alanine).

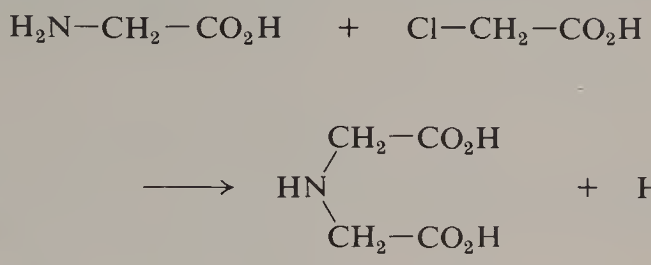
Preparation of α-amino-acids

1. By reaction of a 2-chloro-acid with concentrated ammonia solution, for example:

$$Cl{-}CH_2{-}CO_2H \xrightarrow{2NH_3} H_2N{-}CH_2{-}CO_2^-\ NH_4^+ \xrightarrow{HCl} H_2N{-}CH_2{-}CO_2H + NH_4Cl$$

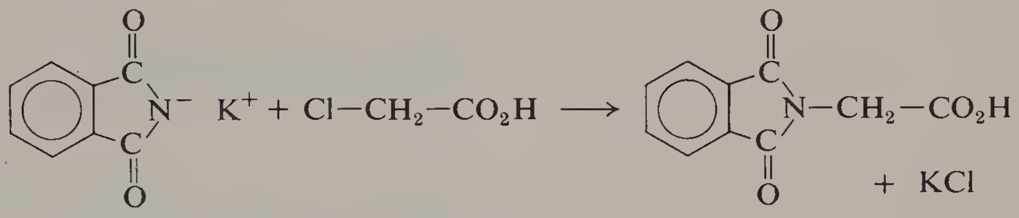
Glycine

The disadvantage of this method is that the amino group which is introduced can react with a second molecule of the chloro-acid:

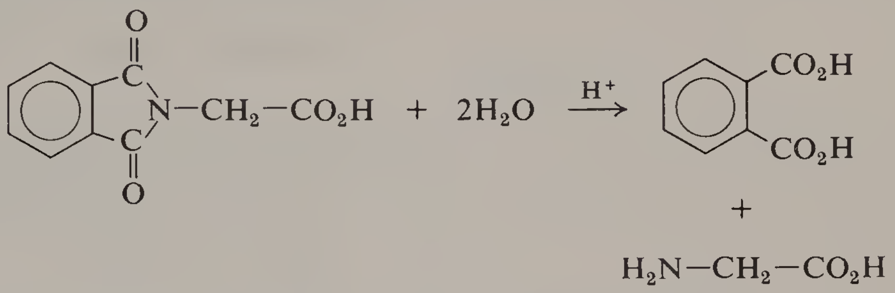


$$H_2N{-}CH_2{-}CO_2H \quad + \quad Cl{-}CH_2{-}CO_2H \longrightarrow HN\begin{array}{l} / \, CH_2{-}CO_2H \\ \backslash \, CH_2{-}CO_2H \end{array} \quad + \quad HCl$$

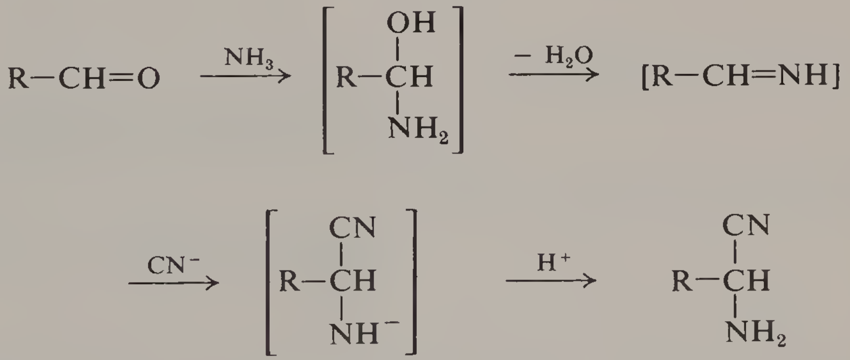
A mixture of products is therefore formed. This problem is overcome by using potassium benzene-1,2-dicarboximide as the source of the nitrogen atom:



The resulting derivative is hydrolysed with acid:



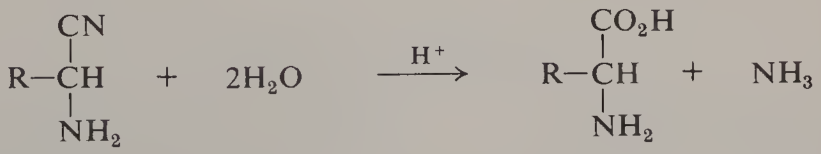
2. By reaction of an aldehyde with a mixture of potassium cyanide and ammonia:



$$R{-}CH{=}O \xrightarrow{NH_3} \left[\begin{array}{c} OH \\ | \\ R{-}CH \\ | \\ NH_2 \end{array}\right] \xrightarrow{-\,H_2O} [R{-}CH{=}NH]$$

$$\xrightarrow{CN^-} \left[\begin{array}{c} CN \\ | \\ R{-}CH \\ | \\ NH^- \end{array}\right] \xrightarrow{H^+} \begin{array}{c} CN \\ | \\ R{-}CH \\ | \\ NH_2 \end{array}$$

followed by hydrolysis of the nitrile:



$$\begin{array}{c} CN \\ | \\ R{-}CH \\ | \\ NH_2 \end{array} \quad + \quad 2H_2O \xrightarrow{H^+} \begin{array}{c} CO_2H \\ | \\ R{-}CH \\ | \\ NH_2 \end{array} \quad + \quad NH_3$$

Chemical properties of α-amino-acids

α-Amino-acids show reactions of both acids and amines individually, as well as some reactions dependent on the presence of both groups. Typical reactions, illustrated for glycine, are:

Reactions of the carboxyl group

1. Formation of esters, for example:

$$H_2N{-}CH_2{-}CO_2H + CH_3{-}OH \overset{H^+}{\rightleftharpoons} H_2N{-}CH_2{-}CO{-}O{-}CH_3 + H_2O$$

2. Decarboxylation, when heated with soda-lime (cf. the decarboxylation of ethanoic acid, p. 199):

$$H_2N{-}CH_2{-}CO_2H + 2NaOH \rightarrow \underset{\text{Methylamine}}{H_2N{-}CH_3} + Na_2CO_3 + H_2O$$

Reactions of the amino group

1. Formation of acyl derivatives, for example:

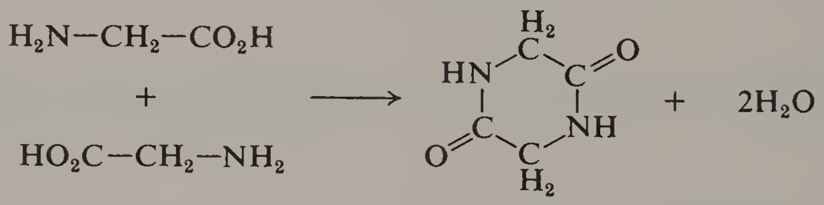
$$H_2N{-}CH_2{-}CO_2H + CH_3{-}CO{-}Cl \rightarrow CH_3{-}CO{-}NH{-}CH_2{-}CO_2H + HCl$$

2. Reaction with nitrous acid:

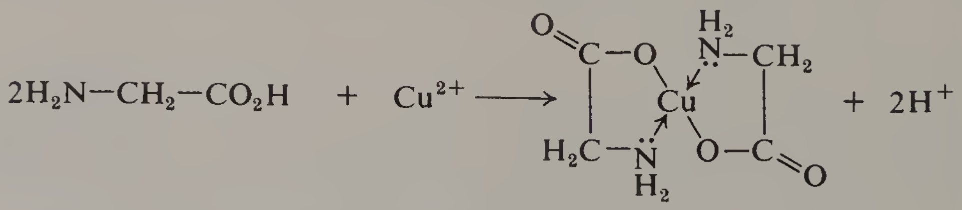
$$H_2N{-}CH_2{-}CO_2H + HNO_2 \rightarrow \underset{\text{Hydroxyethanoic acid}}{HO{-}CH_2{-}CO_2H} + N_2 + H_2O$$

Reactions dependent on the presence of both groups

1. When heated, a cyclic compound (diketopiperazine) is formed:



2. When treated with copper(II) ion in water, a deep blue colour is produced due to the compound, copper(II)-glycine:



Copper(II)-glycine

16.8 Aromatic diazonium salts

Primary aromatic amines react with nitrous acid in acid solution below about 10°C to form aromatic diazonium salts, for example:

$$C_6H_5{-}NH_2 + HNO_2 + HCl \rightarrow \underset{\text{Benzenediazonium chloride}}{C_6H_5{-}\overset{+}{N}{\equiv}N\ Cl^-} + 2H_2O$$

The process is known as **diazotisation** and was discovered by Griess in 1858.

Diazonium salts are stable in solution provided that the temperature is kept low. However, most of them are explosive in the solid state, and so they are usually not isolated from the aqueous solutions in which they are made. They are useful in synthesis because the substituent $—\overset{+}{N}{\equiv}N$ can be replaced by a variety of other groups by treating the aqueous solution of the salt with an appropriate reagent.

Their reactions can be divided into two groups: (a) those in which the two nitrogen atoms are replaced, and (b) those in which the nitrogen atoms are retained.

(a) Reactions in which the nitrogen atoms are replaced

1. Replacement by the **hydroxyl** group. If the solution of the diazonium salt is warmed, a phenol is formed, for example:

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- + H_2O \rightarrow \underset{\text{Phenol}}{C_6H_5—OH} + N_2 + HCl$$

2. Replacement by a **halogen** atom.

(i) **Iodine.** When the solution of the diazonium salt is warmed with an aqueous solution of potassium iodide, an iodo compound is formed, for example:

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5—I} + N_2 + KCl$$

(ii) **Chlorine** and **bromine.** A solution of a copper(I) halide dissolved in the concentrated halogen acid is added to the solution of the diazonium salt, for example:

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- \xrightarrow{CuCl/HCl} \underset{\text{Chlorobenzene}}{C_6H_5—Cl} + N_2$$

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- + HBr \xrightarrow{CuBr/HBr} \underset{\text{Bromobenzene}}{C_6H_5—Br} + HCl + N_2$$

These are known as *Sandmeyer reactions.*

(iii) **Fluorine.** When a solution of potassium tetrafluoroborate, KBF_4, is added to the solution of the diazonium salt, a precipitate of a diazonium fluoroborate is formed, for example:

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- + KBF_4 \rightarrow C_6H_5—\overset{+}{N}{\equiv}N\ BF_4^- + KCl$$

This salt, which is more stable than diazonium chlorides, is filtered and dried. On being heated carefully to about 120°, the aryl fluoride is formed:

$$C_6H_5—\overset{+}{N}{\equiv}N\ BF_4^- \rightarrow \underset{\text{Fluorobenzene}}{C_6H_5—F} + N_2 + BF_3$$

3. Replacement by the **nitrile** group. Copper(I) cyanide dissolved in aqueous potassium cyanide is added to the solution of the diazonium salt, for example:

$$C_6H_5—\overset{+}{N}{\equiv}N\ Cl^- + CuCN \xrightarrow{KCN} \underset{\text{Benzonitrile}}{C_6H_5—CN} + N_2 + CuCl$$

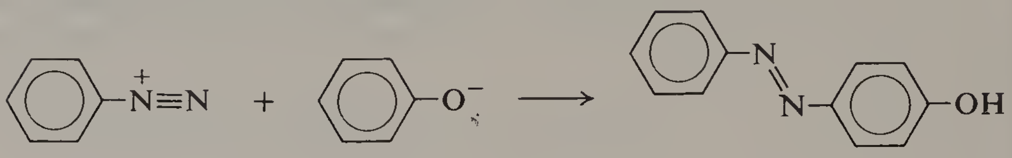
4. Replacement by a **hydrogen** atom. Hypophosphorous acid is added to the solution of the diazonium salt, for example:

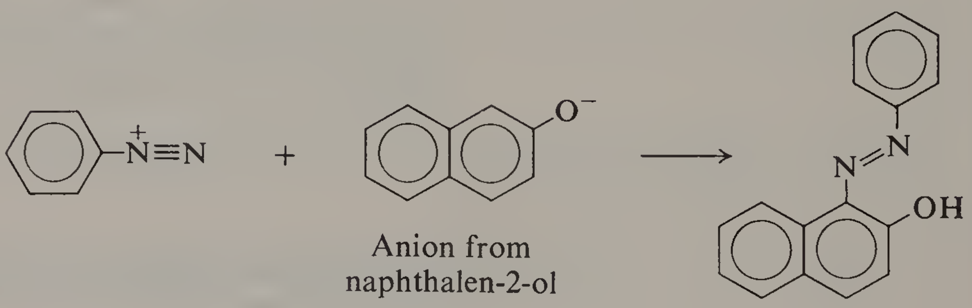
$$C_6H_5{-}\overset{+}{N}{\equiv}N\ Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

(b) Reactions in which the nitrogen atoms are retained

1. Diazonium salts react with phenols and tertiary aromatic amines to form bright-coloured **azo-compounds**.

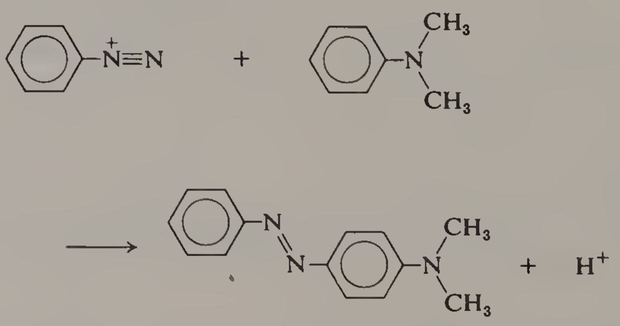
The reaction with phenols is carried out in alkaline solution (that is, with the phenoxide ion), for example:



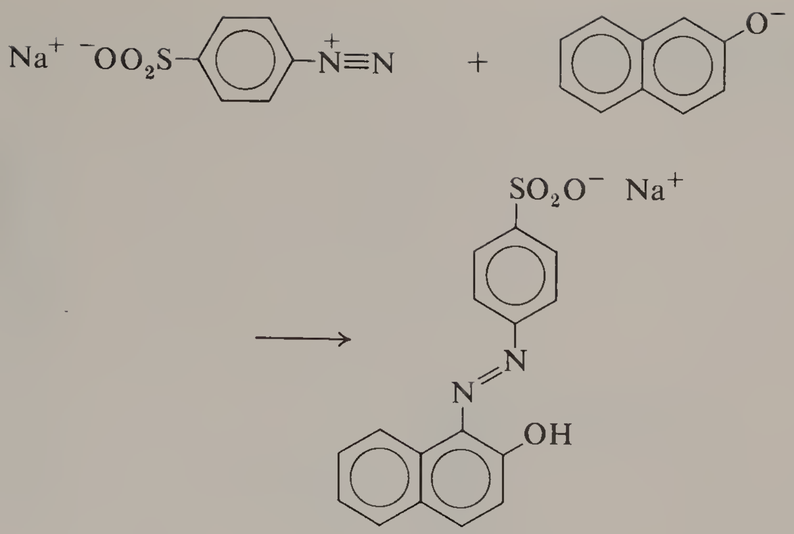


The products formed with naphthalen-2-ol are insoluble, mostly red compounds. Thus, the formation of a red precipitate when an amine is treated with nitrous acid and the solution is poured into an alkaline solution of naphthalen-2-ol shows that the amine is a primary aromatic one; this provides a useful test.

The reaction of diazonium salts with tertiary aromatic amines is carried out in neutral solution. An example is:



Azo-compounds are coloured because the group —N=N— absorbs light; the group is known as a **chromophore**. The particular colour depends on what other substituents are present; these are called **auxochromes**. Many of the compounds are used as dyes; an example is Orange II, which is made by diazotising the sodium salt of 4-aminobenzenesulphonic acid and coupling the product to naphthalen-2-ol:



Orange II

2. Diazonium salts are reduced by a solution of sodium sulphite to arylhydrazines, for example:

$$C_6H_5-\overset{+}{N}\equiv N\ Cl^- + 2Na_2SO_3 + 2H_2O \rightarrow$$
$$\underset{\text{Phenylhydrazine}}{C_6H_5-NH-NH_2} + 2Na_2SO_4 + HCl$$

16.9
Practical work

Small-scale preparation of methylamine and methylammonium chloride: The Hofmann degradation

To 2 g of ethanamide and 2 cm^3 of bromine in a boiling-tube, add 2 g of sodium hydroxide dissolved in 10 cm^3 of water, while shaking the tube under a stream of cold water. A solution of sodium *N*-bromoethanamide is formed, which is pale yellow.

In a separate boiling-tube, dissolve 4 g of sodium hydroxide in 10 cm^3 of water, and pour this solution into the flask (Fig. 16.2). Place the solution of sodium *N*-bromoethanamide in the dropping funnel.

Heat the flask to 70°C in a water-bath and add the sodium *N*-bromoethanamide solution dropwise. Keep the mixture at this temperature for a further 10 minutes. Remove the beaker of water and boil the solution, using a bunsen burner, to drive over methylamine. The base will be absorbed in the acid to yield methylammonium chloride, a salt.

Transfer the solution of the salt to an evaporating basin and evaporate the solution to dryness, using a water-bath.

Transfer a few crystals of methylammonium chloride to a test-tube and add dilute sodium hydroxide solution. Warm and test the gas evolved by (a) smell, (b) moist red and blue litmus papers.

If there is time, transfer the rest of the methylammonium chloride to a boiling-tube, add 5 cm^3 of ethanol and warm the mixture in a beaker of boiling water. Filter (to remove any solid ammonium chloride which may have been formed from the alkaline hydrolysis of ethanamide), and allow the filtrate to cool. Filter off crystals of methylammonium chloride and dry them between pads of filter papers. Find the m.p.

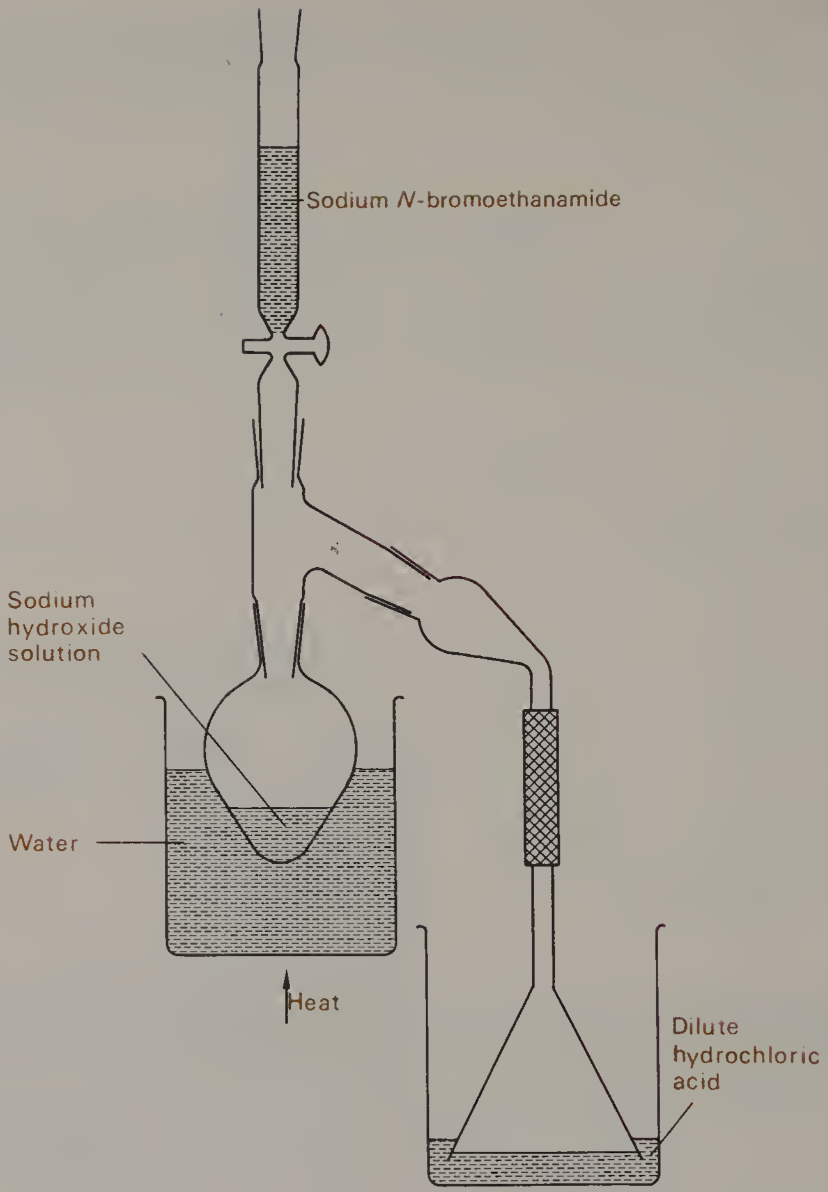


FIG. 16.2. *Preparation of methylammonium chloride by the Hofmann reaction*

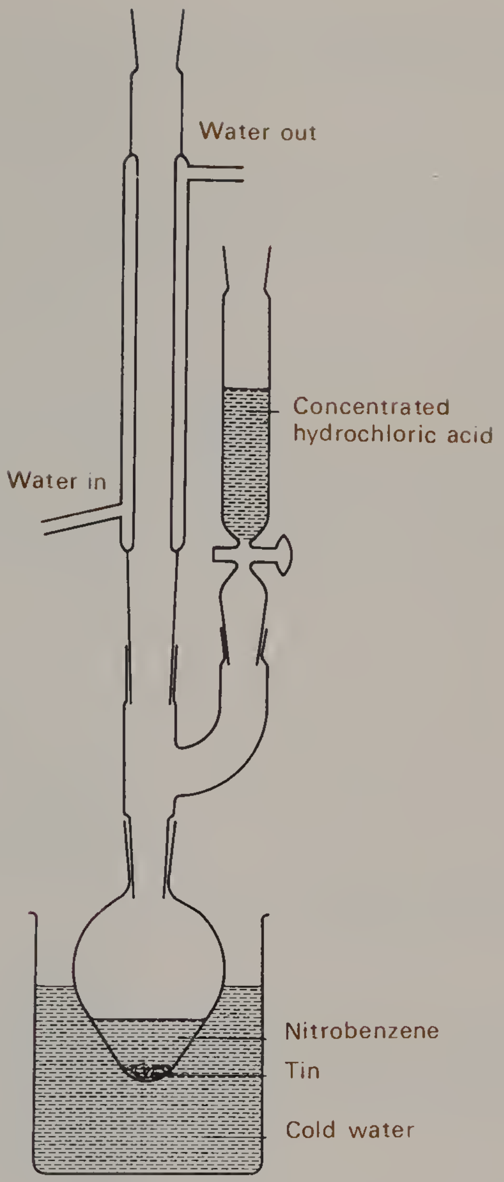
Small-scale preparation of phenylamine

To 2 cm^3 of nitrobenzene and 4 g of tin in a flask, add 10 cm^3 of *concentrated* hydrochloric acid from the dropping funnel (Fig. 16.3). Shake the mixture, immersing the flask in cold water if the reaction becomes too vigorous.

Remove the flask-head and heat the flask in boiling water for 30 minutes (to complete the reduction of nitrobenzene). If some tin remains, add *concentrated* hydrochloric acid dropwise until it has dissolved. Phenylammonium chloride and phenylammonium hexachlorostannate(IV) are soluble in water, but when excess of concentrated sodium hydroxide solution is added, phenylamine is liberated as an oil and the tin salts are precipitated and then dissolve to sodium stannate(IV).

Set up the flask for steam distillation (Fig. 2.6), keeping a low bunsen flame below the centre flask to prevent undue condensation of steam from the steam flask. Distil until no more oily drops of phenylamine can be seen distilling over. Transfer the distillate to a separating funnel and add about 2 g of sodium chloride and shake. (The salt reduces the solubility of phenylamine in water). Run off the organic layer into a test-tube and add some potassium carbonate to remove water. After standing for a few minutes, the turbidity should disappear.

FIG. 16.3. *Preparation of phenylamine*



Redistil phenylamine, using an air condenser (cf. Fig. 2.3), collecting the fraction boiling between 180 and 185°C.

Reactions of ammonia, methylamine, phenylamine and (phenylmethyl)amine

To compare their reactions as bases

1. (a) Place 2 cm^3 of an aqueous solution of ammonia, 2 cm^3 of an aqueous solution of methylamine, 3 drops of phenylamine and 3 drops of (phenylmethyl)amine in separate test-tubes, and test the solutions with Universal Indicator solution.

(b) To 3 drops of phenylamine and 3 drops of (phenylmethyl)amine in separate test-tubes, add 5 drops of water. Shake to see whether the amine dissolves. Then add dilute hydrochloric acid dropwise, with shaking.

2. To 1 g of methylammonium chloride in a test-tube, add 5 cm^3 of dilute sodium hydroxide solution. Boil gently. Test the vapour with moist red litmus paper. Note the smell of the gas.

Repeat the experiment with phenylammonium chloride.

Formation of amides

3. (a) A test-tube experiment to demonstrate the formation of *N*-phenylethanamide is described on p. 227, and a small-scale preparation is described below.

(b) *The Schotten-Baumann* reaction to form *N*-phenylbenzamide is described on p. 227.

Reactions with nitrous acid

4. Make up a solution of about 3 g of sodium nitrite in 10 cm^3 of water, and cool it to about 5°C.

In separate test-tubes, make up *solutions* of a few crystals of methylammonium chloride in water, a few drops of phenylamine in *concentrated* hydrochloric acid and of (phenylmethyl)amine is *concentrated* hydrochloric acid. Cool these solutions and add the cool solution of sodium nitrite to each. Observe what happens (a) in the cold, (b) when the phenylamine solution is warmed.

The reaction between phenylamine and nitrous acid is studied further below.

Reaction of the phenyl group

5. To 5 drops of phenylamine in a test-tube, add *concentrated* hydrochloric acid dropwise until the base dissolves. Add bromine water carefully until nothing more is seen to occur.

Compare the rate of, and the products formed by, the reaction of bromine and phenylamine with those of bromine with (a) methylbenzene (p. 113), (b) phenol (p. 162).

Small-scale preparation of *N*-phenylethanamide

Cool a flask containing 4 cm^3 of glacial acetic acid and 4 cm^3 of ethanoic anhydride in a beaker of cold water, and add 4 cm^3 of phenylamine dropwise with gentle shaking.

Reflux the mixture for 30 minutes (cf. Fig. 2.1) and then pour the liquid into a beaker containing 100 cm^3 of water. Filter the crystals of *N*-phenylethanamide using a Buchner funnel and flask, and wash them with cold water.

Transfer the crystals to a boiling-tube, dissolve them in the minimum quantity of boiling water and allow the solution to cool. Filter the crystals again and dry between pads of filter paper. M.p. 114°C.

Small-scale preparation of benzenediazonium chloride solution

To 3 cm^3 of phenylamine and 10 cm^3 of water in a boiling tube, add 8 cm^3 of *concentrated* hydrochloric acid. Cork and shake the tube until the amine has dissolved.

Cool the solution in a beaker containing ice to about 5°C, and add a solution of sodium nitrite (3 g in 8 cm^3 of water), previously cooled to 5°C. Make sure that the temperature of the mixture does not rise above 10°C.

Reactions of benzenediazonium chloride solution

(a) *Replacement reactions*

1. Boil 2 cm^3 of the diazonium solution. Note the odour of phenol which separates as an oily liquid.

2. To 2 cm^3 of the diazonium solution at 5°C, add, drop by drop, 1 cm^3 of a 10 per cent solution of potassium iodide, previously cooled to 5°C. Allow to stand for 5 minutes and then gently boil. Observe oily drops of iodobenzene.

3. *Sandmeyer reaction*. Dissolve 1 g of copper(I) chloride in *concentrated* hydrochloric acid in a test-tube. Put the test-tube in a beaker of water at 60°C, and add 2 cm^3 of benzenediazonium chloride solution. Note whether the product is soluble in water and its smell.

(b) *Coupling reactions*

4. To 2 cm^3 of benzenediazonium chloride solution in a test-tube, add phenylamine (cooled to below 5°C) dropwise.

5. Dissolve 2 or 3 crystals of phenol in 2 cm^3 of dilute sodium hydroxide solution. Cool the solution in ice, and add the diazonium solution drop by drop. A yellow precipitate of a dye, the sodium salt of 4-hydroxyazobenzene, is obtained.

6. Repeat experiment 5 using napthalen-2-ol instead of phenol.

Reactions of glycine

1. Test the solubility of glycine in (a) water, (b) ethanol, (c) ether.

(a) *Properties of the amino group*

2. Dissolve about 1 g of glycine in the minimum quantity of *concentrated* hydrochloric acid. Cool the mixture and observe whether a white crystalline solid is formed.

3. To about 1 cm^3 of an ice-cold solution of sodium nitrite in a test-tube, add 1 cm^3 of dilute hydrochloric acid. Some decomposition of the nitrous acid formed will occur. When the effervescence has subsided, introduce a few crystals (or a few drops of a concentrated aqueous solution) of glycine. Effervescence occurs again as nitrogen is evolved.

(b) *Properties of the carboxyl group*

4. To a solution of glycine in water, add some solid sodium hydrogencarbonate.

(c) *Properties due to both groups*

5. To a solution of 1 g of glycine in 10 cm^3 of water, add copper(II) carbonate until it is in excess. Filter the mixture using a Buchner funnel, and transfer the filtrate to a boiling-tube and allow it to stand. Observe whether crystals are formed, their colour and shape. Suggest what reaction has taken place.

16.10 Film and Videotape

Azodyes (F,V) Open University. S246/10F.

16.11 Questions

1 Give **two** methods by which pure ethylamine may be prepared. How does ethylamine react with (a) iodoethane, (b) sodium nitrite and dilute hydrochloric acid, (c) ethanoic anhydride, (d) trichloromethane and ethanolic potash?

2 Outline **two** general methods which could be used to prepare a pure primary aliphatic amine, and state whether they could be applied to the preparation of phenylamine.

Give **three** types of reaction which both ethylamine and phenylamine undergo.

Describe **two** tests which may be used to distinguish between solutions of ethylamine and phenylamine in dilute hydrochloric acid.

3 An organic base *A* contains 61·01 per cent C, 15·25 per cent H, and 23·73 per cent N. When treated with nitrous acid *A* yields an alcohol *B*, and nitrogen is evolved. *B* contains 60·00 per cent C, and 13·33 per cent H, and on careful oxidation yields *C*, which has a vapour density of 29. *C* forms an oxime and an addition compound with sodium hydrogen sulphite, but does not react with Fehling's solution. Suggest structures for *A*, *B* and *C*, and indicate the course of the above reactions. (L)

4 A compound *A* gave on analysis C, 61·0 per cent; H, 15·2 per cent; N, 23·7 per cent. Treatment of *A* with acid and sodium nitrite yielded a compound *B* of molecular formula C_3H_8O. Oxidation of *B* with chromic acid gave *C* with a molecular formula C_3H_6O. The product *C* gave a positive iodoform reaction and formed a crystalline derivative with sodium hydrogen sulphite but did not react with ammoniacal silver nitrate. The compound *B* when treated with ethanoic anhydride gave a product *D* corresponding to $C_5H_{10}O_2$.

2,4 DNP

Deduce the identity of *A*, *B*, *C* and *D*. Explain the sequence of reactions by means of equations involving structural formulae for the organic molecules. (W)

5 A pungent-smelling liquid *A* was analysed and found to contain carbon, hydrogen, chlorine and possibly oxygen. Upon reaction with aqueous ammonia a neutral compound *B* was formed. When this was treated with bromine and potassium hydroxide a base *C* resulted. In acidic solution substance *C* reacted with sodium nitrite, giving nitrogen and an alcohol *D*. Upon mild oxidation, the alcohol *D* was converted into compound *E* of molecular formula C_2H_4O which gave a positive test with ammoniacal silver nitrate solution.

Describe the chemistry involved in these reactions and identify the compounds *A*, *B*, *C*, *D* and *E*. (L)

6 How would you prepare a specimen of phenylamine in the laboratory starting from nitrobenzene? Compare the reactions, if any, of phenylamine with those of methylamine towards the following reagents: (a) nitrous acid, (b) ethanoic anhydride, (c) water. (L)

7 (a) How and under what conditions does butylamine react with
  (i) concentrated hydrobromic acid;
  (ii) aqueous copper(II) sulphate;
  (iii) ethanoyl chloride (acetyl chloride);
  (iv) nitrous acid (nitric(III) acid)?

In each case, indicate the experimental conditions for the reaction, describe what happens, write an equation and give the names and formulae of the reaction products.

(b) Describe and explain the tests you would perform in order to demonstrate the presence of nitrogen in butylamine. (SUJB)

8 State, with equations, **three** methods by which primary amines can be prepared.

How, and under what conditions, do primary amines react with (a) nitrous acid, (b) ethanoic anhydride, and (c) dilute sulphuric acid?

Describe the chemical properties and reactions of glycine.

9 Phenylamine (b.p. 184°C) is prepared in the laboratory by the *reduction of nitrobenzene with tin and concentrated hydrochloric acid.* When the reduction is complete, this mixture is made alkaline with an *excess* of *sodium hydroxide* and *steam distilled. Salt is added* to the distillate, and then the resulting solution is extracted *twice* with *ether*.

Explain fully the reasons for the instructions in the above preparation which are printed in italics. (O)

10 What happens when an organic compound containing nitrogen is heated with copper(II) oxide?

Calculate the percentage of each of the elements in phenylamine, $C_6H_5NH_2$.

How does phenylamine react with (a) hydrochloric acid, (b) ethanoyl chloride, (c) bromine water, (d) nitrous acid? (AEB)

11 Define the term *base*. Arrange the following compounds in order of increasing base strength: ammonia, phenylamine, ethanamide, methylamine, ethylamine.

Compare the action of nitrous acid on phenylamine and ethylamine. Outline how ethanamide may be converted into (a) methylamine, (b) ethylamine (W)

12 (a) Describe briefly how ethane could be converted into (i) ethylamine and (ii) ethanol. In each case give the necessary conditions, reagents and mechanistic equations and comment on any side reactions which may occur.

(b) Explain why ethylamine and ethanol are not prepared in these ways on an industrial scale.

(c) Account for (i) the relative acidity of ethanol, phenol and ethanoic (*acetic*) acid and (ii) the relative basicity of ethylamine and phenylamine (*aniline*).

(JMB)

13 How would you prepare, in the laboratory, a pure specimen of phenylamine from nitrobenzene?

Compare and contrast the behaviour of phenylamine and methylamine towards (i) nitrous acid, (ii) bromine, (iii) sulphuric acid, (iv) ethanoyl chloride.

14 *A* is a gaseous organic compound containing carbon and hydrogen only. A volume of *A* requires an equal volume of hydrogen for complete reduction to *B*, the volumes of gases being measured at the same temperature and pressure. *A* reacts with hydrogen chloride to produce a very volatile liquid *C*, with a composition C, 37·2 per cent; H, 7·75 per cent; Cl, 55·0 per cent. *C* reacts with potassium cyanide to produce *D*.

D reacts with sodium hydroxide to evolve an alkaline gas; and with dilute sulphuric acid to produce *E*, of which 1·00 g dissolved in water requires 27·0 cm^3 of 0·5M (0·5N) sodium hydroxide for complete reaction.

D reacts with zinc dust and an excess of concentrated hydrochloric acid to produce a solution, which, when made strongly alkaline with sodium hydroxide and warmed, evolves an alkaline gas *F*.

Identify the compounds *A* to *F* and write equations for the reactions in the above scheme. Outline the preparation of a sample of *A* in the laboratory.

(C(T))

15 Read the following instructions for the preparation of phenylamine. Explain, as fully as possible, the reasons for using the *apparatus, techniques, materials and conditions* printed in italics.

'Into a 250 cm^3 *wide-necked* flask, fitted with an *air condenser*, place 8·4 cm^3 of *nitrobenzene* and 18 g of granulated *tin*. Pour about 6 cm^3 of *concentrated hydrochloric acid* down the condenser. *Shake thoroughly for* 5 *minutes*. Continue to add the acid in 5 *cm^3 portions at* 5 *minute intervals* with continued shaking until 40 cm^3 has been added. During the addition of acid the flask can be immersed in a *cold water bath* but this should not be done *more than is judged to be necessary*. *Heat* the mixture on a boiling water bath for *30 minutes*. Cool. Add *gradually* a solution of 30 g of *sodium hydroxide* in 50 cm^3 of water until the precipitate dissolves and the mixture, after shaking, is *alkaline*. Cool. *Steam distil* until the distillate is no longer *turbid*. Saturate the distillate with *salt*, transfer to a separating funnel and add about 20 cm^3 of *ether*. Shake, releasing the tap momentarily. Allow to stand, separate the upper layer and place it in a corked conical flask with some *anhydrous magnesium sulphate*. Shake for several minutes. *Filter* and distil the *lower fraction* of the filtrate using a *warm water bath* and *water condenser*. With the lower fraction now removed, distil the higher fraction by *direct heating over a wire gauze* using an *air condenser*. The yield of phenylamine is 7·0 g.'

(SUJB)

16 Outline the preparation of a solution of a benzenediazonium salt. (Full practical details are not required.)

How does benzenediazonium chloride react with (i) copper(I) chloride, (ii) phenol, (iii) potassium iodide, and (iv) water? What is the industrial importance of diazonium salts?

17 A compound *Z* is boiled with excess alkali. Ammonia is expelled. The resulting mixture is evaporated to dryness and on prolonged heating, benzene is evolved. Acidification of the cold residue causes an effervescence of carbon dioxide.

Suggest a structure for *Z* to account for the reactions described and name the compounds involved.

Outline briefly reactions for converting *Z* into (a) phenylamine, (b) isocyanobenzene, (c) (phenylmethyl)amine, $C_6H_5.CH_2.NH_2$.

Explain why ammonia is a weaker base than trimethylamine. (SUJB)

18 What is the diazo reaction? Illustrate the use of this reaction to prepare each of the following compounds starting from phenylamine: (a) benzoic acid, (b) 2,4,6-tribromobenzene, (c) methyl phenyl ether, (d) phenylhydrazine, (e) 4-hydroxyazobenzene. (W(S))

19 When the neutral compound *A*, $C_{10}H_{13}NO$, was refluxed with dilute acid it formed two products *B*, C_2H_7N and *C*.
On analysis, *C* was found to contain 70·59% carbon, 23·53% oxygen and 5·88% hydrogen by weight. The relative molecular mass of *C* was found to be 136.
On reaction with alkaline potassium manganate(VII) (permanganate) solution, *C* was oxidized to *D*, $C_8H_6O_4$.
D, which was acidic, was readily dehydrated to the neutral substance *E*, $C_8H_4O_3$.
B reacted with gaseous hydrogen chloride to form the ionic solid, *F*, C_2H_8NCl.
When *F* was dissolved in dilute hydrochloric acid and sodium nitrite solution added, a yellow oil, *G*, was formed and no effervescence occurred.

(a) What is the empirical formula of *C*?
(b) What is the molecular formula of *C*?
(c) Write the structural formulae for substances *A* to *G*.
(d) What are the names of substances *B*, *C* and *F*? (SUJB)

20 A compound *X* is believed to have the structure

$$H_2N.CH_2.CONH.CH_3.$$

How would you:

(a) show that *X* contains nitrogen;
(b) show that *X* contains an amine group?

How would *X* react with:

(i) soda-lime;
(ii) sulphuric acid;
(iii) ethanoyl chloride?

Suggest a series of reactions by which *X* could be prepared from ethanoic acid. (C(S))

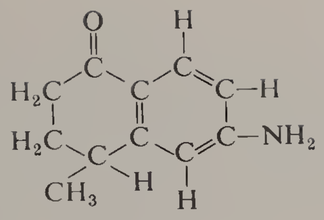
21 Illustrate, with examples, the difference in:

(a) the acidity of the —OH group in ethanoic acid, ethanol and phenol;
(b) the basicity of the —NH_2 group in ethanamide, phenylamine and methylamine.

How do you account for such differences?

How would you expect the basicity of (phenylmethyl)amine $C_6H_5CH_2NH_2$ to compare with that of phenylamine and why? (L(S))

22 A compound was found to have the structural formula illustrated below. From your knowledge of the typical groups it contains give an account of the principal chemical properties which you would expect it to possess.



(L(X, S))

23 Hydrolysis of a compound **L**, $C_{15}H_{15}NO$ with 50% sulphuric acid gave two products, an acid **M**, $C_8H_8O_2$, and a base **N**, C_7H_9N. Reaction of **N** with nitrous acid at 5°C followed by warming the solution on a hot water bath at 50°C gave 4-hydroxymethylbenzene. Addition of phenol to the solution obtained from reaction between **N** and nitrous acid at 5°C gave an orange solid **O**, $C_{13}H_{12}N_2O$. Oxidation of the acid **M** with alkaline potassium manganate(VII) gave **P**, $C_8H_6O_4$, which reacted with methanol in the presence of concentrated sulphuric acid to afford **Q**, $C_{10}H_{10}O_4$. Under suitable conditions **P** reacts with ethane-1,2-diol to produce poly(ethylene terephthalate)*.

Identify the compounds **M**, **N**, **O** and **Q**, and suggest a structure for **L**. Write down equations for the reactions involved.

* terephthalic acid = benzene-1,4-dicarboxylic acid. (C(S))

24 Describe degradative, analytical, and synthetic methods you would employ to establish the structure of 3-methylphenylamine. (W(S))

25 (a) Compare the *physical* properties of aminoethanoic acid with those of methylamine and of ethanoic acid.

Explain what is meant by the term *zwitterion*, and draw a diagram to show the variation of pH with the amount of added hydroxide ion when hydroxide ion is gradually added to a solution containing the ion $^{+}NH_3CH_2CO_2H$ until the solution has become strongly alkaline.

(b) How does urea react with **four** of the following reagents:
- (i) aqueous sodium hydroxide;
- (ii) aqueous sodium bromate(I) (sodium hypobromite);
- (iii) concentrated nitric acid;
- (iv) an aqueous solution containing urease;
- (v) aqueous nitrous acid?

(O(S))

26 An optically active compound *M*, $C_3H_7O_2N$, forms a hydrochloride, but dissolves in water to give a neutral solution. On heating with soda-lime, *M* yields *N*, C_2H_7N; both *M* and *N* react with nitrous acid, the former yielding a compound *P*, $C_3H_6O_3$, which on heating is converted to *Q*, $C_6H_8O_4$. Account for the above reactions and suggest how *M* may be synthesised.

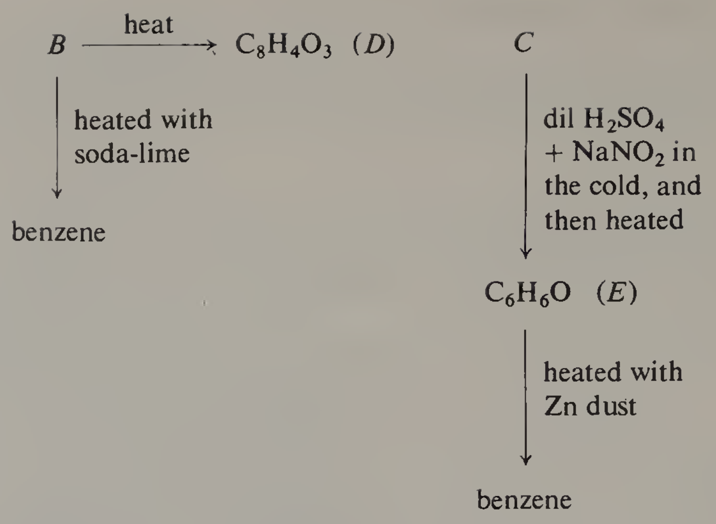
27 (a) Starting from ethanal, suggest a reaction scheme for the preparation of 2-aminopropanoic acid (alanine) $CH_3CH(NH_2)COOH$ stating the necessary reagents and conditions.

(b) Give the structure of the products obtained by reacting 2-aminopropanoic acid with
- (i) aqueous sodium hydroxide solution,
- (ii) dilute hydrochloric acid,
- (iii) ethanoyl chloride (acetyl chloride),
- (iv) an acidified aqueous solution of sodium nitrite.

(c) 2-aminopropanoic acid is said to exhibit *optical isomerism*. What is meant by this statement? Explain why this term can be applied to this amino acid. Give the name and structure of an alkane which also exhibits optical isomerism.

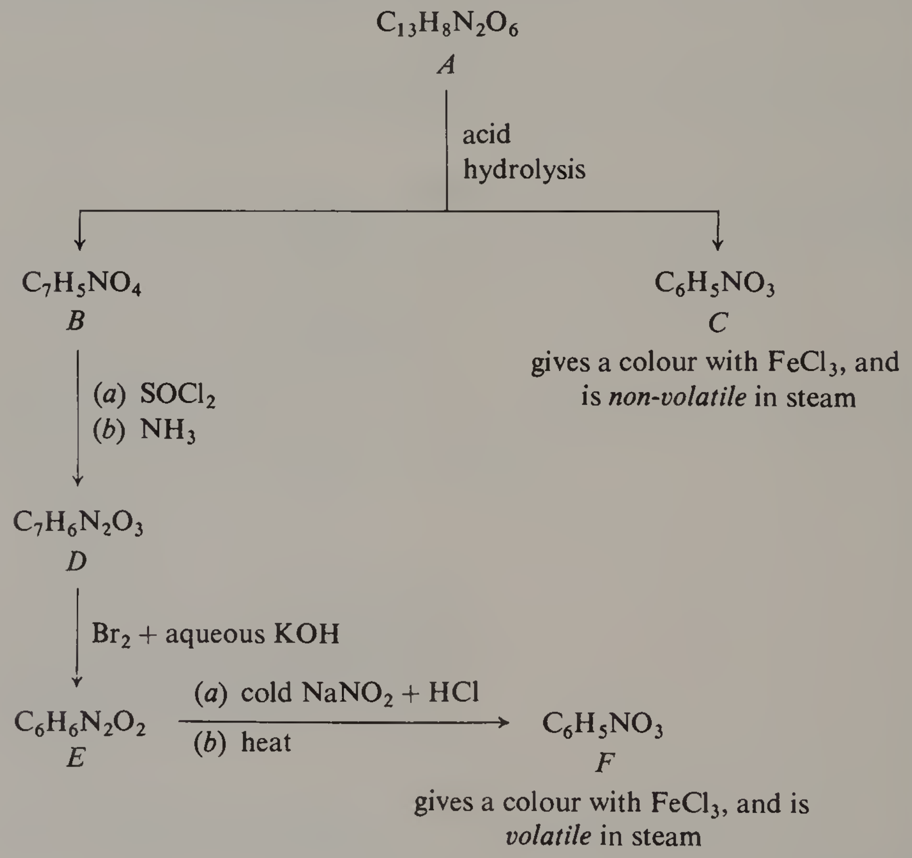
(C)

28 A compound *A*, $C_{14}H_{10}N_2O$, when heated with dilute sulphuric acid gave ammonium sulphate, a compound *B*, $C_8H_6O_4$, and a compound *C*, C_6H_7N (as its sulphate). Compounds *B* and *C* behaved as follows:



Suggest a formula for *A* and account for the above reactions. (C Schol.)

29 Explain the following changes, and deduce the nature of the compounds *A* to *F*:



(O and C(S))

30 What are the principal reactions of the primary amino-group in an amine such as ethylamine? How do the properties of this group differ when it is present in an amide, e.g. ethanamide?

Is the structural formula $NH_2.CH_2.COOH$, satisfactory for glycine (amino-ethanoic acid) which is soluble in water, very sparingly soluble in ether and benzene and which is still solid at 200°C? Give your reasons. (O Schol.)

31 An amino-acid NH_2RCOOH functions both as an acid and as a base in its reactions with water, according to the following equations.

(a) as an acid:

$$NH_2RCOOH + H_2O = NH_2RCOO^- + H_3O^+ \qquad K_a = 10^{-10}M.$$

(b) as a base:

$$NH_2RCOOH + H_2O = {}^+NH_3RCOOH + OH^- \qquad K_b = 2 \times 10^{-12}\ M.$$

At the isoelectric point the concentrations of the cationic and anionic forms of the amino-acid are equal. Calculate the pH of an aqueous solution of the amino-acid at its isoelectric point from the acidic and basic dissociation constants given above and the fact that the ionic product of water is $10^{-14}M^2$.

The amino-acid is a crystalline solid which melts at 250°C. What do you deduce about its chemical structure in the crystal? (O Schol.)

Chapter 17

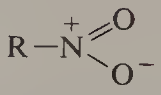
Nitro compounds

17.1 Introduction

General formula

$$R{-}NO_2$$

Nitro compounds have the structure

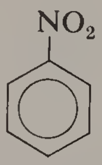


where R is an alkyl group or an aromatic ring. They are isomeric with nitrites, R—O—N=O.

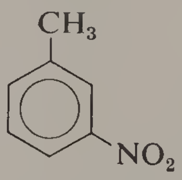
17.2 Nomenclature

Nitroalkanes are named by combining the prefix **nitro** with the name of the corresponding alkane, together with a number to indicate the position of the nitro group in the carbon chain where more than one position is possible.

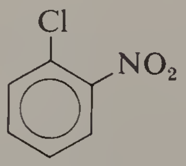
Aromatic nitro compounds which contain the benzene ring are named as derivatives of nitrobenzene, for example:



Nitrobenzene



Methyl-3-nitrobenzene



Chloro-2-nitrobenzene

Table 17.1. Some nitro compounds

NAME	FORMULA	B.P./°C
Nitromethane	$CH_3{-}NO_2$	101
Nitroethane	$CH_3CH_2{-}NO_2$	115
1-Nitropropane	$CH_3CH_2CH_2{-}NO_2$	132
2-Nitropropane	$(CH_3)_2CH{-}NO_2$	120
Nitrobenzene	$C_6H_5{-}NO_2$	210

17.3 Physical properties of nitro compounds

The lower nitroalkanes are colourless liquids which are sparingly soluble in water. Most aromatic nitro compounds are yellow crystalline solids (except for nitrobenzene and methyl-2-nitrobenzene which are yellow liquids) and are insoluble in water and may be purified by steam distillation.

17.4 Methods of preparation of nitro compounds

Laboratory methods

1. Nitroalkanes are prepared by the action of a solution of silver nitrite in ethanol on an alkyl halide, for example:

$$C_2H_5{-}Br + AgNO_2 \rightarrow \underset{\text{Nitroethane}}{C_2H_5{-}NO_2} + AgBr$$

Ethyl nitrite ($C_2H_5{-}ONO$) is also formed (p. 123).

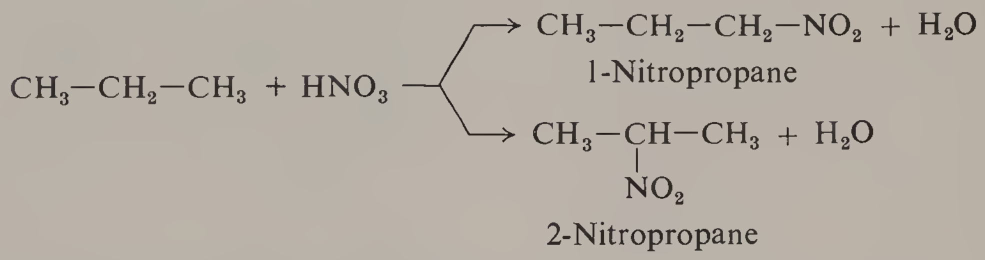
2. Aromatic nitro compounds are prepared by the nitration of the aromatic compound with nitric acid. The choice of conditions depends on the reactivity of the aromatic compound. For benzene, a mixture of concentrated nitric acid and concentrated sulphuric acid is necessary (8.3):

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5{-}NO_2} + H_2O$$

For compounds which are much less reactive than benzene (e.g. 1,3-dinitrobenzene), fuming nitric acid and fuming sulphuric acid are required, whereas for compounds which are much more reactive than benzene (e.g. phenol), dilute nitric acid is suitable.

Manufacture

Nitroalkanes are obtained by the reaction of alkanes with nitric acid in the vapour phase at about 350°C. Alkanes with more than two carbon atoms give mixtures of products which are separated by fractional distillation, for example:



$$CH_3{-}CH_2{-}CH_3 + HNO_3 \longrightarrow \underset{\text{1-Nitropropane}}{CH_3{-}CH_2{-}CH_2{-}NO_2} + H_2O$$

$$CH_3{-}CH_2{-}CH_3 + HNO_3 \longrightarrow \underset{\text{2-Nitropropane}}{CH_3{-}\underset{\large NO_2}{\underset{|}{C}H}{-}CH_3} + H_2O$$

Aromatic nitro compounds are obtained industrially by the same methods as are used in the laboratory.

17.5 Chemical properties of nitro compounds

1. The most important general property of nitro compounds is their reduction to primary amines. This can be effected with hydrogen on nickel:

$$R{-}NO_2 + 3H_2 \xrightarrow{\text{Ni as cat.}} R{-}NH_2 + 2H_2O$$

and with lithium tetrahydridoaluminate:

$$R{-}NO_2 \xrightarrow{LiAlH_4} R{-}NH_2$$

Aromatic nitro compounds are conveniently reduced with tin and hydrochloric acid (16.4), for example:

$$C_6H_5{-}NO_2 \xrightarrow{Sn/HCl} (C_6H_5{-}\overset{+}{N}H_3)_2SnCl_6^{2-} \xrightarrow{NaOH} \underset{\text{Phenylamine}}{C_6H_5{-}NH_2}$$

2. Nitroalkanes are hydrolysed by mineral acids to form a carboxylic acid and hydroxylamine:

$$R{-}CH_2{-}NO_2 + H_2O \xrightarrow{H_2SO_4} R{-}CO_2H + NH_2OH$$

3. Aromatic nitro compounds undergo electrophilic substitution in the

aromatic ring. The nitro group reduces the reactivity of the ring and is 3-directing; for example, nitrobenzene undergoes nitration less readily than benzene and gives 1,3-dinitrobenzene (p. 110).

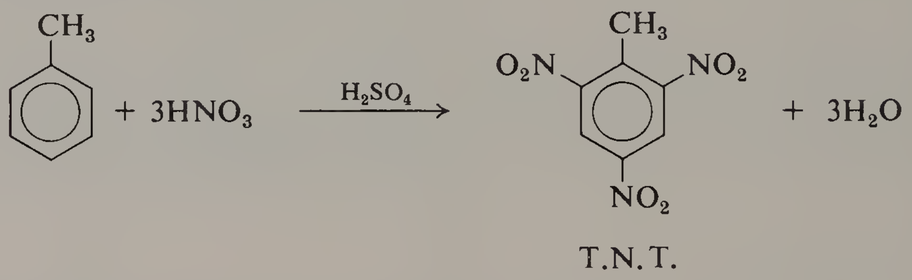
17.6 Uses of nitro compounds

Aliphatic nitro compounds

1. Solvents in industry, particularly for plastics and dyes. They are very useful as they have medium boiling points and do not have obnoxious smells.
2. Specialist engine fuels and rocket propellants.

Aromatic nitro compounds

1. In the preparation of aromatic amines, used for the production of dyes (16.8).
2. A particularly important aromatic nitro compound is methyl-2,4,6-trinitrobenzene (trinitrotoluene, T.N.T.), a powerful explosive made by the nitration of methylbenzene with a mixture of fuming nitric and fuming sulphuric acids:



Small-scale preparation of 1,3-dinitrobenzene

To 8 cm^3 of concentrated nitric acid in a flask, add slowly 10 cm^3 of concentrated sulphuric acid, shaking and cooling the flask under a stream of running water.

Arrange the apparatus (Fig. 17.1) and add 6 cm^3 of nitrobenzene dropwise from the dropping funnel, gently shaking the flask.

Boil the water in the beaker, and heat the mixture for about 40 minutes.

Pour the mixture into 150 cm^3 of cold water in a beaker and stir the contents from time to time for about 15 minutes. Filter off the solid and wash it with distilled water (Fig. 2.8).

Squeeze the crude product between filter papers to absorb any liquid impurities, and then place it in a boiling tube. Add about 20 cm^3 of ethanol (or methylated spirit) and heat in a beaker of boiling water. (If there are any solid impurities, filter.) Allow the solution to cool and filter the product.

Dry the crystals between pads of filter paper (and if possible in an oven at 70°C). Find the m.p. of 1,3-dinitrobenzene.

17.7 Practical work

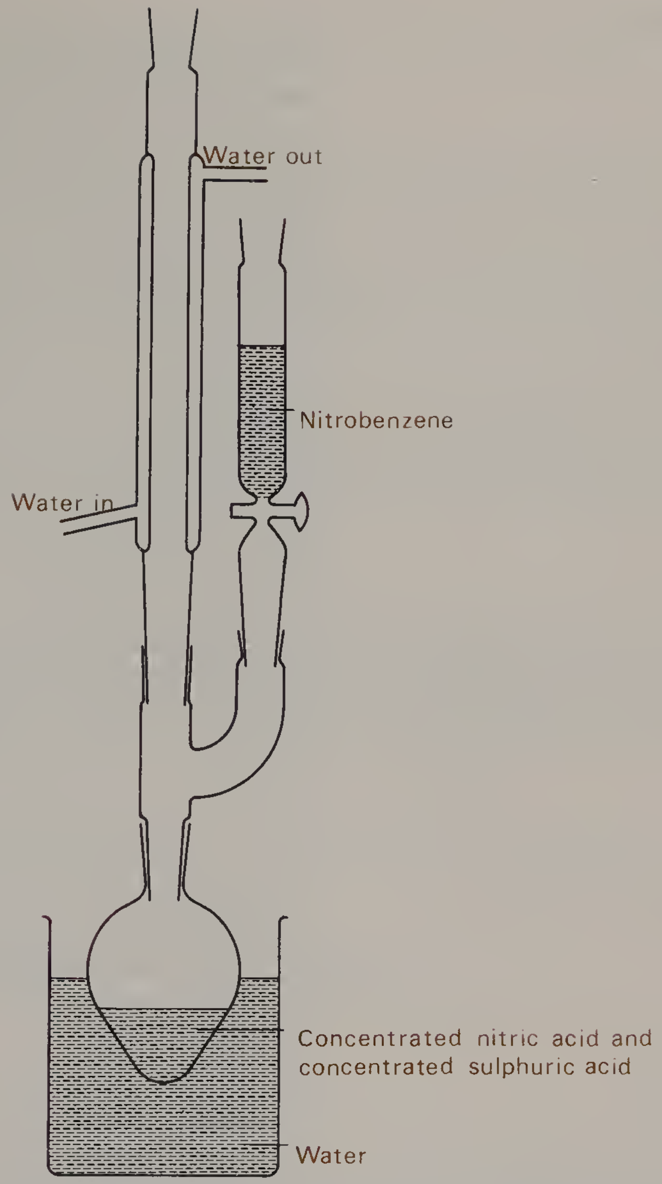
Small-scale preparation of methyl 3-nitrobenzoate

Cool 10 cm^3 of concentrated sulphuric acid in a test-tube, surrounded by ice, to 5°C. Add 5 cm^3 of methyl benzoate with shaking, keeping the temperature at 5°C.

To a separate test-tube, pour in 3·5 cm^3 of concentrated nitric acid and 3·5 cm^3 of concentrated sulphuric acid. Swirl the two acids to mix them and cool this nitrating mixture to 5°C.

Add, using a dropper, the nitrating mixture to the solution of the ester, keeping the temperature to between 20 and 25°C. After the final addition, stand the test-tube for about 15 minutes at room temperature.

FIG. 17.1. *Preparation of 1,3-dinitrobenzene*



Half-fill a 100 cm^3 beaker with crushed ice and pour the mixture onto it. Swirl and filter, using a Buchner funnel (Fig. 2.8). Wash the solid with water and then twice with 5 cm^3 portions of methanol.

Recrystallise a small portion of the nitro compound with methanol, dry it, and determine the melting point (76–77°C).

If time, transfer about 2 g of the ester to a 100 cm^3 beaker and add 20 cm^3 of 2M sodium hydroxide solution. Boil the mixture for about 5 minutes. Then add 2M hydrochloric acid until the solution is just acid (test with litmus paper).

Filter the solid, using a Buchner funnel, and wash thoroughly with water.

Transfer the solid to another 100 cm^3 beaker and recrystallise it using water. Determine the melting point of the dry product (132°C). [The melting point is depressed significantly by water. Ensure that the product is dry].

Comparison of the rates of nitration of aromatic compounds

1. *Nitration of methylbenzene*

(a) Dissolve about 2 g of sodium nitrate in 10 cm^3 of dilute sulphuric acid in a test-tube. Add 5 drops of methylbenzene, shake well and pour the mixture into a beaker containing about 10 cm^3 of cold water. Observe whether nitration has occurred (a dense pale yellow liquid with a characteristic smell of almonds should be formed).

(b) Place 10 drops of *concentrated* nitric acid in a test-tube, and add 10 drops of *concentrated* sulphuric acid, shaking and cooling the test-tube under a stream of cold water. Add the mixed acids to 5 drops of methylbenzene in another test-tube. Shake the mixture under a stream of cold water and then pour it into a beaker containing about 10 cm^3 of cold water. Note the colour and smell of the organic compound.

2. *Nitration of chlorobenzene*

(a) Repeat experiment 1 (a), using chlorobenzene instead of methylbenzene.

(b) Repeat experiment 1 (b), using chlorobenzene instead of methylbenzene. The mixture of chlorobenzene and the mixed acids should be gently warmed for 2–3 minutes, and then cooled before being poured into the beaker containing the cold water.

3. *Nitration of phenol*

Dissolve about 2 g of sodium nitrate in 10 cm^3 of dilute sulphuric acid in a test-tube. Cool the solution by placing the test-tube in a beaker of ice.

In a second test-tube, dissolve 1 g of phenol in 2 cm^3 of water (it may be necessary to warm the mixture). Add the solution of phenol dropwise to the solution of sodium nitrate, making sure that the temperature does not rise above 15°C. Allow the reaction mixture to stand for about 1 hour, decant the solution from the dark brown (black) solid formed, and wash it twice, in a separating funnel, with small amounts of water, discarding the aqueous layers.

Transfer the organic liquid to a small beaker and remove the last drops of water with a dropping pipette or the edge of a filter paper.

Identify the products by thin-layer chromatography (p. 31).

Reduction of aliphatic and aromatic nitro compounds

1. To 3 drops of nitrobenzene in a test-tube, add 1 cm^3 of water, 1 cm^3 of *concentrated* hydrochloric acid and 2 or 3 small pieces of tin. Warm. The phenylamine formed goes into solution in the form of its cation $C_6H_5{-}NH_3^+$.

Make alkaline with dilute sodium hydroxide solution, to liberate the phenylamine as an oil. Add enough alkali to dissolve the tin(IV) oxide formed as sodium stannate(IV).

Test for phenylamine by adding 1 drop of the oil to an aqueous suspension of bleaching powder. If phenylamine is present, a blue colour will appear.

2. To 1 cm^3 of nitroethane in a test-tube, add 1 cm^3 of dilute sodium hydroxide solution and a small quantity ($\frac{1}{2}$ cm on the end of a wooden splint) of powdered aluminium. Warm gently to start the reaction.

When the evolution of hydrogen ceases, warm the solution, note the characteristic smell of ethylamine and test the vapour with moist red litmus paper.

17.8 Questions

1 Describe the preparation of a pure sample of 1,3-dinitrobenzene from nitrobenzene.

How would you distinguish between the members of the following pairs by one chemical test in each case:

(i) chlorobenzene and bromobenzene,
(ii) nitrobenzene and phenylamine,
(iii) bromoethane and 1,1-dibromoethane?

2 Describe in detail two experiments which you have seen or performed to illustrate the nitration of the benzene ring under varying conditions, and outline the purification of the products.

3 Give an account of the nitration of benzene. Your account should include the essential conditions for the reaction as well as an indication of the mechanism of the reaction.

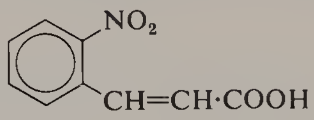
In which **two** ways does the nitration of methylbenzene (toluene) differ from the nitration of benzene? (Mechanisms are not required here.)

Giving the reaction sequences required in the form of equations and the essential conditions and reagents for each, indicate how benzene may be converted into

(a) phenylamine (aniline),
(b) benzonitrile,
(c) (phenylmethyl)amine, $C_6H_5CH_2NH_2$. (O and C)

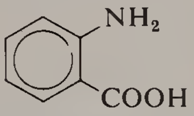
4 Write structural formulae for the isomers corresponding to the molecular formula C_8H_{10} which contain a phenyl group. Give structural formulae for the different main mononitration products of each isomer. Assign possible structural formulae to $C_8H_8(NO_2)_2$ which can yield only two different nuclear monobromosubstitution products. (W)

5 A compound has the structural formula



Outline experiments to

(a) confirm its molecular weight;
(b) identify the functional groups present;
(c) show how many acidic hydrogens are present;
(d) convert the compound to



(JMB Syllabus B)

6 Four bottles contain benzene, ethanonitrile, phenylamine and nitrobenzene, respectively, but the labels have fallen off and have become mixed up. What physical and chemical tests would you apply to these substances so that the bottles may be correctly re-labelled? (L)

7 Illustrate the directive influence of groups in aromatic nuclear substitution by giving the names and structural formulae of the main organic products formed by the reaction of a mixture of concentrated nitric and sulphuric acids on (a) methylbenzene, (b) benzoic acid, (c) methyl-2-nitrobenzene, (d) chlorobenzene.

What is the active nitrating species in a mixture of concentrated nitric and sulphuric acids, and how may the reactivity of the acid mixture be increased?

What procedure is adopted to protect the amino-group when phenylamine is nitrated with the concentrated mixed acids and what is the main product of nitration under such conditions? (W)

8 Nitrobenzene may be prepared in the laboratory by treating benzene with a mixture of concentrated sulphuric and nitric acids. The reaction occurs in several stages.

(i) The reaction of nitric and sulphuric acids to form, firstly, *protonated nitric acid*, and second, *nitronium ions.*
(ii) *Electrophilic* attack of the benzene ring by nitronium ions to form $C_6H_6NO_2{}^+$.
(iii) Loss of a proton to form $C_6H_5NO_2$.

(a) Explain the term *electrophilic*. Give the structures of the intermediates mentioned in (i) and (ii) above, and write equations for the stages involved in the formation of nitrobenzene.

(b) In a typical experiment 39 g of benzene produced 50 g of nitrobenzene. Calculate the percentage yield of nitrobenzene. Suggest TWO reasons why the yield was not 100%.

(c) Nitrobenzene contains a delocalized system of electrons. What do you understand by this statement? Cite THREE pieces of evidence for delocalization in the benzene ring.

(d) Outline the essential practical details of the preparation and purification of an aromatic nitro-compound of your choice.
(Relative atomic masses: H = 1, C = 12, N = 14, O = 16) (L)

Chapter 18

Naturally occurring compounds

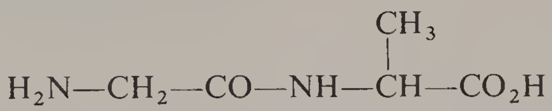
18.1 Introduction

A wide variety of organic compounds can be isolated from living organisms. They include the pigments of birds and flowers, the scents and odours of plants and animals, and compounds in plants such as strychnine and morphine that have powerful physiological effects on animals. From this huge range, four groups of compounds stand out as being common to all forms of life: the proteins, carbohydrates and lipids (fats), which have become household words owing to their importance in nutrition, and the nucleic acids DNA and RNA which are heard about increasingly owing to their importance in genetics (the science of inheritance) and genetic engineering. This chapter is specifically concerned with proteins, nucleic acids and carbohydrates.

18.2 Proteins

Protein accounts for about 80 per cent of the dry mass of all the soft parts of an animal body (i.e. excluding the skeleton). Plants contain a lower proportion.

Proteins are derived from α-amino-acids which are joined together by the elimination of a molecule of water from the carboxyl group of one molecule and the amino group of the next, so that they contain **peptide bonds**, —CO—NH—. When only two amino-acids are joined in this way, as in



$$H_2N{-}CH_2{-}CO{-}NH{-}\underset{}{\overset{\displaystyle CH_3}{\overset{|}{C}H}}{-}CO_2H$$

from glycine and α-alanine, the compound is called a **dipeptide**. A **tripeptide** is made up from three amino-acid molecules, a **tetrapeptide** from four and so on.

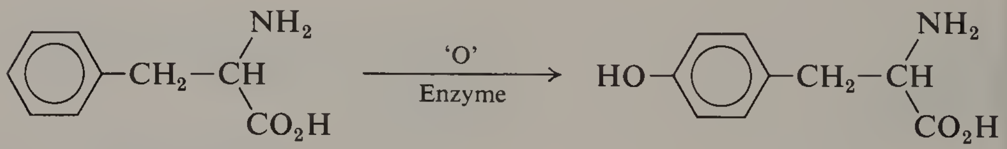
The name protein is given to naturally occurring polypeptides containing more than about 40 amino-acid residues (the term 'residue' is used for an α-amino acid which has lost the elements of water in forming a peptide bond). The number of potentially different proteins is virtually infinite: 20 α-amino-acids are used in their formation, and they can, in theory, be linked in any possible permutations of sequences and total number. In practice, not all possibilities occur, but the total number is nevertheless enormous.

Living organisms need to synthesise new protein continuously, partly to support growth and partly to replace proteins which are broken down during the process of living. Some bacteria can use air as a source of nitrogen for amino-acid, and thence protein, synthesis; this 'nitrogen fixation' involves its reduction to ammonia and occurs at room temperature and pressure (compare this with the Haber process). Some of these bacteria are found in nodules in the roots of plants belonging to the pea family (*Leguminosae*). The excess of fixed nitrogen is available to the host plant which, in return, supplies the nitrogen-fixing bacteria with other necessary nutrients. Other plants and bacteria need a supply of nitrate ions or ammonia from which they make the amino groups of their amino-acids. An interesting area of current research is to try to develop, possibly by genetic engineering (p. 345), a variety of bacterium which would form root nodules in cereals and other commercially important crops and thereby reduce the need to supply these plants with nitrogen-containing compounds.

In contrast to plants and bacteria, animals must obtain their α-amino-acids from proteins in their diet. The proteins are first hydrolysed to their constituent amino-acids, in processes catalysed by the enzymes pepsin, in the stomach, and chymotrypsin, trypsin and other enzymes (p. 284) in the intestine. The constituent amino-acids pass into the blood stream and then to the liver and other tissues where, under the influence of nucleic acids (18.3), they are converted into the proteins required by the body.

There are certain clinical conditions, such as diabetes, which are related to the body's inability adequately to synthesise a required protein (insulin in the case of diabetes). These conditions can only be alleviated by injection of the protein, for if it were taken by mouth it would simply be hydrolysed.

Of the 20 α-amino-acids that constitute naturally occurring proteins, 12 can be synthesised in the human body from other amino-acids, for example:



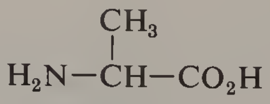
Phenylalanine

Tyrosine

However, eight are described as **essential** α-amino-acids; their residues must be present in the protein diet since they cannot be synthesised in the human body. Examples of α-amino-acids present in proteins, those which are underlined being essential, are:

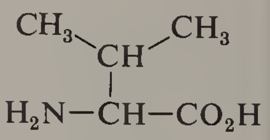
$H_2N-CH_2-CO_2H$

Glycine



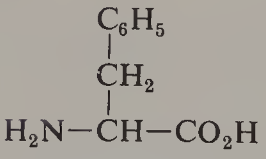
$H_2N-CH(CH_3)-CO_2H$

α-Alanine



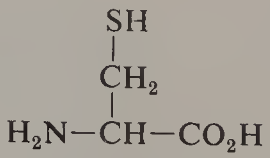
$H_2N-CH(CH(CH_3)_2)-CO_2H$

Valine



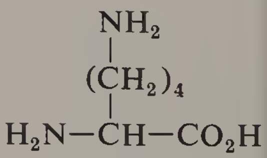
$H_2N-CH(CH_2C_6H_5)-CO_2H$

Phenylalanine



$H_2N-CH(CH_2SH)-CO_2H$

Cysteine



$H_2N-CH((CH_2)_4NH_2)-CO_2H$

Lysine

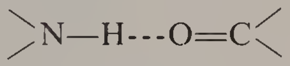
Isolation and purification of proteins

Most proteins occur in mixtures with other proteins of closely similar properties and their separation is therefore difficult. Some purification can usually be achieved by selective precipitation of the protein of interest by careful adjustment of either the pH or the concentration of added salts. Other methods are based on column chromatography (2.6). Crystallisation is normally only attempted if *X*-ray diffraction studies are to be carried out for, although many proteins have now been crystallised, it may take weeks, months or even years to find how to grow satisfactory crystals of a newly isolated protein.

Testing the purity of a protein is also difficult, since they do not have sharp melting-points but decompose on strong heating. Tests are therefore based on other physical differences between proteins. The most reliable method involves electrophoresis, in which the protein is placed as a band on a column of a suitable solid support (for example, polyacrylamide gel) and a voltage is applied to the column. Different proteins move at different rates along the column and can be identified (after staining) as bands on the column. A pure protein produces a single band, and a further advantage of this method is that it can also be used to estimate, with reasonable precision, the relative molecular mass of the protein.

Structure of proteins

Each protein is defined by the number and nature of its constituent amino-acid residues and the sequence in which these are arranged. In its natural environment each protein folds up into a specific well-defined shape, known as its **native structure**, which is held together by a combination of different kinds of interaction between atoms and groups in the molecule. One of the most important of these interactions is the hydrogen bond which occurs between the N—H group of one residue and the C=O group of another:



$$>N{-}H\cdots O{=}C<$$

This can lead to the twisting of the protein chain into a helix. Several model helical structures can be built, but the one which occurs most frequently in proteins is the **α-helix** in which the amino group of one residue is bonded to the carbonyl group of the fourth residue along. In Fig. 18.1 the spacing between the turns of the helix is 540 pm.

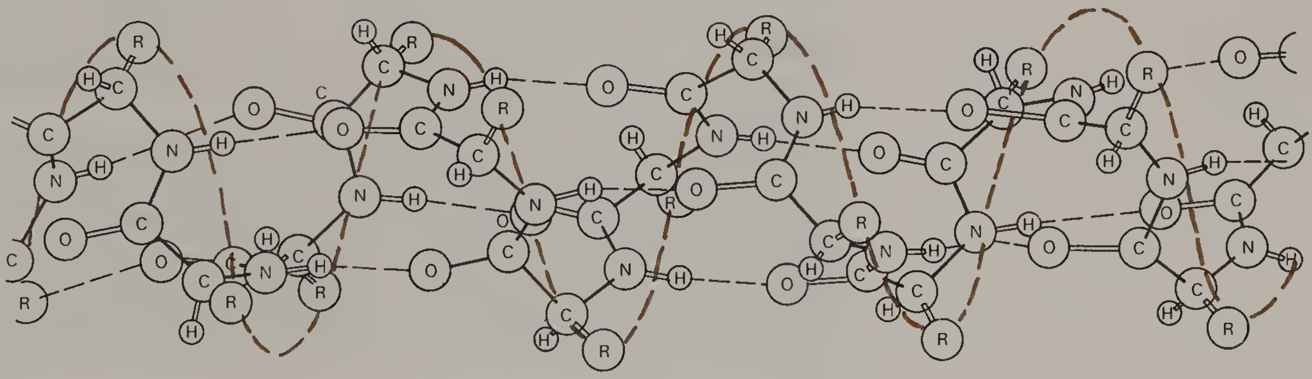
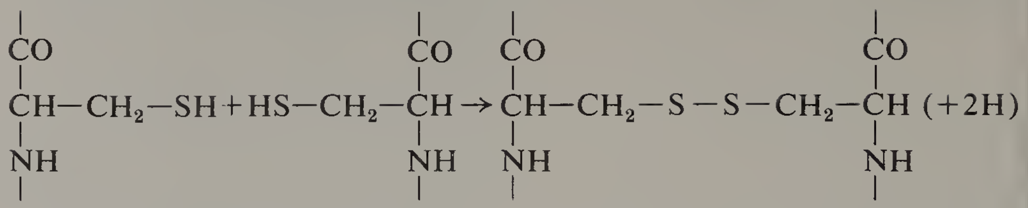


FIG. 18.1. *α-Helix of a protein. The change in angle between one unit and the next occurs at the carbon atom to which the side group R is attached. The helix is held rigid by hydrogen-bonding*

Another important factor determining the shape of a protein is the inability of some groups on the protein (the —$CH(CH_3)_2$ group of valine is an example) to interact with water. This leads to a tendency for these non-polar groups to clump together in the centre of a protein from which water is excluded.

Covalent bonds (other than those defining the sequence of amino-acids) are not needed to make a protein fold up. However, in some folded proteins, it happens that two cysteine residues are brought close enough to each other for them to be linked by oxidation:



$$\begin{array}{c}|\\ \mathrm{CO}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH}\\ |\end{array}\!\mathrm{-CH_2-SH+HS-CH_2-}\!\begin{array}{c}|\\ \mathrm{CO}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH}\\ |\end{array}\rightarrow\begin{array}{c}|\\ \mathrm{CO}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH}\\ |\end{array}\!\mathrm{-CH_2-S-S-CH_2-}\!\begin{array}{c}|\\ \mathrm{CO}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH}\\ |\end{array}(+2\mathrm{H})$$

Once these covalent bonds have been formed, they add greatly to the stability of the folded structure.

Folded proteins can be assigned to one of two groups, the **fibrous proteins** and the **globular proteins**, which can be distinguished by various physical properties. In fibrous proteins each molecule is folded to form a long, thin shape. These proteins are usually insoluble in water and form important structural features. An example is **keratin** (in hair and feathers) in which the basic structure is the α-helix; several helical molecules coil together rather like a rope and the elastic nature of these structures results from the ability of the protein chains to stretch out from their helices into extended chains. A more universal fibrous protein is **collagen**, the material which makes up tendons, ligaments and the sheets of connective tissue which separate the individual muscles of a joint of meat. In collagen, three molecules coil round each other to form a triple-stranded helix.

In globular proteins each molecule is folded into an approximately spherical shape, giving a compact structure; the proteins are mostly soluble in water.

Enzymes are a particularly important group of globular proteins. They are the catalysts which enable living organisms to bring about necessary reactions at body temperature. Some consist solely of protein and others of a protein joined to another molecule (a **prosthetic group**).

Enzymes are more specific than artificial catalysts, being able to catalyse only the making and breaking of one type of bond, and usually that bond must be located in one of a very limited range of compounds. This specificity arises from the requirement that the molecules in which reaction is to occur (the substrates) must fit exactly into the contours of the enzyme surface to which it must be attached by non-covalent bonds (such as hydrogen bonds).

Since the forces that determine the shape of a protein are relatively weak (e.g. a hydrogen bond is far weaker than a covalent bond), the shape can readily be disrupted, and this is known as **denaturation**. It occurs, for example, when an aqueous solution of a protein is warmed, or when the pH is altered, and it is accompanied by changes in physical characteristics and the loss of biological activity. Denaturation can usually be reversed, and biological activity then returns, showing that a protein folds spontaneously into its native state.

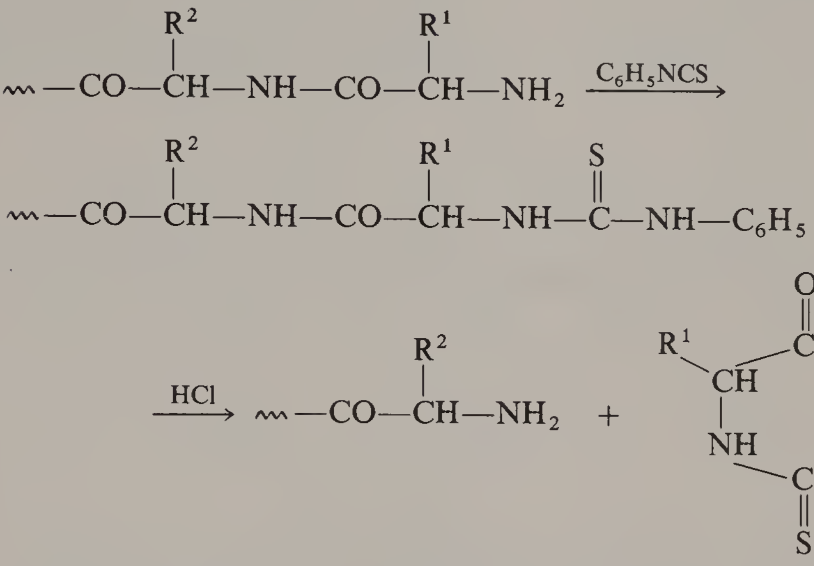
However, do not expect to be able to 'unboil' an egg. Although boiling the egg brings about denaturation, the high temperature also causes disulphide bonds to break and reform in the wrong places, and these covalent changes cannot be easily reversed.

Determination of protein structure and shape

The problem is usually approached by finding (a) which amino-acids are present and in what relative amounts, (b) what their sequence is, and (c) the detailed shape of the folded protein.

(a) The protein is hydrolysed with mineral acid and the resulting amino-acids are separated by chromatography on an ion-exchange resin. With modern methods, this analysis can be done with a fraction of 1 mg of protein within 24 hours. (The older method, using paper chromatography, is much harder to make quantitative.)

(b) For a polypeptide, one approach is to treat the compound with phenylisothiocyanate, $C_6H_5{-}N{=}C{=}S$. This reacts with the $-NH_2$ group at the end of the chain, but not with the $-NH-$ groups in the peptide bonds. The product is then hydrolysed with hydrogen chloride in an organic solvent, conditions which remove the terminal amino-acid as a cyclic derivative but are not so vigorous as to hydrolyse the peptide bonds:



$$\sim{-}CO{-}\overset{R^2}{\overset{|}{C}H}{-}NH{-}CO{-}\overset{R^1}{\overset{|}{C}H}{-}NH_2 \xrightarrow{C_6H_5NCS} \sim{-}CO{-}\overset{R^2}{\overset{|}{C}H}{-}NH{-}CO{-}\overset{R^1}{\overset{|}{C}H}{-}NH{-}\overset{S}{\overset{\|}{C}}{-}NH{-}C_6H_5$$

$$\xrightarrow{HCl} \sim{-}CO{-}\overset{R^2}{\overset{|}{C}H}{-}NH_2 \; +$$

The cyclic product can be identified by comparison of its behaviour on chromatography with that of known compounds, and the degraded polypeptide, with a new terminal $-NH_2$ group, can be subjected to the sequence again. The yields are good enough for a skilled scientist to determine a sequence of about 30 amino-acid residues. With larger molecules, this method must be combined with hydrolysis of the protein to polypeptides. It is usually possible to find conditions in which a protein is hydrolysed in different ways (for example, by the use of two different enzymes). The natures of the resulting shorter sequences are then determined, and the original full sequence pieced together. For example, if one method of hydrolysis yields, amongst others, the polypeptides, A—B—C—D—E and F—G—H—I, and a second yields C—D—E—F—G and H—I—J, then the full sequence is A—B—C—D—E—F—G—H—I—J.

(c) Detailcd knowledge of the shape of a protein molecule can only be obtained by *X*-ray diffraction studies on protein crystals. The first structure to be worked out in sufficient detail for individual atoms to be resolved was that of myoglobin in 1962. This was a remarkable feat, for the relative molecular mass is nearly 17 000 and there are about 2500 atoms in the molecule. With modern methods, including fast computers, it is now possible to determine the structures of even more complex molecules rapidly.

18.3
Nucleic acids

A cell which synthesises proteins needs to be able to store information about the sequences of amino-acids in those proteins and to translate the coded information into a real sequence. Both these properties are conferred by nucleic acids.

Nucleic acids are polymers formed from **nucleotides**. A nucleotide is composed of a carbohydrate, a phosphate group and a nitrogen base, and in the nucleic acids the polymer chain consists of alternating carbohydrate and phosphate units; this is shown schematically in Fig. 18.2. There are only two general types of nucleic acid: **ribonucleic acid (RNA)**, in which the carbohydrate is ribose and the bases are cytosine and uracil (members of the pyrimidine group) and adenine and guanine (members of the purine group); and **deoxyribonucleic acid (DNA)**, in which the carbohydrate is deoxyribose and the bases are the same as in RNA except that thymine replaces uracil (Fig. 18.3). However, there is an enormous number of individual compounds in each of these two categories because of the variety of possible sequences for the four bases in each case.

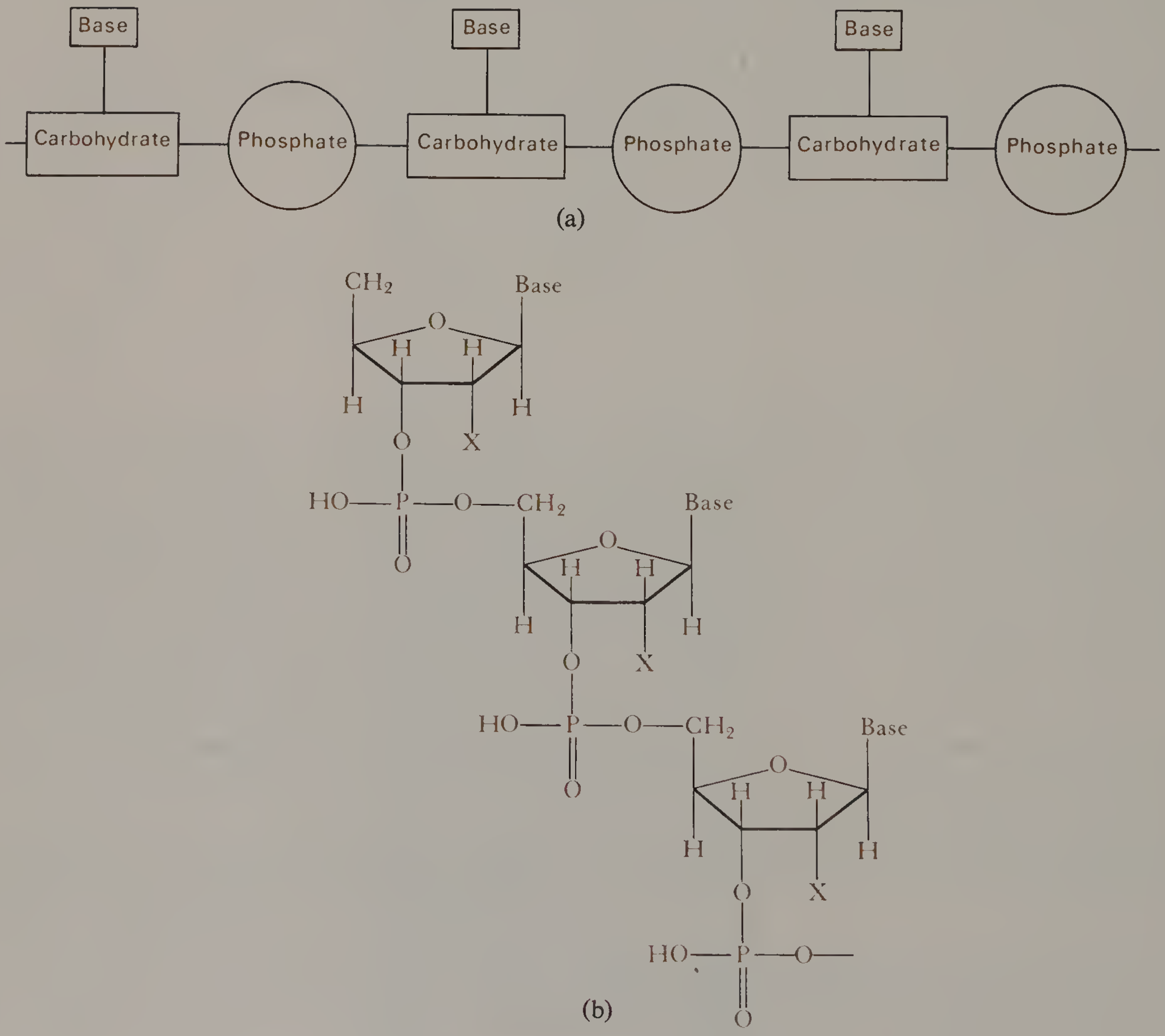


FIG. 18.2. *Alternating phosphate and carbohydrate residues in a nucleic acid. A base is attached to each carbohydrate. In (b), the bonding between the carbohydrate residues and the phosphate residues is shown. X represents H in deoxyribose and OH in ribose*

In DNA, two nucleic acid chains, each in the form of a helix, are intertwined. The two strands are held together by hydrogen bonds between the bases. This arrangement is only possible when the right pairs of bases are opposite each other: Fig. 18.4 shows the geometrical fit which occurs when adenine and thymine come together and when guanine and cytosine come together. The pairs have exactly the same overall dimensions, even though neither the two purines nor the two pyrimidines are identical, so that when

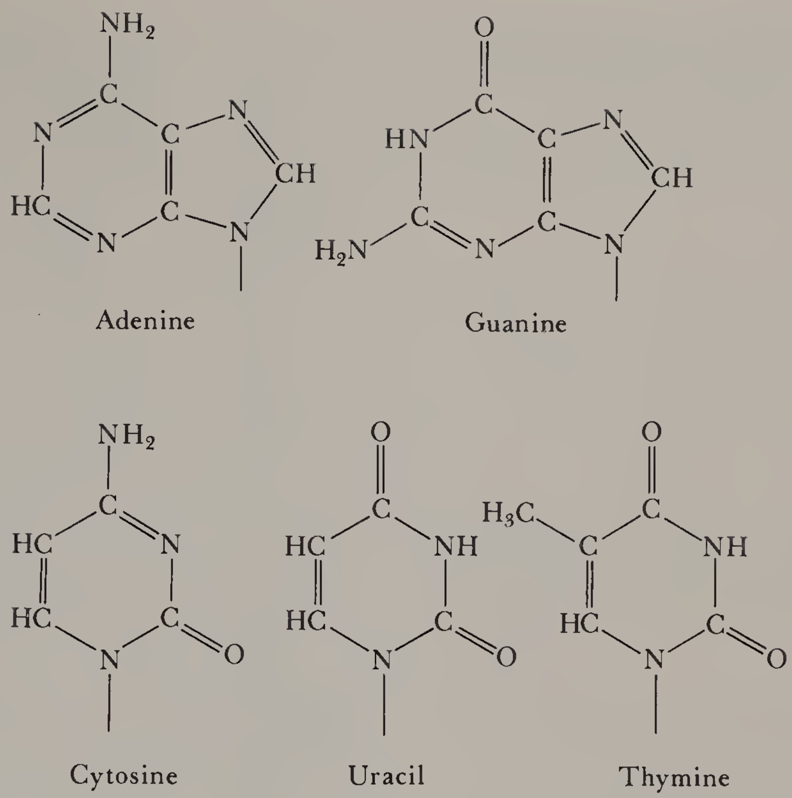


FIG. 18.3. *The bases present in RNA and DNA. The bond that attaches the base to the carbohydrate is shown*

the bases are paired in this way, but in no other, they can be stacked neatly on top of each other and the chains of alternating phosphate and carbohydrate can take up a regular helical structure irrespective of the sequence of bases along it (Fig. 18.5). Because of this matching geometry the pairs A:T and G:C are known as **complementary** base pairs. In DNA the sequences of the two strands are always complementary to each other: for example, if the sequence of one strand is AGTCG then the sequence of the other will be TCAGC.

The double-helical structure of DNA fits it exactly for its role as a store of information, since each strand of the DNA carries enough information for the complementary strand to be synthesised on it. When a cell reproduces itself, the DNA molecules first separate into their individual strands and each then acts as a template for the synthesis of a new strand. The synthesis is carried out by an enzyme which moves along the single strand of DNA, selecting the nucleotide with the appropriate complementary base and linking them together to form a new complementary chain.

The translation of this coded information for specifying the sequence of amino-acids in a protein involves RNA. RNA molecules have only a single strand, and they are synthesised, using one of the two strands of DNA as a template, in an exactly analogous way to the synthesis of a complementary strand of DNA. In RNA, uracil replaces the thymine of DNA, but again the dimensions are right for a geometrical fit corresponding to that of Fig. 18.4.

The relative molecular mass of an RNA is much less than that of a DNA, so that only a comparatively short length of a DNA molecule is needed to make an RNA molecule, and each DNA carries enough information to make several different RNA molecules.

Two types of RNA molecules are synthesised: a smaller type (80–100 nucleotides long) known as **transfer RNA** (tRNA), each cell having at least as many types of tRNA as there are amino-acids; and a larger type (up to

FIG. 18.4. *The hydrogen-bonding between thymine and adenine and between cytosine and guanine*

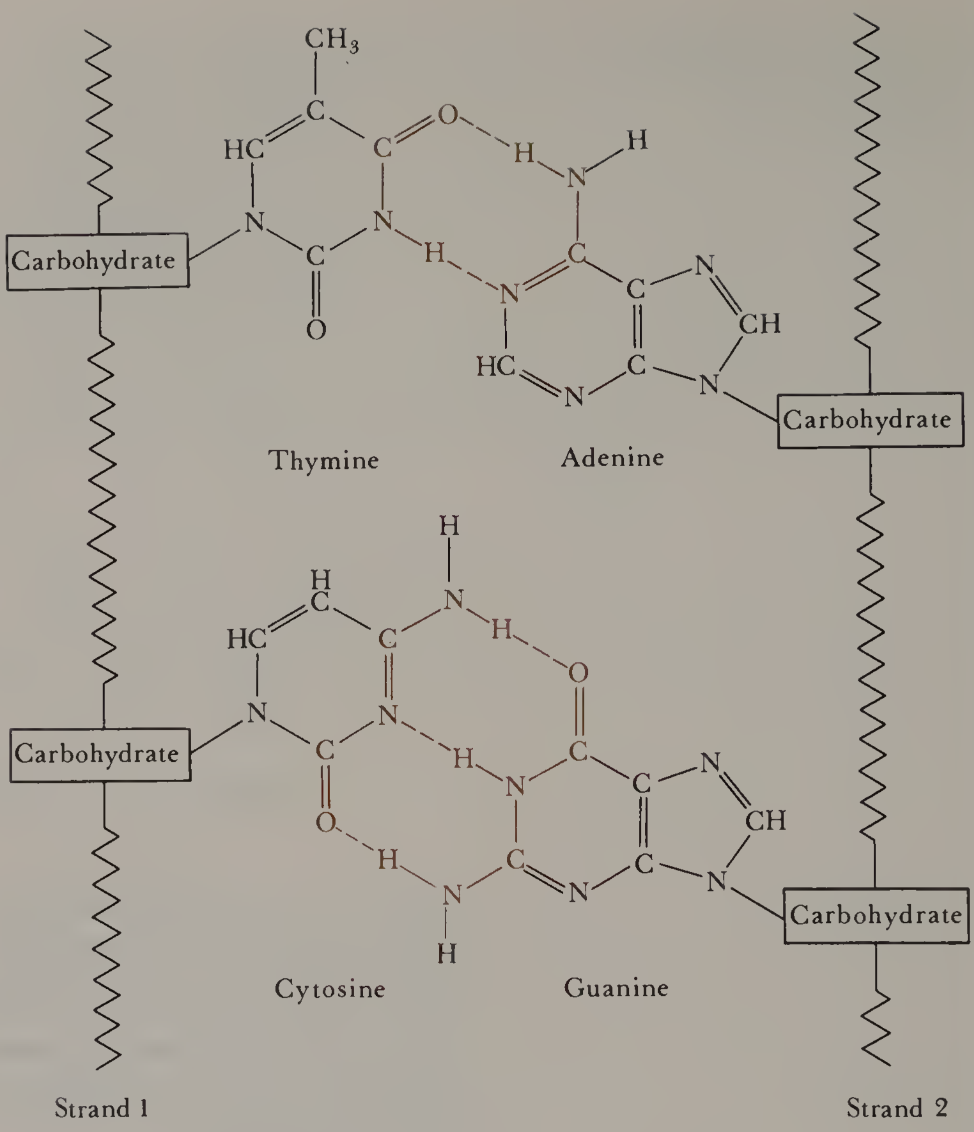
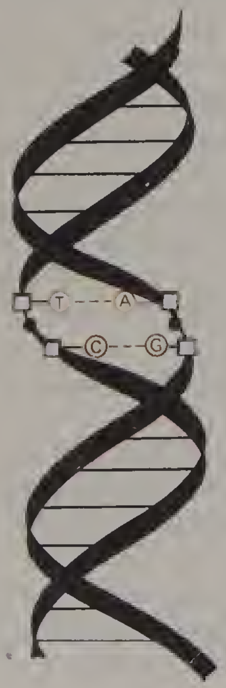


FIG. 18.5. *Part of the double helix of DNA. The helix consists of two strands of alternate carbohydrate (☐) and phosphate (●) residues. To each carbohydrate residue, a base is attached. Hydrogen-bonding between two bases, one from each strand, holds the helix together. This is represented by the rungs of the ladder, and two of these rungs are shown in more detail (A = Adenine, T = Thymine, G = Guanine, C = Cytosine)*



10,000 nucleotides long) known as **messenger RNA** (mRNA). They have different roles in protein synthesis: mRNA specifies the sequence of amino-acids in the protein, and for this reason the piece of DNA from which a particular RNA is copied (transcribed) may be called a **gene**; and tRNA translates the message in the mRNA by ensuring that a particular amino-acid recognises the appropriate sequence of three bases in the mRNA. These roles are achieved as follows.

Each amino-acid forms an ester bond, through its carboxyl group, to a specific tRNA. Each tRNA is folded into a particular shape so that a unique sequence of three bases (a **triplet**) is positioned on the surface where it can interact with a complementary set of bases on a mRNA molecule; for example, if a mRNA sequence has a sequence of six bases, AGUCGA, it will interact with the exposed triplets UCA and GCU of two tRNA molecules. This brings the two amino-acids carried by the two tRNA molecules into close proximity to each other, and an enzyme then breaks the ester bond of one of them and forms instead a peptide bond between it and the amino-group of the other amino-acid. Other amino-acids are brought successively into position in this way and further peptide bonds are formed so that eventually the coded message in the RNA has been completely translated and the new protein is released from the template.

18.4 Carbohydrates

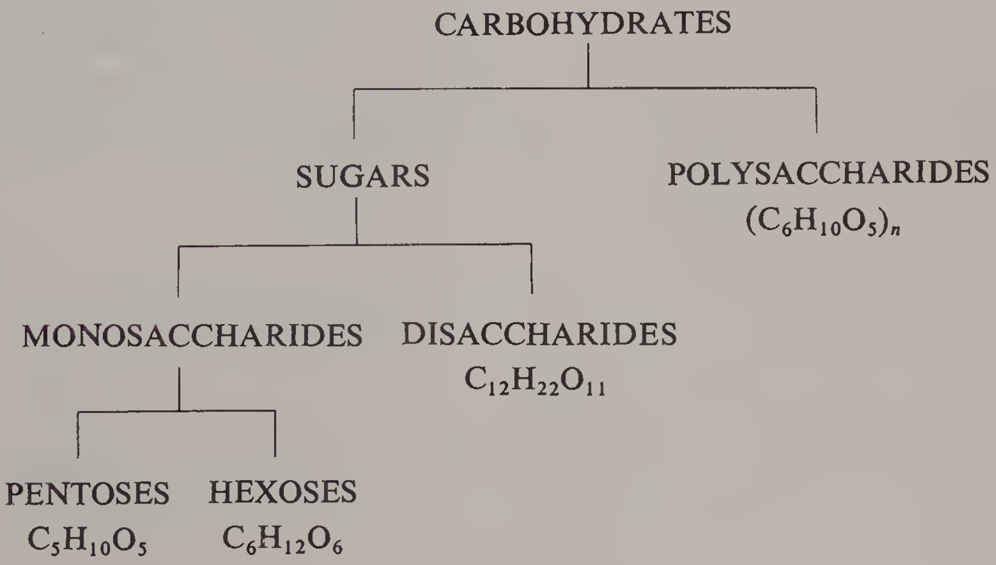
Carbohydrates are so called because of the historical observation that they have the empirical formula $C_x(H_2O)_y$—that is, they correspond to 'hydrates of carbon'. However, the name gives a misleading impression of their true molecular structure, and furthermore several compounds (such as deoxyribose found in nucleic acids) have been discovered which do not have this general formula but which it is convenient to classify as carbohydrates.

Plants are the main source of carbohydrates for both human food and other commercial uses. They synthesise carbohydrate from carbon dioxide and water (photosynthesis) and use it as an oxidisable fuel (source of energy to the plant), store it for later use as a fuel (for example, starch in potatoes or grain and sucrose in sugar-beet or sugar-cane) or convert it into structural material (for example, cellulose).

Animals can synthesise carbohydrate from excess of amino-acids in their diet, but most obtain their carbohydrate by eating plant material directly or indirectly. Vertebrate animals use carbohydrate primarily as an oxidisable fuel (to provide the energy for life) and the form in which they store it for this purpose is **glycogen**. In many invertebrates, **chitin**, which is closely related to cellulose, forms a structural material.

The monomeric units of carbohydrates are called **monosaccharides**; most of the naturally occurring ones have the formula $C_5H_{10}O_5$ (the **pentoses**) or $C_6H_{12}O_6$ (the **hexoses**). When two monosaccharides are condensed together by the elimination of a molecule of water, a **disaccharide** is formed; naturally occurring disaccharides are made up from two hexoses and therefore have the formula $C_{12}H_{22}O_{11}$. Together the monosaccharides and the disaccharides are known as the **sugars**. They are crystalline solids which dissolve readily in water.

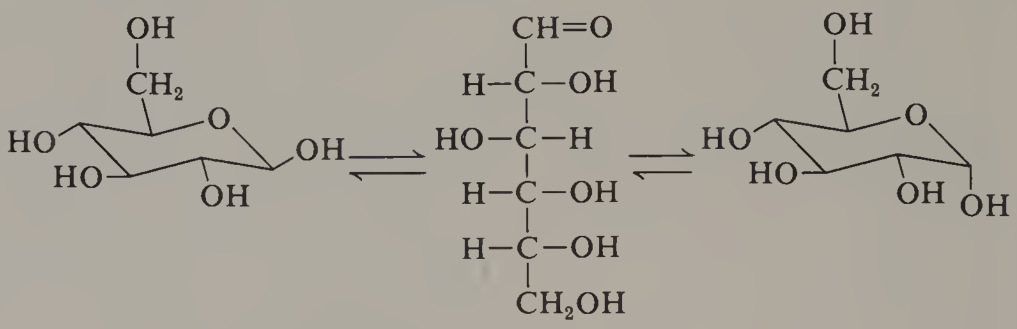
Polysaccharides are formed when many hexose units are joined together to give compounds of formula $(C_6H_{10}O_5)_n$ where n can range from about 200 to several thousands (naturally occurring polysaccharides based on pentoses are unknown). Polysaccharides may be extremely insoluble in water (such as cellulose) or rather soluble (such as glycogen). In summary, carbohydrates can be classified in the following way:



Monosaccharides

The most commonly occurring group of monosaccharides is the hexoses, with general formula $C_6H_{12}O_6$, and of these the most important are glucose and fructose.

In aqueous solution, glucose consists of a mixture of three structures in equilibrium:



The left-hand structure corresponds to the major component and the non-cyclic structure is present in the smallest proportion. However, equilibrium between the three is fairly rapidly established, so that if a reagent is introduced which reacts with aldehydes, for example Fehling's solution, it removes the non-cyclic isomer but more is then formed from the cyclic isomers to maintain the equilibrium; eventually the entire quantity of glucose reacts.

Preparation of glucose and fructose

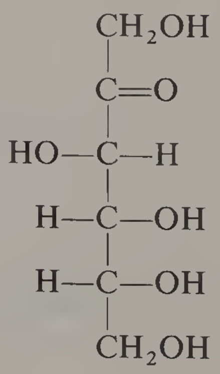
Glucose is obtained by the hydrolysis of starch with dilute sulphuric acid at high temperatures under pressure:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

There are four asymmetric carbon atoms in glucose so that (since there is no internal compensation) it is optically active and has $2^4 - 1 = 15$ stereoisomers (p. 243), some of which also occur naturally.

Glucose can be obtained in the solid state in two crystalline forms, which correspond to the two cyclic structures. When either form is dissolved in water, equilibrium between all three structures is soon established. The process, known as **mutarotation**, can be followed with a polarimeter (p. 240) since the isomeric forms have different molar optical rotatory powers.

Fructose, too, occurs in solution as an equilibrium mixture of cyclic and non-cyclic structures; the non-cyclic structure is:



$$\begin{array}{c} CH_2OH \\ | \\ C{=}O \\ | \\ HO{-}C{-}H \\ | \\ H{-}C{-}OH \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

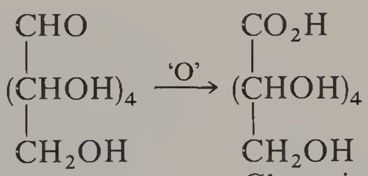
Fructose is obtained by the hydrolysis of sucrose (p. 294) with dilute sulphuric acid:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Properties of glucose

Glucose is a white crystalline solid, soluble in water but insoluble in most organic solvents. It behaves like an aliphatic aldehyde in the following respects:

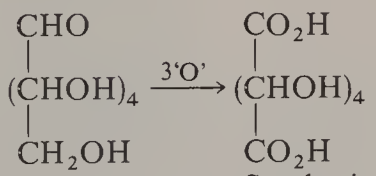
1. It reduces Fehling's solution to copper(I) oxide and ammoniacal silver nitrate to silver.
2. With weak oxidising agents, such as bromine water, it forms gluconic acid:



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{\text{'O'}} \begin{array}{c}CO_2H\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$$

Gluconic
acid

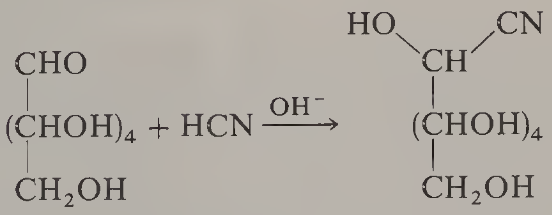
With strong oxidising agents, such as nitric acid, the primary alcohol group is also oxidised:



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{3\text{'O'}} \begin{array}{c}CO_2H\\ |\\ (CHOH)_4\\ |\\ CO_2H\end{array}$$

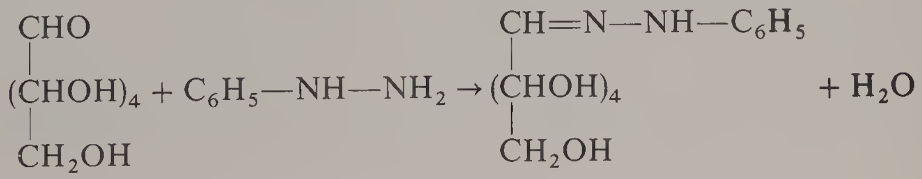
Saccharic
acid

3. It forms a cyanohydrin:



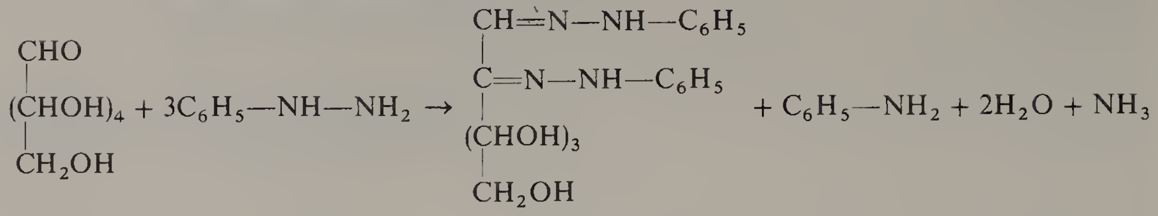
$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + HCN \xrightarrow{OH^-} \begin{array}{c}HO\diagdown\;\;\diagup CN\\ CH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$$

4. It undergoes condensation reactions with hydroxylamine, phenylhydrazine, etc, for example:



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + C_6H_5{-}NH{-}NH_2 \rightarrow \begin{array}{l}CH{=}N{-}NH{-}C_6H_5\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + H_2O$$

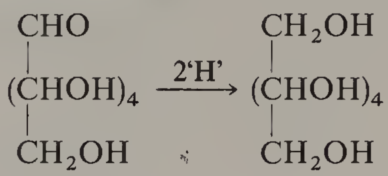
With excess of phenylhydrazine, it forms an **osazone**:



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\end{array} + \mathrm{3C_6H_5{-}NH{-}NH_2} \rightarrow \begin{array}{l}\mathrm{CH{=}N{-}NH{-}C_6H_5}\\ |\\ \mathrm{C{=}N{-}NH{-}C_6H_5}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array} + \mathrm{C_6H_5{-}NH_2} + \mathrm{2H_2O} + \mathrm{NH_3}$$

Glucosazone

5. It is reduced, for example by sodium amalgam and water, to a polyhydric alcohol:



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\end{array} \xrightarrow{2\text{‘H’}} \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Glucose as a source of energy

Glucose is commonly used as a source of energy by plants, animals and bacteria. Animals normally ingest it in the form of starch and sucrose (cane sugar) which are hydrolysed to glucose by enzymes. Mammals do not possess an enzyme capable of hydrolysing cellulose to glucose, which is why cellulose is useless as a foodstuff.

Energy is obtained from glucose by oxidation. Complete oxidation is summarised by:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Energy}$$

The amount of energy released is 2870 kJ $\mathrm{mol^{-1}}$ of glucose.

Oxidation occurs in the cell by a sequence of enzyme-catalysed reactions. Glucose is first phosphorylated (i.e. converted into a phosphate ester) to give glucose-6-phosphate by reaction at its $\mathrm{{-}CH_2OH}$ group. Glucose-6-phosphate then isomerises to fructose-6-phosphate, and a second phosphorylation occurs to give fructose-1,6-diphosphate. This compound forms two 3-carbon molecules which, by oxidation, give 2-oxopropanoic acid, $\mathrm{CH_3{-}CO{-}CO_2H}$ (which, at cellular pH, is ionised).

$\mathrm{HO{-}CH_2{-}(CHOH)_3{-}CH(OH){-}CHO} \rightarrow$

Glucose

$P\mathrm{{-}O{-}CH_2{-}(CHOH)_3{-}CH(OH){-}CHO} \rightarrow$

Glucose-6-phosphate

$P\mathrm{{-}O{-}CH_2{-}(CHOH)_3{-}CO{-}CH_2OH} \rightarrow$

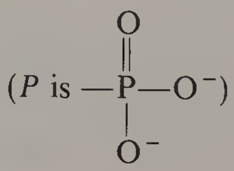
Fructose-6-phosphate

$P\mathrm{{-}O{-}CH_2{-}(CHOH)_3{-}CO{-}CH_2{-}O{-}}P \rightarrow$

Fructose-1,6-diphosphate

$P\mathrm{{-}O{-}CH_2{-}CH(OH){-}CHO} + \mathrm{HO{-}CH_2{-}CO{-}CH_2{-}O{-}}P \rightarrow$
$\mathrm{CH_3{-}CO{-}CO_2^-}$

2-Oxopropanoate ion



$$(P \text{ is } \begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{{-}P{-}O^-}\\ |\\ \mathrm{O^-}\end{array})$$

Oxidation and decarboxylation of this leaves an ethanoyl group, $CH_3CO—$, which is attached *via* a sulphur atom to a large organic molecule known as Coenzyme A; this coenzyme itself contains an —SH group, so that the ethanoyl derivative is a thiol ester containing the group $CH_3—CO—S—$. This is then oxidised by a pathway known as the **Krebs cycle**:

$$CH_3\text{—}CO\text{—}CO_2^- \rightarrow CH_3\text{—}CO\text{—Coenzyme A} \rightarrow CO_2 + H_2O$$

The Krebs cycle is also involved in the oxidation of fats, and this link between the oxidation pathways of the body's two chief fuels plays an important part in the control of their use.

Human beings obtain most of their energy from oxidising fat rather than carbohydrates. But the use of carbohydrate gives added flexibility since it can provide a supply of energy during particularly intense muscular activity when oxygen cannot be obtained rapidly enough. In this situation 2-oxopropanoate (formed as described earlier) is reduced to 2-hydroxypropanoate to give an overall equation for glucose breakdown

$$C_6H_{12}O_6 \rightarrow 2CH_3\text{—}CH(OH)\text{—}CO_2H + \text{Energy}$$

This process produces much less energy than the oxidation of glucose, but it does avoid the need for oxygen. The 2-hydroxypropanoate is later reoxidised to 2-oxopropanoate which is either oxidised through the Krebs cycle or resynthesised into glycogen.

Disaccharides

Disaccharides have the molecular formula $C_{12}H_{22}O_{11}$, and consist of two monosaccharide molecules, $C_6H_{12}O_6$, joined together with the loss of a molecule of water. Three disaccharides occur naturally; these are maltose, lactose and sucrose. They all have similar physical properties, being white crystalline solids which are soluble in water.

Manufacture of sucrose

Sucrose is obtained from either sugar-cane or sugar-beet. The cane is cut into small pieces and crushed, and the juice is pressed out. The juice is made alkaline with calcium hydroxide, impurities being precipitated and filtered off. The proteins are precipitated by passing steam through the liquid, and the clear juice is concentrated by evaporation under reduced pressure. The syrup is cooled and some sugar crystallises out. The residual sugar remains in the thick liquid, known as **molasses**, and sucrose is recovered by dilution and recrystallisation.

The brown sugar obtained is dissolved in water, and is treated with calcium hydroxide and carbon dioxide, and more impurities are precipitated. The filtrate is decolorised by boiling with charcoal, and the solution is filtered and concentrated by vacuum distillation. The sugar is allowed to crystallise out and may be granulated or moulded into cubes. The molasses are used in the manufacture of ethanol by fermentation or for cattle foods.

Chemical properties of sucrose

1. Sucrose, like all disaccharides, is hydrolysed by dilute mineral acids to two monosaccharide molecules. Sucrose yields glucose and fructose:

$$\mathrm{C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}}$$

Sucrose is dextrorotatory, and glucose and fructose are dextro- and laevorotatory, respectively. Although an equimolar mixture is formed, the resulting solution is laevorotatory as fructose has a higher rotatory power than glucose. This hydrolysis is known as the **inversion of sucrose**, and the resultant mixture is known as **invert sugar**. The reaction may also be effected by the enzyme invertase, present in yeast.

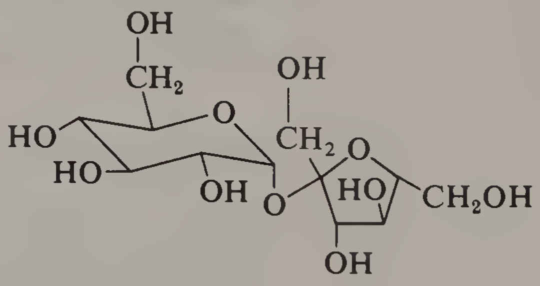
2. Concentrated sulphuric acid dehydrates sucrose, leaving almost pure carbon, known as sugar charcoal:

$$\mathrm{C_{12}H_{22}O_{11} \xrightarrow{conc.\ H_2SO_4} 12C + 11H_2O}$$

3. Sucrose is a **non-reducing sugar**; it does not reduce Fehling's solution to copper(I) oxide or an ammoniacal solution of silver nitrate to silver.

Structure of sucrose

An examination of the chemical properties above suggests that sucrose is made up of a molecule of glucose and a molecule of fructose, with the elimination of a molecule of water. Further, the absence of reducing properties suggests that the glucose and fructose 'residues' cannot equilibrate with non-cyclic carbonyl-containing structures with which the reducing properties of sugars are associated and that therefore these residues are joined through the carbon atoms which, in the corresponding monosaccharides, form carbonyl groups. The structure of sucrose has been deduced, from this and other evidence, as:



Chemical properties of maltose and lactose

1. They are hydrolysed by dilute mineral acids to two monosaccharide molecules:

$$\mathrm{\underset{Maltose}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{Glucose}{2C_6H_{12}O_6}}$$

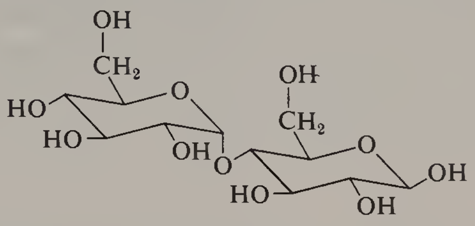
$$\mathrm{\underset{Lactose}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{Glucose}{C_6H_{12}O_6} + \underset{Galactose}{C_6H_{12}O_6}}$$

2. Concentrated sulphuric acid dehydrates both disaccharides to charcoal.

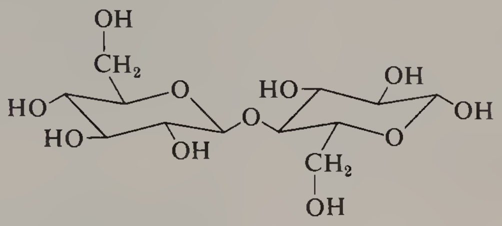
3. Both disaccharides reduce Fehling's solution to copper(I) oxide and an ammoniacal solution of silver nitrate to silver. They are known as **reducing sugars**.

Structures of maltose and lactose

An examination of the chemical properties above suggests that both are made up of two monosaccharide 'residues'. However, their reducing properties suggest that one or both residues can equilibrate with a non-cyclic, aldehydic structure. The structures have been deduced, from this and other evidence, as:



Maltose



Lactose

Polysaccharides

Polysaccharides are polymers, made up of monosaccharide units, which occur in both animals and plants. They are hydrolysed by mineral acid to monosaccharides:

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

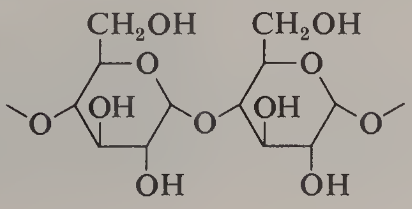
The two most widely occurring polysaccharides are starch and cellulose.

Starch

Starch occurs in wheat, barley, rice, potatoes and all green plants. It is the main carbohydrate reserve of plants. It is also an important ingredient of animal foods since it provides a source of glucose; it is hydrolysed to glucose by enzymes in saliva.

Starch has two components: α-amylose and β-amylose (amylopectin).

α-Amylose is composed of long chains of glucose units:



Its formula weight is between 10,000 and 60,000, depending on the degree of polymerisation. It is water-soluble and is used for making starch solutions.

β-Amylose also contains long chains of glucose units, but these are joined together at various points by other glucose chains and complex glucose derivatives, so that the structure is a complex three-dimensional network. Its formula weight is in the range 50,000–100,000 and it is insoluble in water.

Hydrolysis of starch

If a solution of starch is warmed to about 70°C in the presence of the enzyme amylase (present in human saliva), it is hydrolysed to the disaccharide, maltose:

$$2(C_6H_{10}O_5)_n + nH_2O \rightarrow \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

The hydrolysis is also catalysed by a mixture of enzymes known as diastase (present in malt) (see below).

However, if starch is boiled with dilute sulphuric acid, it is hydrolysed to the monosaccharide, glucose:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Presumably, starch is first hydrolysed to maltose, which, in turn, is hydrolysed to glucose.

Fermentation of starch

Wheat or barley is 'mashed' with hot water and then filtered to extract a solution of starch. The aqueous solution is heated to about 55°C with malt, which is germinated barley and contains a mixture of enzymes known as diastase. Starch is hydrolysed to maltose.

The liquid is cooled to 35°C, and yeast, which contains the enzyme maltase, is added to catalyse the hydrolysis of maltose to glucose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

Glucose is then broken down to 2-oxopropanoate exactly as it would be by any other organism using glucose as a fuel. However, in the absence of oxygen, 2-oxopropanoate is not reduced to 2-hydroxypropanoate in pressence of yeast, unlike the processes that take place in mammalian muscle; instead, it is decarboxylated to give ethanal which is then reduced to ethanol, giving the overall equation:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \text{Energy}$$

When the concentration of ethanol in the fermented liquor reaches about 10 per cent it is toxic to the yeast so that further fermentation is not possible. The resulting liquor can be used for alcoholic drinks (for example, beer from barley and malt) or purified to obtain pure ethanol. Purification by distillation is discussed on p. 146.

Most strains of yeast contain enzymes which catalyse the oxidation by molecular oxygen (in air) of 2-oxopropanoate to carbon dioxide and water *via* the ethanoyl derivative of Coenzyme A (p. 293), which explains the necessity for keeping oxygen out of fermenting liquors, and when storing, for example, beer, cider and wines.

Cellulose

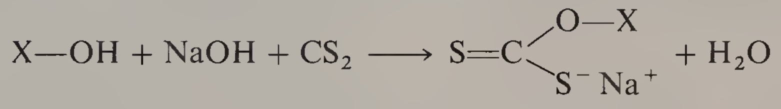
Cellulose is the principal constituent of the cell walls of plants. It consists of a three-dimensional network of chains of glucose units and some complex glucose derivatives.

Cotton is almost pure cellulose, but cellulose is usually manufactured from wood, which is a mixture of cellulose and a material known as lignin. In this process, wood shavings are heated with calcium hydrogensulphite to dissolve the lignin and the cellulose is removed by filtration. It can be purified by dissolving it in a solution of ammonia containing a copper(II) salt and then adding mineral acid to precipitate the pure cellulose.

Rayon

Rayon is the name given to cover all fibres manufactured from cellulose. **Cellulose ethanoate**, celanese silk, is made by ethanoylating cellulose with ethanoic anhydride. Cellulose ethanoate does not burn readily, and is used to make films, lacquers and varnishes.

Viscose rayon is manufactured by treating cellulose with sodium hydroxide and carbon disulphide, and the reaction can be represented thus:



$$\text{X—OH} + \text{NaOH} + CS_2 \longrightarrow S{=}C\begin{matrix}\diagup \text{O—X} \\ \diagdown S^- Na^+\end{matrix} + H_2O$$

Cellulose

Cellulose xanthate

The viscose solution is forced through fine jets into a bath of dilute sulphuric acid, giving a fine thread of viscose rayon. The thread is spun and made into fabrics which are lustrous and supple, and can be easily dyed. Although rayon is cheaper than natural silk, it is not as strong or durable.

Cellophane is manufactured by forcing the viscose solution through slits into the acid.

If cellulose is treated with dilute nitric acid, cellulose mononitrate and dinitrate are formed; the mixture is known as **pyroxylin**. A solution of pyroxylin in ethanol, ether or propanone is known as **collodion**, and is used as an adhesive. If pyroxylin is heated with ethanol and camphor, **celluloid** is formed.

18.4
Practical work with proteins

Preparation of a protein solution

Beat an egg-white with about five times its volume of water, adding about 1 g of sodium chloride to help the albumen to dissolve. Filter carefully through a muslin cloth.

Reaction of the protein solution

1. *Denaturing*. Test 2 cm^3 portions for precipitation by (a) boiling, (b) adding M sulphuric acid, (c) adding 2M sodium hydroxide solution, (d) adding ethanol.

2. *Biuret test*. To a 2 cm^3 portion of protein solution, add 2 cm^3 of 2M sodium hydroxide solution, followed by 2 or 3 drops of copper(II) sulphate solution. Note the violet colour.

3. *Reactions catalysed by enzymes.*

(a) *The hydrolysis of carbamide (urea) catalysed by the enzyme urease.*

The hydrolysis of carbamide in neutral solution is catalysed by the enzyme, urease. Dissolve about 0·1 g of urea in 2 cm^3 of water in a test-tube, and add a few grains of urease powder.

Stand the test-tube in a beaker of water at 40°C, and test the gas evolved by (a) smell, (b) moist red litmus paper. It may take about 5 minutes to obtain enough gas to test with the litmus paper.

(b) *The hydrolysis of starch by enzymes present in saliva* (p. 299).

(c) *The decomposition of hydrogen peroxide catalysed by the enzyme, catalase.*

The decomposition of hydrogen peroxide solutions is catalysed by the enzyme, catalase. Catalase can be obtained as a pure powder and is also present in blood and in potatoes.

Set up an apparatus similar to that in Fig. 7.1, except with a boiling-tube as the receiver. The boiling-tube should first be calibrated in 10 cm^3 portions, by running in water from a burette and marking the heights for 10, 20, 30 and 40 cm^3 with a crayon or dab of paint.

Place 1 cm^3 of catalase solution (made up by dissolving about 0·01 g of catalase in 100 cm^3 of water) in the test-tube, and 2 cm^3 of 20-volume hydrogen peroxide in the dropping pipette. Squeeze the rubber teat so that all the hydrogen peroxide solution is added and collect the gas evolved in the boiling-tube.

Repeat the experiment using (a) a solution of 1 small drop of blood in 2 cm^3 of water, (b) a mixture made by chopping up a small piece of potato and water, instead of the solution of catalase in water.

If time, repeat the experiment using a small amount (ca. 0·1 g) of solid manganese(IV) oxide in place of the enzyme. By diluting the solution of catalase used above, see how active the enzyme is as a catalyst compared with manganese(IV) oxide.

N.B. If blood is to be drawn, it is important that the correct procedure is used. A useful guide is 'Human blood sampling: recommended procedures' *Education in Science*, No. 82, p. 27 (1979).

18.5 Practical work with carbohydrates

Reactions of glucose (a monosaccharide)

1. Heat about 1 g of glucose in a test-tube. It first melts, then gives off water of crystallisation and finally chars, smelling of burnt sugar.

2. Heat about 0·5 g of glucose with 2 cm^3 of concentrated sulphuric acid. Warm. Note charring with formation of carbon.

3. *Fehling's test* (p. 185). Use about 0·1 g glucose in place of the aldehyde.

4. *Silver mirror test* (p. 185). Use about 0·1 g glucose in place of the aldehyde.

5. *Formation of an osazone*. Dissolve 0·5 g of glucose in 5 cm^3 of water. Dissolve 1 g of phenylhydrazine in 1 g of ethanoic acid and dilute to 10 cm^3. Mix the solutions, and warm on a waterbath. Filter the crystals, wash with water and with ethanol. Recrystallise from ethanol. Study the crystalline structure of the osazone under a microscope. M.p. of the osazone is 204°C.

Reactions of fructose (a monosaccharide)

6. Repeat the experiments above with fructose in place of glucose.

Reactions of sucrose (a disaccharide)

7. Repeat experiments 1 and 2 above.

8. Dissolve 2 g of sucrose in 10 cm^3 of water and divide into two portions. With one, repeat experiment 3. Acidify the second portion with 5 drops of M sulphuric acid and boil for a few minutes. Neutralise by adding 2M sodium hydroxide solution dropwise and then test the solution with Fehling's solution.

Reactions of starch (a polysaccharide)

9. Make a paste with about 0·1 g of soluble starch and about 1 cm^3 of water. Pour 10 cm^3 of boiling water into the paste and shake the solution. Divide the solution into three parts.

To the first part, add 2 drops of iodine solution. Note the blue coloration.

Add 5 drops of M sulphuric acid to the second portion and boil for a few minutes. Neutralise the solution by adding 2M sodium hydroxide solution drop by drop. Divide the solution into two parts. Test one with iodine solution to show the absence of starch. Test the second with Fehling's solution to show the presence of a reducing agent (glucose).

Add a little saliva to the third portion and warm to about 70°C for a few minutes. Test the solution as in the previous experiment with iodine and with Fehling's solution.

Small-scale preparation of cellulose ethanoate

Mix 20 cm^3 of ethanoic acid, 5 cm^3 of ethanoic anhydride and 2 drops of concentrated sulphuric acid in a beaker. Then add, with stirring, 0·5 g of shredded cotton wool.

Continue to stir so that the cotton wool is evenly distributed throughout the mixture and there are no air bubbles. Leave the mixture for about a day, stirring occasionally. The mixture gradually becomes less viscous, ending in a clear liquid.

Pour the liquid slowly into a large beaker containing 500 cm^3 of water. A precipitate of cellulose ethanoate separates out, which should be filtered using a small Buchner funnel (Fig. 2.8). Wash it with water and dry it between pads of filter paper.

Take about a quarter of the ester and dissolve it in about 15 cm^3 of trichloromethane in a boiling tube. If the solution is turbid, place some anhydrous calcium chloride in the tube and shake the solution. Decant the solution into a basin and allow it to evaporate in a fume cupboard. Remove the film of cellulose ethanoate.

18.6 Further reading

The Chemistry of Proteins. R. J. Taylor. Unilever Educational Booklet, Advanced Series.

Carbohydrates. Unilever Educational Booklet, Advanced Series.

A Guidebook to Biochemistry. 4th ed. (1980). M. Yudkin and R. Offord. Cambridge University Press.

The Double Helix. James D. Watson. (1968). Weidenfeld and Nicholson. Paperback, Penguin 1970.

Introducing Biochemistry (1982) E. J. Wood and W. R. Pickering, John Murray.
Molecules to Living Cells. (1980) A collection of papers from Scientific American. Introduction by P. C. Hamawalt. W. H. Freeman and Co.

18.7 Film and Videotape

The Structure of Protein (F) Unilever.
'Pruteen' Food for the Future (V) ICI

18.8 Questions

1 What is meant by the term *sugar*? Give a brief account of the sources of sucrose and glucose, and their relationships with one another and with starch and ethanol.

How would you obtain a sample of ethanol from glucose and show it to be ethanol?

2 Give an account of the natural occurrence and properties of two types of polysaccharide. Write down structural formulae for glucose and fructose, and describe the principal reactions of these substances. Describe the preparation and chemical properties of sucrose.

3 How, if at all, do (a) glucose and (b) sucrose react with (i) dilute sulphuric acid, (ii) concentrated sulphuric acid, (iii) phenylhydrazine, (iv) hydrogen cyanide.

4 (a) Distinguish between an aldose and a ketose by drawing structural formulae for a named example of each, and show how each may be represented by both open chain and ring structures.

(b) Explain why such compounds may be optically active. Suggest why the optical activity of a solution of dextro-rotatory sucrose alters during hydrolysis to monosaccharides.

(c) How might starch be converted into monosaccharides? Illustrate this change by a block diagram or an equation. Describe and explain TWO instances of difference in chemical behaviour between starch and its constituent monosaccharides. (L)

5 (a) '*α-amino acids* are the final products of the hydrolysis of *proteins*.'
Explain what you understand by the terms *α-amino acid* and *protein*. Describe how the hydrolysis may be effected.

(b) State how an α-amino acid may be formed from propanoic acid, and explain why an aqueous solution of a pure α-amino acid prepared in this way is neutral to litmus, and optically inactive.

(c) By what chemical reaction has the chemist synthesized nylon and in what way are proteins and nylon structurally similar?
(Note: α-amino acids are also called 2-amino acids.) (L)

Chapter 19

Petroleum

19.1 Introduction

The term **petroleum** is used to describe the mixture of hydrocarbons in oil, including the gases above the liquid in oil wells and the gases and solids which are dissolved in the liquid. Well over 200 different hydrocarbons can be identified in a sample of crude petroleum.

Petroleum was formed in remote periods of geological time. Some was formed over 500 million years ago. Even the newest deposits are over 50 million years old. It was produced from the remains of living organisms. It is, therefore, a *fossil fuel*. Weathered rock material eroded from land masses and carried to the sea accumulated in layers over millions of years in subsiding basins, and the remains of large quantities of marine plant and animal organisms became incorporated in the sediment (Fig. 19.1). Owing to the great thickness of the sediments, high pressures built up which, probably in conjunction with biochemical activity, led to the formation of petroleum, although the detailed mechanism is obscure. It is probable, though, that anaerobic microbes lowered the oxygen and nitrogen content of what had been living matter.

Subsequent earth movements which caused uplift of the sedimentary basins also caused migration of the petroleum through pore spaces in the rocks, sometimes to areas distant from the formation zones. In the course of migration, some of the petroleum came to accumulate in *traps* where the porous rock was bounded by impermeable rock. The principal types of trap in oil fields such as those in the Middle East, North America and

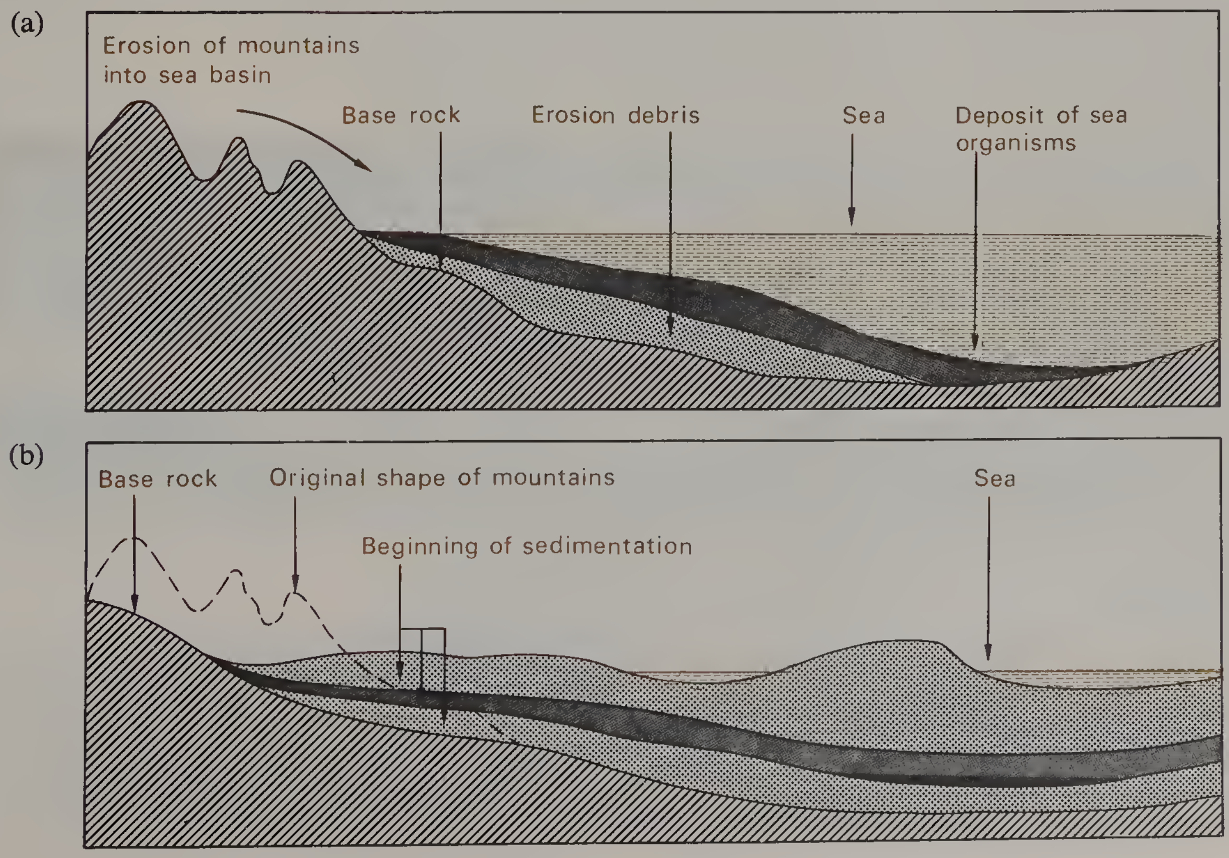


FIG. 19.1. (a) *Debris accumulates by erosion of the mountains, together with the bodies of marine organisms.* (b) *Pressure from the debris on the organisms contributes to the formation of oil*

the North Sea are the *anticline* (an upfold in the strata), the *fault* trap and the *salt dome* (Fig. 19.2).

The gas is principally methane, with smaller amounts of other alkanes. The liquid contains mainly alkanes (with up to about 125 carbon atoms in the chain), with smaller amounts of cycloalkanes and aromatic hydrocarbons. The relative amounts of the three classes of compound vary with the oil-field; for example, petroleum from the Middle East and Pennsylvania contains a high proportion of alkanes, whereas that from Venezuela is relatively rich in cycloalkanes and that from California in aromatic hydrocarbons. The length of the carbon chains also varies. For example, the petroleum from Mexico has a high proportion of heavy oils and residues, while the oils from the Middle East and the North Sea are much lighter.

Crude oil does not just consist of hydrocarbons. Also present are a variety of nitrogen- and sulphur-containing compounds which must be removed during its refining.

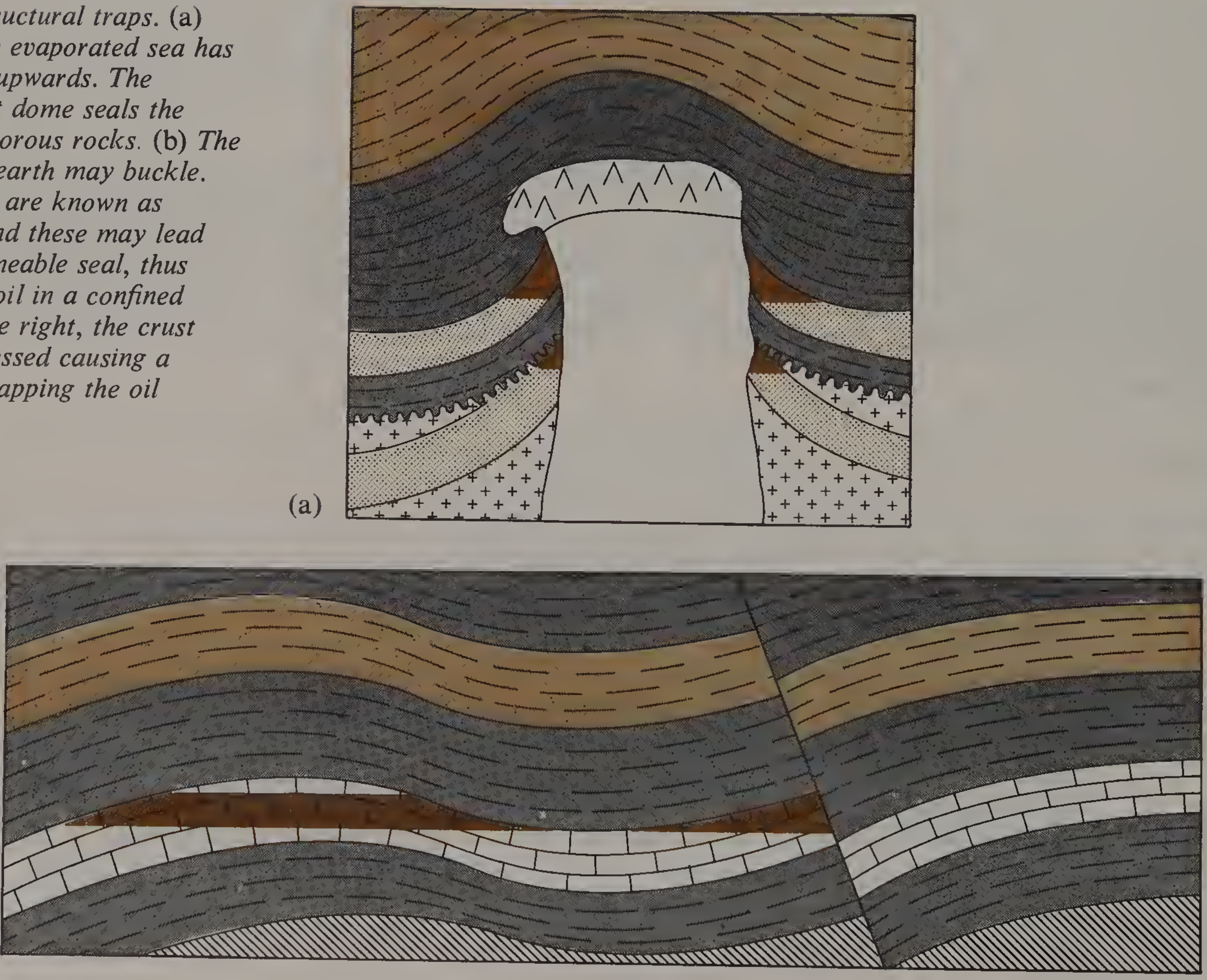


FIG. 19.2 *Structural traps.* (a) *Salt from an evaporated sea has been forced upwards. The resulting salt dome seals the oil-bearing porous rocks.* (b) *The crust of the earth may buckle. The up-folds are known as anticlines, and these may lead to an impermeable seal, thus keeping the oil in a confined space. On the right, the crust has been stressed causing a fault, thus trapping the oil*

19.2 Natural gas

The discovery of natural gas fields under the North Sea in 1967 has focused our attention on this very important material which serves both as a fuel and as a source of chemicals. Many fields all over the world are now exploited commercially, including those in Libya (from which gas is transported to other countries in the liquid state in specially constructed, refrigerated tankers), Italy, Holland and the U.S.A.

Plate 19.1. An aerial photograph of the San Andreas fault in California. There is a sharp line between mountains and farmland (Esso Petroleum Co. Ltd.)

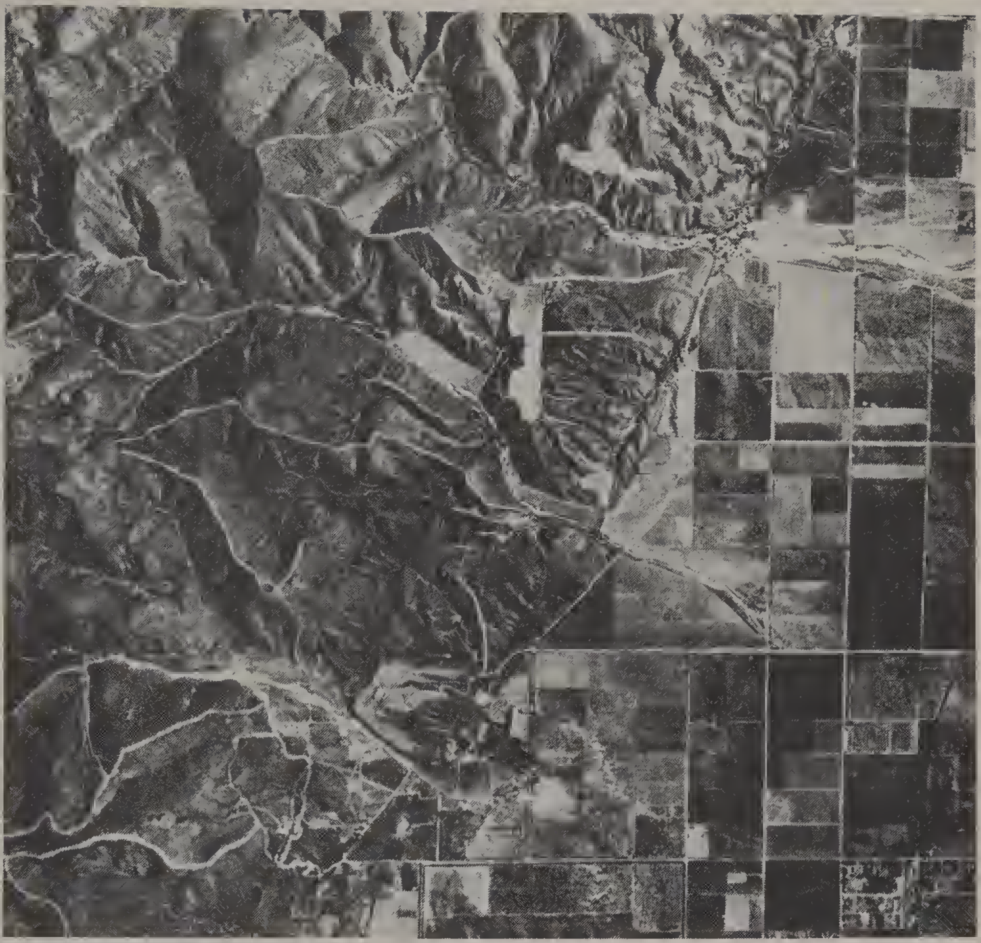


Plate 19.2. An aerial photograph of an anticline in Iran (Shell Petroleum Co. Ltd.)

It is believed that natural gas is formed from the decomposition of petroleum or coal deposits. It contains principally methane (if it is more than 95 per cent methane it is known as 'dry' natural gas). It may contain larger amounts of ethane, propane and butane ('wet' natural gas). The large North Sea natural gas fields are 'dry', but those in the U.S.A. are 'wet', and the higher alkanes are recovered and used as fuels ('bottled' gases) and to make alkenes (20.4).

Natural gas may also contain inert gas and, occasionally, hydrogen sulphide. Gas from the Lacq field in France contains about 15% of hydrogen sulphide, providing an important source of sulphur. Certain gas fields in the United States contain up to 5% helium and these have become a major source of the noble gas. On the other hand, the gas from the Groningen field in the Netherlands contains 14% nitrogen which merely reduces its calorific value.

Natural gas from the North Sea contains over 95% methane. Its sulphur content is so low that organic sulphur compounds are added by law before it is pumped into the grid so that it can be detected by a very unpleasant smell.

19.3 Distillation of crude petroleum

When crude petroleum is underground, it is under pressure. Hydrocarbon gases, the lower members of the alkane family (methane, ethane, propane and the butanes), are both above and dissolved in the liquid. When the liquid is obtained, it is allowed to degas at the oil field and the gas is either 'flared' or is used for generating power or as a feedstock for organic chemicals. For example, it is pumped ashore from the North Sea and is generally liquefied. In this form it is known as **liquefied petroleum gas** (LPG). It is a very useful source of ethane and propane (5.5 and 20.3) for chemical feedstocks.

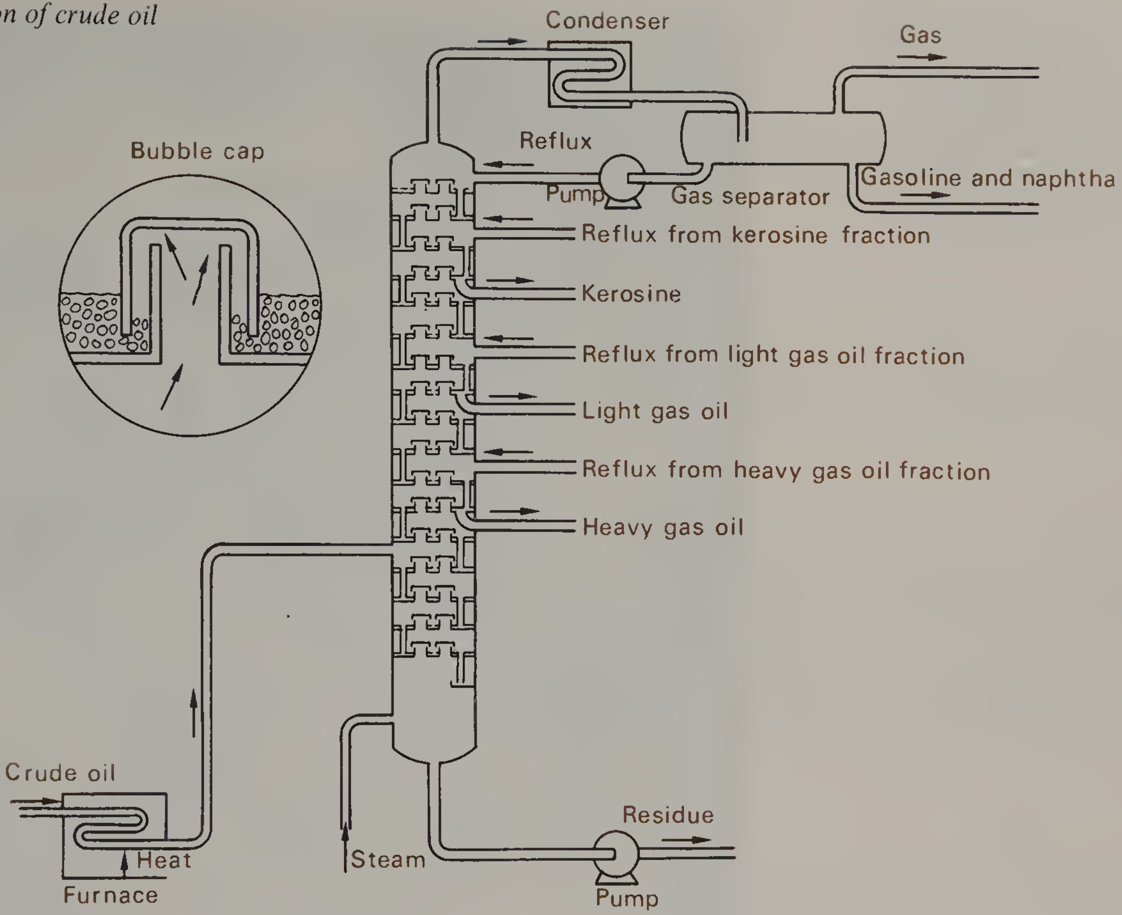
Once the gas is removed, the crude petroleum is said to be 'stabilised' and is transported to refineries, which are generally located in the countries where the products are to be used. The crude petroleum is distilled into fractions with different boiling ranges (Fig. 19.3).

CRUDE PETROLEUM

	GAS	GASOLINE	NAPHTHA	KEROSINE	LIGHT GAS-OIL	HEAVY GAS-OIL	RESIDUE (Residual crude)
B.P./°C	<40	40–100	100–160	160–250	250–300	300–350	>350
% wt	3	7	7	13	9	9	52
Numbers of C atoms in the alkanes	<4	4–10		10–16	16–20	20–25	>25

The values for percentage composition are approximate and vary widely, depending on where the crude petroleum is found (19.1). The residue, known as **residual crude**, is used both as a fuel for large industrial furnaces and as a source of lighter fractions on cracking. Some is distilled under vacuum to yield fractions suitable for lubricating oils and waxes. The residue is bitumen (19.8).

FIG. 19.3. *Distillation of crude oil*



19.4
The gasoline and naphtha fractions

Petrol (gasoline) is a mixture of volatile liquid hydrocarbons which is vaporised before entering the cylinder of the engine. The straight-chain alkanes, as obtained from crude petroleum, are not ideal as engine fuels because they do not burn uniformly in the cylinder, the process being known as 'knock'. This leads to both wear in the engine and wastage of petrol. However, the highly branched alkanes, as well as the cycloalkanes and the aromatic hydrocarbons, are less susceptible to knock. It is convenient to have a measure of the suitability of petrols as fuels, and for this purpose each compound is given a rating known as the **octane number**, which is determined by experiment. Two arbitrary reference points are used in the scale: heptane, octane number 0 (a poor fuel), and an isomer of octane, 2,2,4-trimethylpentane, octane number 100 (a good fuel). The fraction obtained by the distillation of crude petroleum has an average octane number of less than 60, whereas modern car engines, which have high compression ratios, require petrol with an octane number between 90 (2 star) and 98 (4 star).

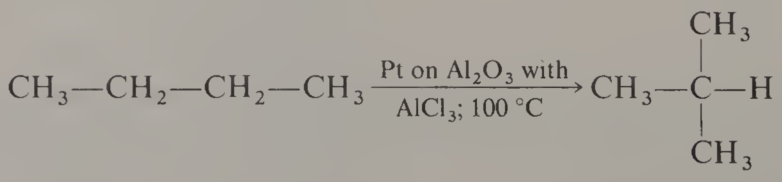
It is therefore necessary to enrich the petrol obtained from crude petroleum with branched-chain alkanes, cycloalkanes and aromatic hydrocarbons, and these compounds are themselves made from other fractions obtained by the distillation of crude petroleum. The methods for doing this include the **isomerisation** and **alkylation** of the smaller alkanes obtained from the gas fraction, the **reforming** of straight-chain alkanes obtained from the gasoline and naphtha fractions, the **cracking** of long-chain alkanes

Plate 19.3. An aerial photograph of a salt dome in Louisiana. The salt has been forced upwards under high pressure and is now acting as a seal, preventing the escape of oil upwards from the porous rocks (Esso Petroleum Co. Ltd.)

obtained from the kerosine and gas-oil fractions, and the **polymerization** of small alkenes.

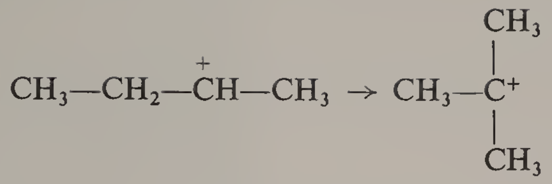
Isomerisation

Isomerisation is said to occur when a molecule undergoes a rearrangement to give an isomer. This process is used to convert straight-chain into branched alkanes over an acid catalyst. For example, butane is isomerised to 2-methylpropane when it is passed over a catalyst:



$$CH_3{-}CH_2{-}CH_2{-}CH_3 \xrightarrow[\text{AlCl}_3\text{; 100 °C}]{\text{Pt on Al}_2\text{O}_3\text{ with}} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}H$$

Reaction occurs *via* carbonium ions: initially, a secondary carbonium ion is formed and this, by rearrangement, gives the more stable tertiary carbonium ion (6.4):



$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightarrow CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C^+}}$$

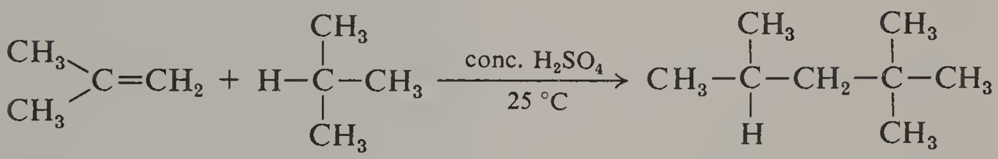
This reaction is important because it gives a supply of 2-methylpropane for the alkylation process (below).

Isomerisation of a mixture of pentanes and hexanes, from naphtha, can increase the octane number of a fuel from 70 to over 90.

Alkylation

As the use of lead compounds to improve the octane number of fuels becomes less, methods of increasing the proportion of branched-chain alkanes in the fuel become more important. One way is by **alkylation**.

Alkenes (obtained by cracking, p. 309) react with alkanes in the presence of acid to form larger alkanes. For example, 2-methylpropene reacts with 2-methylpropane (obtained by isomerisation as above) to give 2,2,4-trimethylpentane:

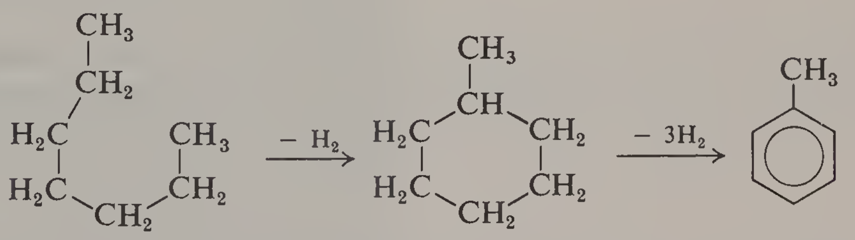


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}CH_2 + H{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH_3 \xrightarrow[25\ ^\circ C]{\text{conc. } H_2SO_4} CH_3{-}\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH_3$$

2,2,4-Trimethylpentane

Reforming

Reforming is another important way in which the octane number of a fuel can be increased. If the gasoline and naphtha fractions are passed over a catalyst at 500°C, the straight chain alkanes undergo cyclisation and dehydrogenation to form a mixture of cycloalkanes and aromatic hydrocarbons. For example:



The process is known as **catalytic reforming** and the catalyst is generally platinum suspended on aluminium oxide. During the process some of the alkane decomposes to carbon. However, if an excess of hydrogen is mixed with the gasoline and naphtha vapours before they are passed over the catalyst, formation of carbon is suppressed. Platforming is thus sometimes referred to as **hydroforming**. If carbon is formed, the catalyst is purified by removing it and burning off the carbon. In recent processes, the catalyst is continuously repurified and regenerated.

The catalyst, which contains a metal and an oxide acting as an acid, is known as a **bifunctional catalyst**: the platinum catalyses the dehydrogenation reaction while the aluminium oxide catalyses the rearrangement of the skeleton of carbon atoms. Recently, rhodium has also been added to promote the yield of aromatic hydrocarbons in place of cyclohexanes.

As well as being employed for the enrichment of petrol, the product from reforming, known as the *reformate*, is the major source of aromatic hydrocarbons such as benzene and methylbenzene for the petrochemical industry (20.5). The reformate contains over 60% of aromatic hydrocarbons.

Polymerization

Propene in the presence of traces of an acid (e.g. sulphuric acid) forms a mixture of branched chain alkenes, containing 3 or 4 propene units; these are known as trimers and tetramers and have the molecular formulae C_9H_{18} and $C_{12}H_{24}$. On hydrogenation, they form alkanes which, because of the branched chain, are added to petrol with a low octane number to improve its rating.

Tetraethyllead

The octane number of petrols can be improved significantly by additions of small amounts of chemicals known as 'anti-knocks'. Tetraethyllead, $Pb(C_2H_5)_4$, is the most effective.

In recent years, there has been considerable concern that the exhaust gases of cars, which contain volatile lead compounds, could be a serious hazard to health. Although there is no direct proof, lead is certainly a cumulative poison; for this reason, the permitted level in the U.K. has been reduced from 0·84 g dm^{-3} in 1972 to 0·15 g dm^{-3} in 1985. The debate on whether the addition of lead compounds to petrol leads to a health hazard or not has been overtaken in the United States by another factor. In order to remove carbon monoxide and unchanged hydrocarbons from car exhausts, many cars are now fitted with a converter, under the car, between the engine and the exhaust pipe. Some of the most advanced exhaust systems contain two converters. One (with a rhodium—platinum alloy) catalyses the *reduction* of oxides of nitrogen by the excess of hydrocarbons and carbon monoxide in the exhaust gases. The second (based on palladium), using the excess of air which is pumped in, catalyses the *oxidation* of the remaining hydrocarbons and carbon monoxide. Lead compounds poison the catalyst and so there is a considerable demand for lead-free petrol.

There is therefore more demand for branched-chain, cyclic and aromatic hydrocarbons, so that isomerisation, alkylation, reforming and polymerisation are becoming increasingly important. An interesting development has been the use of methyl t-butyl ether, which is sometimes added to improve the octane number.

An alternative strategy is to build engines that can run efficiently on lower grade petrols, and this too is being pursued vigorously by engine manufacturers in collaboration with the oil companies.

19.5
The kerosine fraction

The kerosine fraction boils between 160 and 250°C and contains alkanes with 10–16 carbon atoms. Kerosine is used in space- and radiant-heaters; the 'blue flame stoves' burn the fuel without smell or smoke. The kerosine is marketed under such names as Aladdin Pink and Esso Blue.

Kerosine is the principal constituent of jet (gas-turbine) fuels. The fuel must have the correct viscosity (so that the fuel spray is atomised), volatility and freezing point, for the temperature of the air at 10,000 metres is below −90°C.

When there is an excess of kerosine available from the distillation of petroleum, it is cracked (19.6).

19.6
The light gas-oil fraction

The light gas-oil fraction has a boiling point range of 250–300°C; the number of carbon atoms in the alkane molecules varies from 16 to 20. Much of the fraction is used as a heating oil and in high-speed diesel engines (DERV: Diesel Engine Road Vehicle). In the diesel engine, the fuel is injected as a fine spray; the engine, which does not have a sparking plug, relies on the heat of compression to ignite the mixture of fuel and air.

That part of the fraction not needed as a fuel is heated in the presence of a catalyst, at high temperature; the large molecules are thereby broken into two or more smaller molecules. The process is known as **catalytic cracking** or **'cat-cracking'**. The gas-oil or kerosine vapour is passed through a fine powder made of silica and aluminium oxide (sometimes containing small quantities of nickel or tungsten) at 400–500°C. The powder acts as a fluid and continuously flows out of the reactor into a second chamber through which air is passed. In this way, any carbon deposited on the catalyst is burnt off, so reactivating the catalyst which then flows back to the reactor (Fig. 19.4).

The products from cat-cracking are: (a) a gas, known as **refinery gas**, of which the alkenes, ethene and propene, are major constituents; this is used to make many chemicals (20.4); (b) a liquid containing a high yield of branched-chain alkanes, cycloalkanes and aromatic hydrocarbons, which can be used as high-grade petrol; (c) a residue of high boiling point, used as a fuel-oil.

A variant of the process is called **hydrocracking**. The catalyst is a sodium aluminosilicate in which some of the sodium ions are replaced by platinum. In the presence of excess of hydrogen, no alkenes can be formed and all the products are saturated. For example, the gases produced contain a high proportion of 2-methylpropane used to make high-grade petrol by alkylation (p. 307).

19.7
The heavy gas-oil fraction

The heavy gas-oil fraction has a boiling-point range of 300–350°C, and the number of carbon atoms in the alkanes varies from 20 to 25. It is used as a fuel for slow speed (e.g. stationary or marine) diesel engines.

19.8
The residue

The residue from the primary distillation of petroleum is known as **residual crude** (p. 304). As this consists of over half of the crude petroleum and has often been transported over very large distances from the oil field to the refinery, it is important that as great a use is made of it as possible.

Much of the residual crude is burnt as a fuel, widely used to generate steam in the production of electricity. This is of vital importance to countries which do not have the other main fossil fuel, coal. Modern ships also

FIG. 19.4. *A 'cat-cracker' using a fluid catalyst*

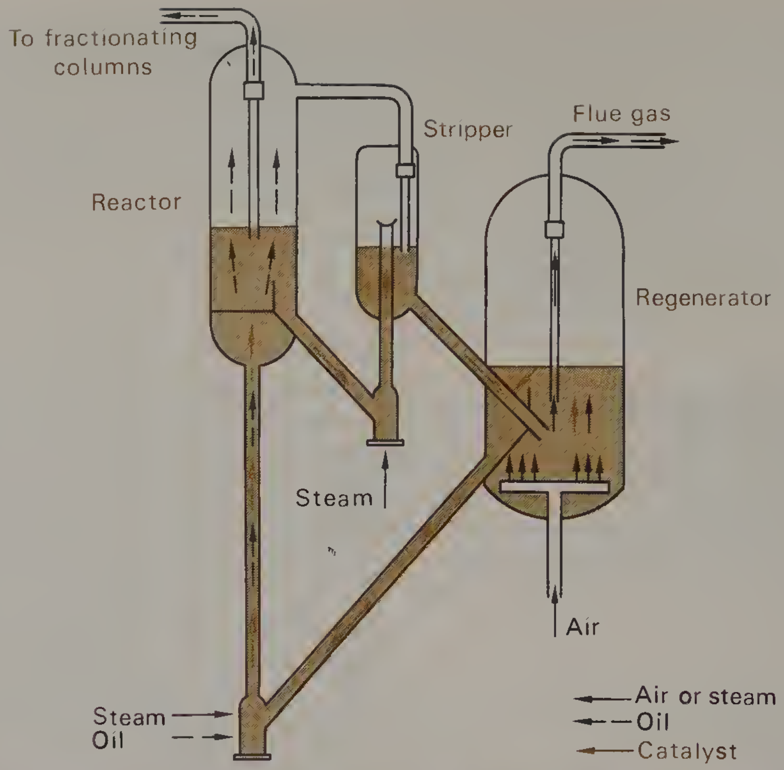
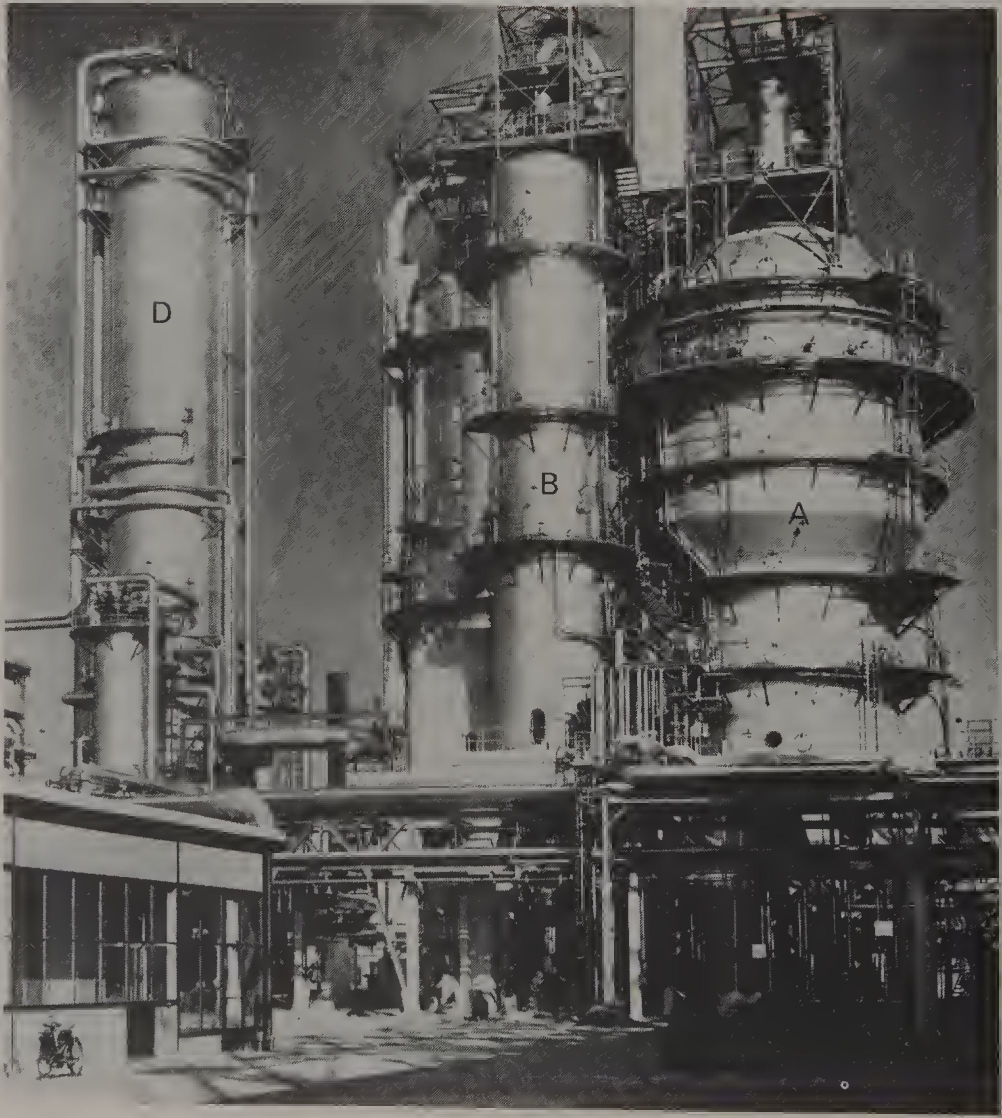


Plate 19.4. A cat-cracker (a fluid catalytic cracking unit). The regenerator (A) and stripper (B) are in front of the reactor (C), which is partly hidden. On the left is a fractionating column (D) (Shell Petroleum Co. PLC.)



use residual crude as a fuel oil and indeed the technology of modern ship design now depends on its use. Some is distilled in vacuum to yield light and heavy lubricating oils, greases, waxes and a residue, bitumen.

The viscosity of lubricating oils changes with temperature; the oils are too thick when cold and too thin when hot. Recent developments in producing multigrade oils (for example, BP Viscostatic and Super Shell multigrade) have ensured that the viscosity changes relatively little with temperature. In particular, a polymer of 2-methylpropene is added whose viscosity is almost constant over a wide temperature range. Detergents are also added to keep any sludge formed as a fine dispersion.

The effect of engine wear has been studied with pistons which have been irradiated in an atomic pile and so contain a radioisotope of iron; the occurrence of wear leads to the enrichment of the oil with the radioactive iron and so can be followed by 'monitoring' the circulating oil. It has been found that most wear occurs while the engine is at rest; it results from attack on the metal by acids formed in the oxidation of oils. Chemicals, such as substituted phenols, are therefore added to inhibit the oxidation of oil.

Paraffin wax, deposited on distillation of the residue, is used for waterproofing paper cartons and in the manufacture of candles and polishes.

By cracking the wax in the presence of excess of steam at 500°C, straight-chain alkenes with terminal double bonds (i.e. $RCH{=}CH_2$) and 5–18 carbon atoms are formed; they are separated by fractional distillation. The lower members are used to make branched-chain alkanes for high-grade petrol (p. 307), and the higher members are used in the manufacture of detergents by a number of routes (13.10).

Bitumen (the residue from the vacuum distillation of residual crude) is mainly used in making the surfaces for roads and in part for coating materials such as cables to give them water and electrical insulation.

19.9 Practical work

Distillation of crude oil

Pour in some crude oil to a depth of about 2·5 cm in a test-tube with a side arm and push down a plug of Rocksil to soak it up. Set up the apparatus as in Fig. 19.5 and distil the crude oil very slowly, collecting the fractions in different test-tubes:

Fraction 1—up to 70°C
Fraction 2—70–130°C
Fraction 3—130–180°C
Fraction 4—180–240°C
Fraction 5—the residue.

Pour each fraction on to a separate watch glass and light it with a burning match or splint.

Cracking of oil to form alkenes

Pour some paraffin oil in a test-tube to a depth of about 2·5 cm. Add Rocksil until the oil has been soaked up, and then fill the tube to a depth of about 5 cm with porous pot chips (Fig. 19.6). Heat the chips and collect the gases in test-tubes, placing corks in them when they are full of gas.

FIG. 19.5. *Distillation of crude oil*

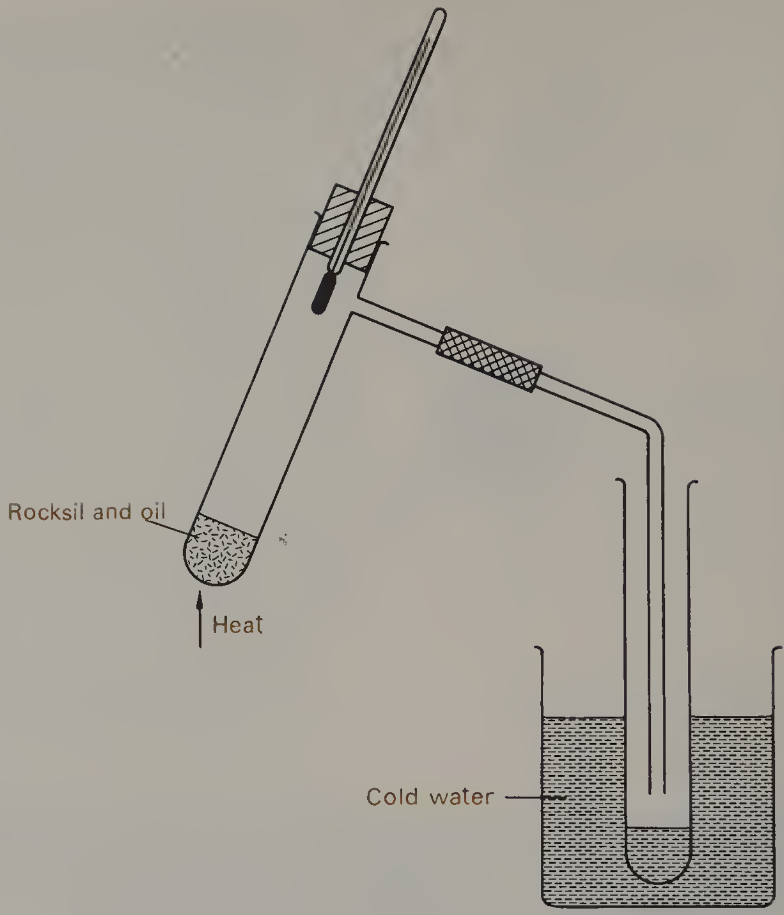
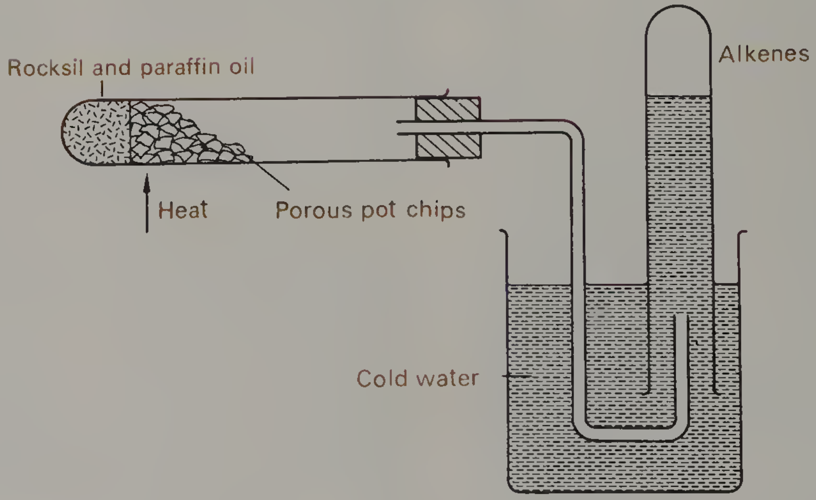


FIG. 19.6. *Cracking of oil to form alkenes*



Tests for alkenes

1. To one test-tube, apply a lighted splint. Note the colour of the flame and compare it with the colour of the flame of an alkane.

2. To another test-tube, add 2 drops of a solution of bromine in tetrachloromethane and shake.

3. To a third test-tube, add 2–3 drops of an alkaline solution of potassium manganate(VII) (made by dissolving about 0·1 g of anhydrous sodium carbonate in 1 cm^3 of 1 per cent potassium manganate(VII) solution). Shake the contents of the test-tube. A green solution may be obtained

first [potassium manganate(VI)]. Subsequently, a brown precipitate of mangananese(IV) oxide is formed.

19.10 Further reading

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The Oil Venture. Shell Education Service.
Energy from synthetic fuels. C. A. McAullife. *Education in Chemistry*, Vol. 15, p. 21 (1978).
Energy from oil and gas. C. A. McAuliffe. *Education in Chemistry*, Vol. 15, p. 24 (1978).
Energy from coal. *Journal of Chemical Education*, Vol. 56, p. 186 (1979).

19.11 Films and Videotapes

A wide range of films on prospecting for petroleum and natural gas can be obtained from Shell Film Library, British Petroleum PLC and from the Gas Council.
Of particular interest are
Location North Sea (F, V) B.P. Education Service
Flags under the North Sea (F, V) Shell Film Library
The Origins of Oil (F, V) Shell Film Library
Films covering the distillation of oil can also be obtained from these sources. One such film is: *Oil Refinery* (F, V) Shell Film Library
Another interesting film describing our finite fuel resources is *Energy in Perspective* (F) B.P. Education Service.

19.12 Other resource material

North Sea Challenge. A resource pack including audio-casettes. B.P. Education Service.

Chapter 20

The petrochemical industry

20.1 Introduction

In the United States and Western Europe, about half-a-tonne of organic chemicals is produced every year for every member of the population. It is difficult to imagine how we consume such an enormous amount. But we do—in the clothes we wear, the furniture in our homes, in medicines, in foods, in our cars and planes. It is interesting to spend a few minutes checking on the materials we use in our homes, in the places where we work and in the sports we play.

More than 90% of these organic compounds come from natural gas and petroleum, and the petrochemical industry is one of the vital industries in our developed societies. Yet, to put this in perspective, this only accounts for about 5% of the petroleum used each year—the remainder being used as fuels in one form or another. This ratio will change as the oil deposits become scarcer and this will provide chemists with one of the greatest challenges in the next 20 or 30 years.

As this chapter develops, you will see that the myriad of chemicals is produced from only seven raw materials—methane, ethene, propene, a mixture of C_4 unsaturated hydrocarbons, benzene, methylbenzene, and a mixture of dimethylbenzenes. Indeed, the chemicals we make from ethene account for nearly half the entire petrochemical industry.

20.2 Primary sources

There are four important primary sources for the manufacture of petroleum chemicals: natural gas, gas dissolved in oil deposits (LPG), refinery gas and naphtha. The first three have been discussed in the preceding chapter. Refinery gas, which contains hydrogen, and alkanes and alkenes containing up to four carbon atoms, is obtained from the distillation of petroleum (19.3), catalytic cracking (19.6) and catalytic reforming (19.4).

20.3 Chemicals from alkanes

(a) Methane

Methane is obtained from natural gas. The sulphur compounds are first removed (20.8) and then the natural gas is fractionated to yield pure methane.

The principal use of methane is the formation of a mixture of **carbon monoxide** and **hydrogen** (known as **synthesis gas**) by reaction with steam (5.4). The uses of synthesis gas are discussed in Section 20.7. Suffice to say that this is the main use of methane because the hydrogen co-product is needed for the Haber Process.

Chloromethane and **dichloromethane** are formed when an excess of methane is heated with chlorine at 400°C. Chloromethane is used in the manufacture of **silicones** (p. 339), and dichloromethane is an important solvent.

Methane is the principal source of **hydrogen cyanide**:

$$2CH_4 + 2NH_3 + 3O_2 \xrightarrow[1000^\circ C]{\text{Pt–Rh cat.}} 2HCN + 6H_2O$$

which is used in the manufacture of **hexanedinitrile** (p. 320) and **methyl 2-methylpropenoate** (p. 331).

A more recent and increasingly important use of methane is in the manufacture of **ethyne** (5.4).

The uses of methane as a source of chemicals are summarised in a chart given in Appendix I.

(b) Ethane and propane

Ethane and propane, constituents of 'wet' natural gas (19.2) and liquefied petroleum gas (LPG) (19.3) are important sources of **ethene** and **propene**, which are used to make a very wide range of chemicals (20.3 and 20.4).

Some ethane is chlorinated to form **chloroethane**, used to make **tetraethyllead** (19.4). Some propane is used in bottled fuel and also to make **nitroalkanes**. When it is heated with nitric acid vapour at 350°C, a mixture of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane is formed; the compounds are separated by distillation and used as solvents and as fuels for small engines.

(c) Butane

Butane is generally obtained from refinery gas (20.2). Much is liquefied, bottled and sold as a liquid, portable, fuel (for example, Calor Gas).

Butane is a major source of ethanoic acid (13.4).

2-Methylpropane is used in the manufacture of 2,2,4-trimethylpentane for high-grade petrol (19.4).

(d) Higher alkanes

The naphtha fraction (C_4–C_{10} alkanes) is cracked to form alkenes (20.4). It is also reformed to produce a mixture of aromatic hydrocarbons (19.4). It is an important source of ethanoic acid (13.4).

2-Methylbuta-1,3-diene, required for the synthetic rubber industry (21.4), is obtained in part from 2-methylbutane.

The **kerosine fraction** (C_{10}–C_{16} alkanes) contains both straight-chain and branched alkanes. These are separated by passing them through synthetic zeolites which 'sieve' the molecules, the straight-chain compounds (average diameter of 500 pm) being absorbed and the larger branched-chain compounds (diameter of about 550 pm) passing through. The straight-chain alkanes are then desorbed by washing the column with pentane, and these are converted into **detergents** (13.10).

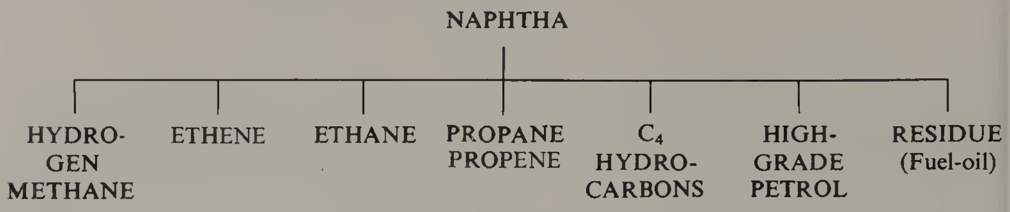
20.4
Chemicals from alkenes

Production of ethene and propene

Ethene and propene are the two most important compounds in the petrochemical industry. As we have already seen, ethene and its products account for about half the tonnage of the industry.

In the UK and in other Western European countries, they are produced principally by the thermal cracking of the naphtha fraction (containing C_5–C_{10} hydrocarbons), obtained from the distillation of crude oil. Naphtha is vaporised, mixed with steam, and passed, very quickly, through tubes made of a special alloy, at 700–900°C. The time taken for the heating of the mixture of naphtha and steam is a few thousandths of a second.

After condensation of the liquid products, the gases are compressed and separated by fractional distillation. The final result is to give the following products:



At 700°C, about 15 per cent of the feedstock is converted into ethene and a further 15 per cent into propene. When the temperature is raised to 900°C, the conversion into ethene increases to 30 per cent, but the amount of high-grade petrol (19.4) decreases from 30 to 25 per cent.

In the United States, ethene and propene are generally manufactured by cracking the ethane and propane obtained from 'wet' natural gas (p. 302). In the United Kingdom, liquefied petroleum gas (LPG (19.3)), a mixture of the smaller alkanes, is becoming available in very large quantities from the stabilisation of North Sea oil sent for export. 'Steam cracking' LPG gives a high yield of ethene, and this source may well become more important than naphtha by the late 1980s.

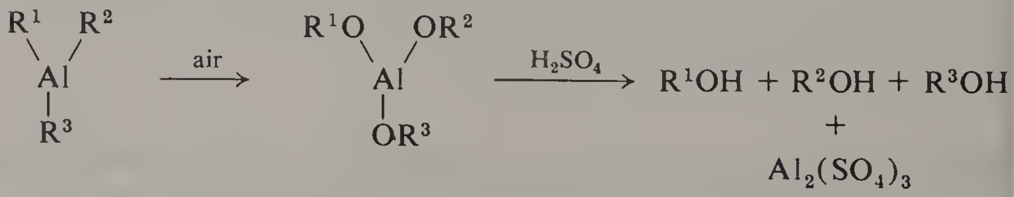
Most of the ethene produced, and the chemicals derived from it, end up as polymers—poly(ethene), poly(chloroethene), poly(phenylethene), poly(ethenyl ethanoate), and the polyesters, which are discussed in Chapter 21. In addition, the Ziegler process for the manufacture of poly(ethene) (p. 328) has been adapted to make longer-chain alkenes and alcohols from ethene. The ethene is heated with triethylaluminium:

$$\mathrm{Al(C_2H_5)_3} + n\mathrm{C_2H_4} \rightarrow \mathrm{AlR^1R^2R^3}$$

For the formation of alkenes, the resulting trialkylaluminium (in which R^1, R^2 and R^3 are alkyl groups larger than ethyl) is heated at 300°C under pressure, for example:

$$\mathrm{Al(CH_2CH_2CH_2CH_2R)_3} \rightarrow \mathrm{Al(C_2H_5)_3} + 3\mathrm{RCH{=}CH_2}$$

For the formation of alcohols, the aluminium trialkyl is oxidised in air to an aluminium alkoxide which is subsequently decomposed with dilute sulphuric acid:



$$\mathrm{AlR^1R^2R^3} \xrightarrow{\text{air}} \mathrm{Al(OR^1)(OR^2)(OR^3)} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{R^1OH + R^2OH + R^3OH + Al_2(SO_4)_3}$$

The alcohols are used in the manufacture of detergents (13.10).

Ethanol is made from ethene, either by direct hydration or *via* ethyl hydrogensulphate (10.4), and is used to make ethanal. Ethanol is used in the manufacture of esters and as a solvent for lacquers and varnishes, cellulose nitrate (used to make cellophane) and in many cosmetic and toilet preparations.

Ethanal is made from ethene by the Wacker process (12.3), and can then be converted into **ethanoic acid** and **ethanoic anhydride**.

Ethene is oxidised directly to **epoxyethane** (11.6), which is used to make **detergents** (13.10) and **ethane-1,2-diol** (10.7). The diol is used as an antifreeze and also to make **Terylene** (p. 337).

Chloroethane, used to make **tetraethyllead** (9.3), the antiknock agent for gasoline, is manufactured from ethene in the gas phase:

$$CH_2{=}CH_2 + HCl \xrightarrow[200°C]{AlCl_3 \text{ as cat.}} CH_3{-}CH_2Cl$$

and by the chlorination of ethane (9.3), while **1,2-dichloroethane** is made in the liquid phase by the addition of chlorine to ethene, with 1,2-dichloroethane itself as the solvent:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow[50°C]{FeCl_3 \text{ as cat.}} Cl{-}CH_2{-}CH_2{-}Cl$$

Chloroethene is manufactured from ethene (p. 85) and is the source of **poly(chloroethene)** (21.2).

The uses of ethene in the chemical industry are summarised in a chart in Appendix I.

Chemicals from propene

By far the greatest use for propene is in the manufacture of raw materials needed to make plastics, the major single outlet being polymerisation to **poly(propene)** (21.2).

Propene is the starting material for **propenenitrile**. This important chemical is formed by passing propene, ammonia and oxygen over a molybdenum-based catalyst at 450°C:

$$CH_3{-}CH{=}CH_2 + NH_3 + \tfrac{3}{2}O_2 \xrightarrow{\text{Bismuth molybdate}} CH_2{=}CH{-}CN + 3H_2O$$

Newer catalysts, based on antimony(V) and uranium(VI) oxides, are being formulated and used.

Propenenitrile is used for the manufacture of **synthetic fibres** (for example, Acrilan) (21.3) and **nitrile rubber** (21.4). A very useful by-product of the process is **hydrogen cyanide**.

If only propene and oxygen are in the reactant mixture which is passed over bismuth molybdate, propenoic acid (acrylic acid) is produced. This can be esterified and polymerised to form the ‘polyacrylates’ used as a base in emulsion paints.

Propene is one of the starting materials in the Cumene process which is used to manufacture **propanone** and **phenol** (p. 156). Propanone is also manufactured from propene *via* propan-2-ol (10.4 and 12.4).

Although propanone is used both as a solvent and in the manufacture of a variety of other products, one of the most important uses is in the manufacture of the thermosoftening plastic, **Perspex** (p. 331).

Large amounts of propene are now converted by the OXO process into **butan-1-ol**. This is described later (20.7) and is an example of how recent advances in catalysis have enabled us to produce ‘tailor-made’ molecules.

Other uses of propene include the manufacture of **propane-1,2,3-triol** (10.7) for **glyptal resins** (p. 335) and **epoxypropane** for **polyurethane foams** (p. 334).

The uses of propene in the chemical industry are summarised in a chart in Appendix I.

Butenes and pentenes

The butenes are obtained from refinery gas. 2-Methylpropene is converted into polymers to improve the viscosity characteristics of lubricating oils for car engines (p. 311). It is used, too, to make branched alkanes, for example, 2,2,4-trimethylpentane, to improve the octane number of petrol (p. 307).

Pentenes are used to make **2-methylbuta-1,3-diene**, the monomer for an **artificial rubber** (p. 339).

Higher alkenes

Higher alkenes are made by polymerisation of ethene (20.4) or the cracking of waxes (19.8). They are used principally for the manufacture of **detergents** (13.10) and long-chain alcohols [via the OXO process (20.7)] for making esters used as **plasticisers** (21.2).

20.5

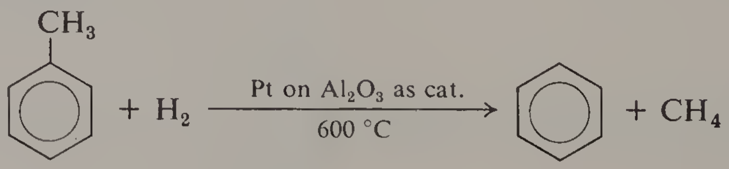
Chemicals from aromatic compounds

Production of aromatic hydrocarbons

The traditional source of benzene, methylbenzene, the dimethylbenzenes and the polycyclic aromatic compounds such as naphthalene was coal-tar. However, by far the most important source of these hydrocarbons is now by reforming the gasoline and naphtha fractions from the distillation of petroleum (19.4). Over 90% of benzene is now produced from petroleum.

In order to obtain pure aromatic hydrocarbons from the reformate, a number of physical processes are used. First, the aromatics are separated from other hydrocarbons by solvent extraction (bis-2-hydroxyethyl ether, $HOCH_2CH_2—O—CH_2CH_2OH$, is often used since aromatic hydrocarbons, unlike aliphatics, dissolve readily in it). Then, the aromatic hydrocarbons are carefully distilled. The first fraction contains **benzene**. The second contains **methylbenzene**, which is purified by further distillation. The third, containing a mixture of the **dimethylbenzenes** and **ethylbenzene**, is purified by both fractional distillation and fractional recrystallization.

More methylbenzene and dimethylbenzenes are formed during the reforming processes than is required, and they are converted into benzene by a process known as **hydrodealkylation**. The vapours of the aromatics are mixed with hydrogen and passed over a catalyst under pressure at about 600°C. For example:



Chemicals from benzene

Most of the benzene which is manufactured is converted into materials needed for the plastics industry; examples are the formation of **phenylethene** and thence **poly(phenylethene)** (p. 329), and **cyclohexane** (p. 320), an intermediate in the manufacture of **nylon** (p. 336).

Benzene is also used to make **phenol** *via* (1-methylethyl)benzene (p. 156). The principal uses of phenol are in the manufacture of cyclohexanol (p. 159) used to make **nylon** (p. 336), thermosetting plastics such as **Bakelite** (p. 333), substituted phenols for **epoxy resins** (p. 335) and selective weed-killers such as **2,4-D** (2,4-dichlorophenoxyethanoic acid) (p. 160).

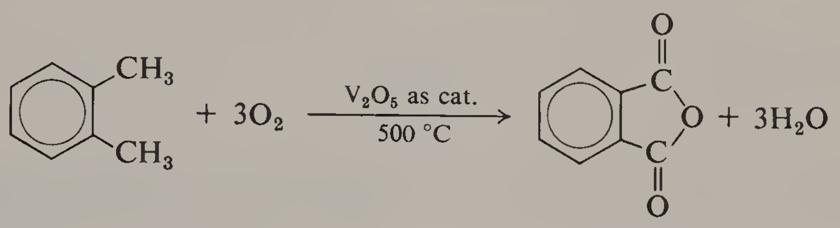
The uses of benzene are summarised further in Appendix I.

Chemicals from methylbenzene

Some methylbenzene is converted into **benzene** by hydrodealkylation, some is used in fuels for aeroplanes and cars and some is employed in the manufacture of the **polyurethane** plastic foams (p. 334).

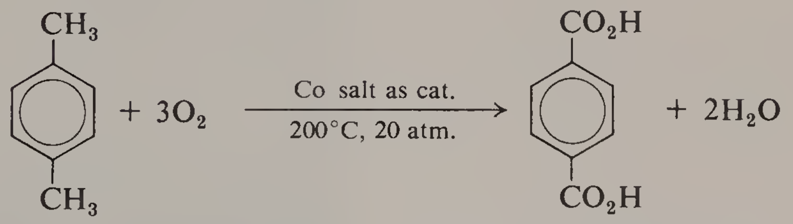
Chemicals from dimethylbenzenes

1,2-Dimethylbenzene is used for making **benzene-1,2-dicarboxylic anhydride**, which is required for **plasticisers** (p. 327) and **glyptal resins** (p. 335):



Benzene-1,2-dicarboxylic anhydride

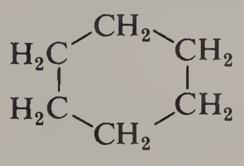
1,4-Dimethylbenzene is oxidised to **benzene-1,4-dicarboxylic acid**, required for **Terylene** manufacture (p. 337). One of the most recent methods for the oxidation is by passing air into the liquid hydrocarbon under pressure in the presence of a cobalt salt as catalyst:



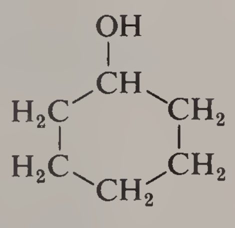
Benzene-1,4-dicarboxylic acid

20.6 Alicyclic compounds

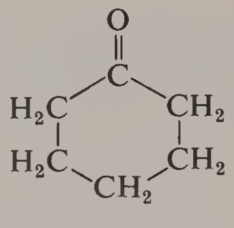
The most important alicyclic compounds used in industry are cyclohexane, cyclohexanol and cyclohexanone, all of which are made from benzene.



Cyclohexane

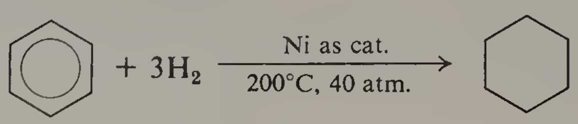


Cyclohexanol

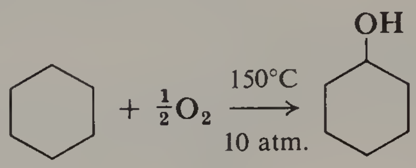


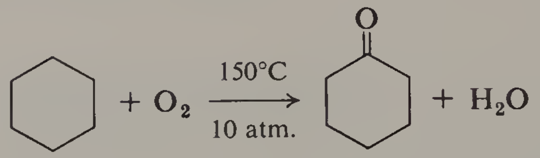
Cyclohexanone

Cyclohexane is manufactured by passing hydrogen through liquid benzene in the presence of a nickel catalyst under pressure:

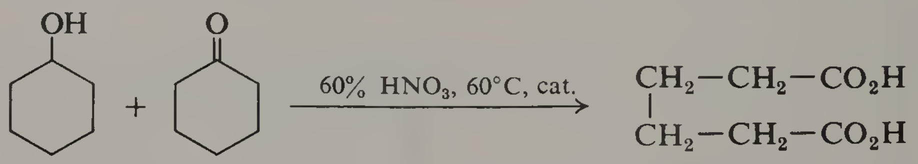


Cyclohexane is oxidised by passing air through the liquid under pressure, in the presence of a catalyst (often a cobalt salt):





The mixture of cyclohexanol and cyclohexanone (known as 'mixed oil' or KA—ketone/alcohol) is oxidised in the liquid phase to **hexanedioic acid** using moderately concentrated nitric acid and a copper salt as catalyst:



Part of the hexanedioic acid is converted into **hexanedinitrile** which is reduced by hydrogen over nickel to **1,6-diaminohexane**. Hexanedioic acid and 1,6-diaminohexane are then used to make **nylon-6.6** (p. 336).

A more recent method for making 1,6-diaminohexane starts with buta-1,3-diene. It is an intriguing process for it would not have been predictable from our basic knowledge of organic reactions.

Hydrogen cyanide is added to buta-1,3-diene to produce an unsaturated nitrile, as expected:

$$CH_2{=}CH{-}CH{=}CH_2 + HCN \rightarrow CH_3{-}CH{=}CH{-}CH_2{-}CN.$$

The product is then treated with more hydrogen cyanide in presence of a catalyst to produce hexanedinitrile direct:

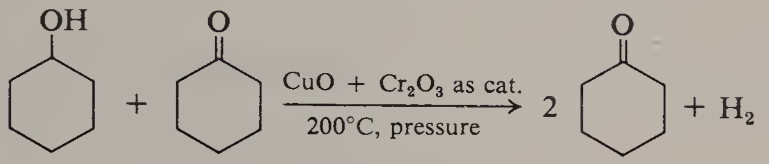
$$CH_3{-}CH{=}CH{-}CH_2{-}CN + HCN \rightarrow NC(CH_2)_4CN$$

A bifunctional catalyst (p. 308) is used. The catalyst is made up of a compound containing a transition element (e.g. Pt, Pd, Ru) and an acid. Apparently the transition element isomerises the unsaturated nitrile to a compound with a terminal double bond

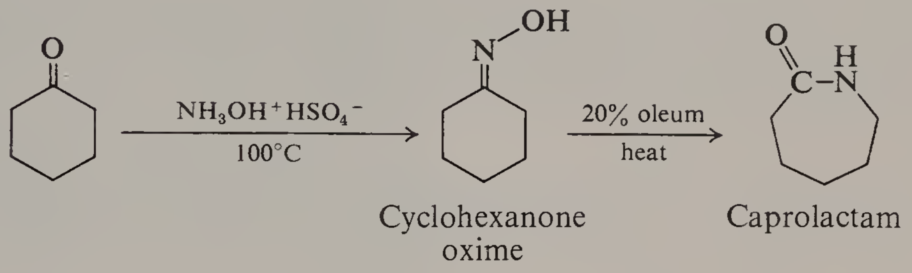
$$H_2C{=}CH{-}CH_2{-}CH_2{-}CN$$

and the catalyst also encourages a molecule of HCN to add in the anti-Markownikoff manner (p. 86). Hexanedinitrile is then hydrogenated to 1,6-diaminohexane.

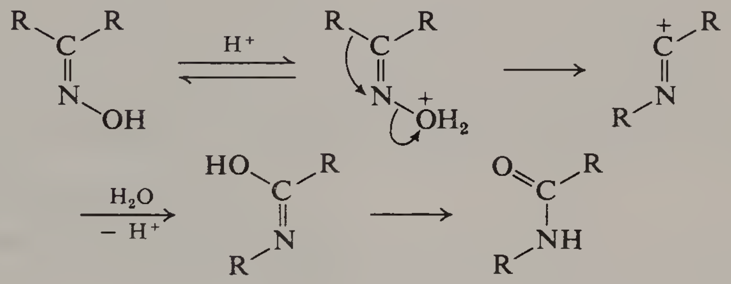
Another important polymer is **nylon-6**, for which pure cyclohexanone is required. When the mixed oil is heated under pressure with copper(II) and chromium(III) oxides, the cyclohexanol, which is a secondary alcohol, is dehydrogenated to the corresponding ketone:



Cyclohexanone is then converted into **caprolactam**, from which nylon-6 is made (p. 336).



The isomerisation of the oxime to caprolactam by sulphuric acid is an example of the **Beckmann rearrangement** in which an oxime is transformed into an amide in the presence of acid:



20.7 Synthesis gas

Manufacture of synthesis gas

'Synthesis gas' is a mixture of carbon monoxide and hydrogen. It is manufactured by heating methane or naphtha with steam on a nickel catalyst, for example:

$$CH_4 + H_2O \xrightarrow[900°C,\ 30\ atm.]{Ni\ as\ cat.} CO + 3H_2$$

Since methane contains a higher ratio of hydrogen to carbon than naphtha, it is the preferred feedstock when a high proportion of hydrogen is required in the product.

Uses of synthesis gas

1. **Methanol** is manufactured from carbon monoxide and hydrogen. Water gas has traditionally been the source of these gases (10.4). However, synthesis gas is purer than water gas and is now used for manufacturing

methanol with an active catalyst, based on copper:

$$CO + 2H_2 \xrightarrow{\text{cat.}} CH_3OH$$

A temperature of 250°C and 70 atmospheres pressure can be employed, and these conditions are milder and therefore more economical than those of the older process using water gas in which the catalyst of zinc and chromium(III) oxides requires a higher temperature and a pressure of 300 atmospheres. The uses of methanol are outlined in Section 10.6. They include the manufacture of **methanal** and thence **Bakelite**, **Perspex**, and **methanoic** and **ethanoic acids.**

2. **Higher alcohols** are manufactured from alkenes by the OXO process. This is an example of a reaction known as hydroformylation (the addition of CH_2O).

The alkene, together with synthesis gas, is heated in presence of a catalyst and an isomeric mixture of aldehydes is produced. However, it has been shown recently that if the catalyst is either cobalt carbonyl, $Co(CO)_8$, or a complex of rhenium and triphenylphosphine, only the more useful straight-chain aldehyde is formed. This is hydrogenated to the primary alcohol. For example:

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + CO + H_2 \rightarrow \underset{\text{Butanal}}{CH_3CH_2CH_2CHO}$$

$$CH_3CH_2CH_2CHO + H_2 \rightarrow \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH}$$

Butan-1-ol is an important solvent. If longer chain alkenes are used, the primary alcohols produced become a basis for **detergents** (13.10).

3. **Carbon monoxide** is produced by cooling synthesis gas, liquefying the carbon monoxide and pumping off the hydrogen. It can be converted into **carbonyl chloride**, $COCl_2$, which is used to make **polyurethane** foam plastics (p. 334).

An important new use of carbon monoxide is in carbonylation reactions (the addition of carbon monoxide to a molecule). The principal route for the manufacture of **methanoic** and **ethanoic acids** is by the reaction of methanol with carbon monoxide (13.4).

4. **Hydrogen** is manufactured by modifying the process used for the production of synthesis gas. Excess of steam is used, encouraging the formation of carbon dioxide, rather than carbon monoxide, and hydrogen:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

However, some carbon monoxide is still present and so the gases are successively passed over iron at 400°C and a more active copper catalyst at 200°C. Carbon monoxide is oxidised by the steam, still present in the mixture:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The gases are passed through an alkali (for example, a solution of potassium carbonate) to remove carbon dioxide. Traces of carbon monoxide can be removed by passing the mixture over nickel:

$$CO + 3H_2 \xrightarrow[300°C,\ 20\ atm.]{Ni\ as\ cat.} CH_4 + H_2O$$

Hydrogen is used to make **ammonia**:

$$N_2 + 3H_2 \xrightarrow[500°C,\ 150\ atm.]{Fe\ as\ cat.} 2NH_3$$

Apart from countries where oil supplies are considered insecure, all ammonia is now manufactured from naphtha or methane. It is used to make nitric acid and inorganic fertilisers such as **ammonium nitrate**. However, an organic nitrogen compound, **carbamide** (urea), is now a very important fertilizer for use in warm climates. It has a high nitrogen content (46%) and it is made by heating ammonia and carbon dioxide under pressure:

$$2NH_3 + CO_2 \xrightarrow{200°C,\ 200\ atm.} H_2N{-}CO_2^-\ NH_4^+ \rightarrow H_2N{-}CO{-}NH_2 + H_2O$$

Carbamide is also used to make plastics (p. 333).

20.8 Sulphur

Crude oil contains both hydrogen sulphide and organic sulphur compounds (which during the various processes in the refinery are converted into hydrogen sulphide). The refinery gas is passed through a solution of a weak base (an amine) which absorbs hydrogen sulphide, which is an acid. The solution is later boiled to release hydrogen sulphide in a concentrated form. Some natural gas also contains hydrogen sulphide and this is removed in the same way.

The removal of sulphur compounds is necessary to avoid pollution. However, it is also economically important since over a quarter of the sulphur now used in industry is recovered from petroleum sources.

It is most convenient to convert the hydrogen sulphide into solid sulphur, which is then in turn converted into **sulphuric acid** by the Contact Process. The hydrogen sulphide is burnt in air to form sulphur dioxide:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

Sulphur dioxide is mixed with excess of hydrogen sulphide and passed over aluminium oxide at 400°C:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Sulphuric acid is used in many ways, for example, in the manufacture of fertilisers (superphosphate and ammonium sulphate), titanium (IV) oxide, rayon and cellophane (p. 297), explosives (p. 276), and detergents (p. 201).

20.9 When the oil runs out

If you had been studying chemistry 30 years ago, you would have been using a book in which a great deal of space was devoted to the use of coal both as a fuel and as a feedstock for the chemical industry. During the 1930s and 1940s there was a revolution in the industry and, in order to give a picture of the organic chemicals industry today, we have concentrated, in Chapters 19 and 20, exclusively on petroleum. This revolution has been remarkable. Just consider its growth. In 1920, less than 100 tonnes of chemicals manufactured in the United States were derived from petroleum. By 1950 the output had grown to 5 million tonnes and, by 1970, to about 30 million. In the 1950s, there was also a swing from coal to oil as an important source of electricity generation.

But petroleum is a non-renewable resource, in the sense that we are using it up faster than it is being made. Sometime in the future—and the estimates of when this will happen vary widely—there will be a major shortage of oil in the world.

Industrial chemists are meeting this new and exciting challenge in two ways. One way is to develop methods for using the petroleum more effectively. For example, ethanoic acid can be made more cheaply by a catalytic process based on synthesis gas than by the oxidation of naphtha.

At the same time, methods are being sought for saving energy, for example, by developing catalysts that enable chemical processes to be operated at lower temperatures and pressures.

But the major question still remains: what will happen when the oil runs out? There are many carbon-containing materials other than oil. Coal is an obvious one and many countries still have vast untapped reserves. Biomass is another, and tropical countries, in particular, are very suitable for the rapid growth of wood and plants like cane sugar.

Much work is being done now to find effective ways of converting coal and biomass into synthesis gas, from which, as we have seen in Section 20.7, a wide range of chemicals such as plastics and detergents can be produced. Petrol, too, can be made from synthesis gas, but at present it is too expensive for most countries to replace oil in this way. However, the economics of the process will become more favourable as oil becomes increasingly scarce and its price rises.

Historians may well see the era of oil-based materials in which we now live as a brief interlude in which man used a valuable and unique material extravagantly and thoughtlessly. But the organic chemist will still provide us with the materials upon which we depend for comfort and our way of life by adapting the feedstocks away from oil to the older feedstock, coal, and a newer one, biomass.

20.10 Further reading

Cracker. I.C.I. Educational Publications.

Chemicals from coal J. Gibson. *Chemistry in Britain*, Vol. 16, p. 26 (1980).

There is a series of articles from 1981 in *Journal of Chemical Education*, entitled 'Real World of Industrial Chemistry', by H. A. Wittcoff, which is a very useful source of information.

ADVANCED READING

Basic Organic Chemistry. Part 5. Industrial Products. J. M. Tedder, A. Nechvatal and A. H. Jubb (1975. Reprinted 1979.). John Wiley and Sons.

Industrial Organic Chemicals in Perspective. Parts 1 and 2. H. A. Wittcoff and B. G. Reuben (1980). John Wiley and Sons.

20.11 Films and Videotapes

A large number of films and videotapes can be obtained from the Shell Film Library and from the British Petroleum Company Ltd.

Three videotapes which illustrate important aspects are:

Catalysis (V) ICI
Ammonia (V) ICI
Organics by the Ton (V) Open University S246/15V
Where from Next (V) Open University P.V. 10 illustrates some developments of the future as oil resources dwindle.

20.12 Questions

1 Most widely used organic compounds are now made directly or indirectly from petroleum. Select THREE important such compounds, preferably of different types. Describe how they are made and indicate briefly what they are used for.
For ONE of the compounds, suggest how it might be made if we had no petroleum. (L)

2 What is the chemical nature of petroleum? Show how petroleum can be processed to give
(a) fuels and
(b) pure compounds, having two or three carbon atoms in their molecules. (NI)

3 In the United States, the simple gaseous hydrocarbons are all readily available. Suggest routes by which certain of these gases could be used for the preparation of propanone, benzene, ethanol, ethanoic acid and poly(ethene).

4 Write an essay on petroleum as a raw material in the production of simple organic compounds of low relative molecular mass.

5 Describe, with the aid of a diagram, the primary refining process used in the treatment of crude petroleum.

Explain, quoting one example in each case, the meaning of: (a) catalytic cracking; (b) alkylation. Say why these processes were introduced into the petroleum industry.

Describe how the following are made from refinery sources: (i) ethanol, (ii) ethane-1,2-diol, (iii) methylbenzene.

6 Write an account of the production of organic chemicals from crude petroleum. (SUJB(S))

7 Outline the means by which the following are industrially produced from petroleum: (a) petrol, (b) benzene, (c) propan-2-ol.

By what means, in the petrochemical industry, are hydrocarbons containing about twelve carbon atoms changed into lower molecular weight homologues?

Indicate all the steps involved in the production of benzene from a different natural source. (SUJB)

8 Ethene is made on an industrial scale by cracking naphtha in the presence of steam at 900°C at just above atmospheric pressure.
(a) (i) State what you understand by the term *cracking*.
(ii) What is the function of the steam in this process?
(iii) Why is the process operated at this comparatively low pressure?
(iv) Show by means of an equation the first chemical step in the purely thermal cracking of octane.
(v) Thence show how ethene is formed.

Ethene is frequently called the *building block chemical.*
(b) (i) Show by means of equations and conditions how ethene can be converted into **either** chloroethene (*vinyl chloride*) **or** phenylethene (*styrene*).
(ii) Name a material in everyday use made from chloroethene or from phenylethene.
(iii) Give the structural formula for the material in (ii). (JMB)

9 Describe the production of the following, writing equations for important chemical processes.
  (a) polyethene (polythene) from petroleum;
  (b) high-grade petrol (gasoline) from petroleum;
  (c) aromatic hydrocarbons from coal.
Candidates should aim to submit clear, concise accounts, rather than voluminous, rambling descriptions. (SUJB)

10 (a) Write a comparative account of the processes involved in obtaining the chief products of commercial importance from coal and petroleum. Details of the industrial plant are not required.
  (b) Comment on the relative importance of coal and petroleum as raw materials in the world today.
  (c) Explain, with an illustrative equation, in each case, what you understand by the terms:
    (i) catalytic cracking,
    (ii) reforming,
  and why these processes are important in the production of large volumes of high-quality petrol. (SUJB)

11 Explain how ethene, trichloroethene, propene and styrene can be obtained from petroleum. How are ethene, propene and styrene converted into polymers of industrial importance? (NI)

12 (a) Discuss the relative importance and availability of coal, oil and natural gas as raw materials in the world today and in the future.
  (b) 'Organic chemists, working in industry, consume scarce natural resources at an alarming rate and produce materials which pollute our environment. Living would be cleaner and more enjoyable without their activities.' Discuss this statement. (SUJB)

13 Alkenes react with alkanes in presence of acid catalysts; the process is known as alkylation. What product(s) would you expect to obtain from propene and 2-methylbutane? Give reasons.

14 Crude petroleum contains over 200 different hydrocarbons and the ratio of short chain to long chain and the proportions of alkanes, cycloalkanes, and aromatic hydrocarbons also vary.

There is a possibility that oil may be discovered near the islands of Egg and Muck, and you, as a member of the oil company exploring for it, are asked what composition you hope that it will have. Giving reasons, outline this composition.

Chapter 21

Polymers

21.1 Introduction

When two or more molecules of a simple compound (a **monomer**) join together to form a new compound (a **polymer**), the process is described as **polymerisation**. In **addition polymerisation**, the polymer has the same empirical formula but a higher formula weight than the monomer; an example is the formation of poly(ethene) from the monomer ethene:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \cdots\mathrm{—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—}\cdots$$

In **condensation polymerisation**, polymerisation of the monomer is accompanied by the elimination of small molecules such as water or ammonia; an example is the formation of nylon-6.6:

$$n\mathrm{H_2N—(CH_2)_6—NH_2} + n\mathrm{HO_2C—(CH_2)_4—CO_2H} \rightarrow$$
$$\mathrm{H{+}NH—(CH_2)_6—NH—CO—(CH_2)_4—CO{+}_{\mathit{n}}OH} + (2n-1)\mathrm{H_2O}$$

Natural polymers such as proteins (18.2) and carbohydrates (18.4) are discussed elsewhere. This chapter is concerned with synthetic polymers.

21.2 Plastics

Many synthetic polymers can be moulded into required shapes and are useful as **plastics** for the manufacture of a wide range of articles. The properties of plastics can be modified by the addition of compounds known as **plasticisers**. For example, esters of benzene-1,2-dicarboxylic acid, made from benzene-1,2-dicarboxylic anhydride (p. 319) with long-chain alcohols such as octanol, are added to PVC (poly(chloroethene)) (p. 330) to produce a softer and more easily worked material. **Dyes** and **pigments** are added to give the plastic colour, and it is sometimes possible to add a cheap material known as a **filler** to increase the bulk of the plastic and make it less expensive, without altering its desirable properties.

Plastics can be subdivided into two groups: the thermosoftening and thermosetting plastics.

Thermosoftening plastics

The characteristic of these plastics is that they become soft when heated and can then be moulded or remoulded. They are **linear** polymers; that is, they are of the general structure:

$$\mathrm{—X—X—X—X—X—X—X—}$$

where X represents the monomer.

Many of the thermosoftening plastics are formed by the polymerisation of monomers which contain a C=C bond; examples are poly(ethene) from ethene, poly(propene) from propene, poly(chloroethene) from chloroethene and Perspex from methyl 2-methylpropenoate.

Poly(ethene) (polythene)

Two types of poly(ethene) are manufactured. One, with a low density and a formula weight ranging from 50,000 to 300,000, softens at a comparatively low temperature (about 120°C). It is made by compressing ethene under very high pressure at about 200°C, in the presence of a very small amount of oxygen:

$$nCH_2{=}CH_2 \xrightarrow[\text{200°C, 1500–2000 atm.}]{O_2\text{ as cat.}} \left(CH_2-CH_2 \right)_n$$

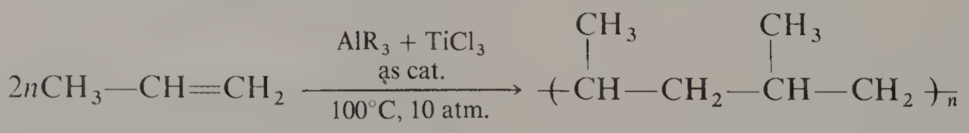
The second form is a high density material with a formula weight in the range 50,000 to 3,000,000 and a higher softening point (about 130°C). It is generally manufactured by a process developed by the Swiss chemist, Ziegler, in which ethene is passed under pressure into an inert solvent (an aromatic hydrocarbon) containing as catalyst triethylaluminium and titanium(IV) chloride. After polymerisation, the catalyst is decomposed by adding dilute acid, and the crystalline polymer is filtered off. Poly(ethene) produced this way has a greater rigidity and higher softening point than the low density polymer.

Poly(ethene) is used without a plasticiser or filler and can be readily coloured. The plastic is an insulator and is acid-resistant. The low density polymer is used as a film for packaging and for coating and as a covering for cables. The high density polymer is particularly suitable for good quality mouldings including bottles.

Poly(propene)

While poly(ethene) has been manufactured since 1939, poly(propene) is a comparatively new material. Its manufacture did not begin in Great Britain until 1962, but the amount produced then increased very rapidly. It can be used in place of poly(ethene), over which it has the advantages of being stronger and lighter and having a higher softening point. Its high tensile strength allows it to be pulled to produce tough fibres which can be used to make ropes and carpets. Carpets made from polypropene are popular as it is possible to mop up spillages from them, so that they are particularly useful in kitchens. Polypropene's impact strength makes the polymer very useful for mouldings, too, and it is used, for example, to make bottles, often replacing metal and glass.

It is manufactured by a method invented by the Italian chemist, Natta, in which propene is passed under pressure into an inert solvent (heptane) which contains a trialkylaluminium and a titanium compound:



$$2nCH_3-CH{=}CH_2 \xrightarrow[\text{100°C, 10 atm.}]{AlR_3 + TiCl_3\text{ as cat.}} \left(\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2 \right)_n$$

This method produces a polymer in which the methyl groups on the alternate carbon atoms all have the same orientation. This can be represented as in Fig. 21.1. Such polymers are described as **isotactic**, and it is this regularity of structure which allows neighbouring molecules of poly(propene) to pack closely together to give a crystalline structure. In **atactic** polymers, the orientations of the side-chains are random and the compounds are non-crystalline.

Ziegler and Natta were awarded a Nobel Prize in 1963 for their work on polymerisation.

FIG. 21.1. *A molecular model of poly(propene), an isotactic polymer*

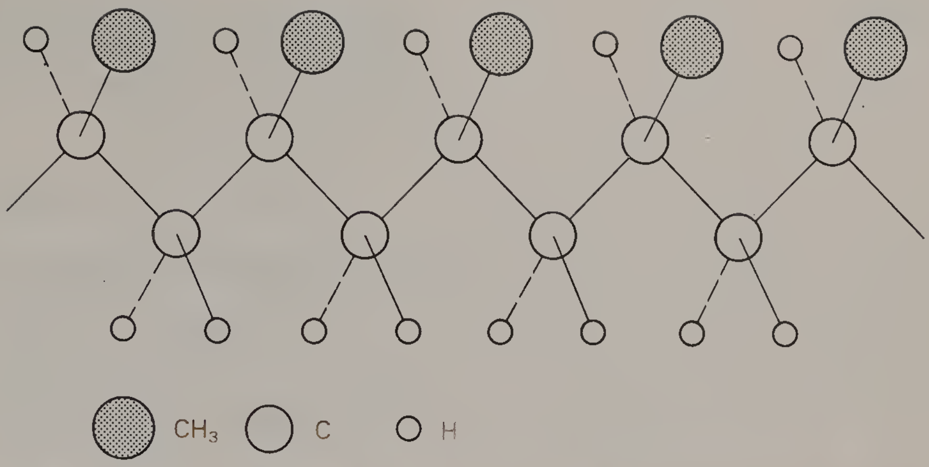


Plate 21.1. The manufacture of poly(propene). Following polymerisation, many polymers are too finely divided and are first melted. In this photograph, molten poly(propene) is being forced through a die into water. The 200 strands are then chopped into lengths of about 0·3 cm, known as moulding powder. This can be used in injection mouldings and for extruders (Shell Petroleum Co. PLC.)

Poly(phenylethene)

Phenylethene, $C_6H_5—CH{=}CH_2$, is being produced on a rapidly expanding scale in order, principally, to make poly(phenylethene) and synthetic rubbers, especially SBR (p. 338). It is made largely by the reaction of benzene with ethene in the presence of aluminium chloride:

$$C_6H_6 + CH_2{=}CH_2 \xrightarrow[300^\circ C,\ 40\ \text{atm.}]{AlCl_3\ \text{as cat.}} \underset{\text{Ethylbenzene}}{C_6H_5—CH_2—CH_3}$$

followed by dehydrogenation of the resulting ethylbenzene at 600°C over a catalyst such as zinc, iron(III) or magnesium oxide supported on charcoal or alumina:

$$C_6H_5—CH_2—CH_3 \xrightarrow[600^\circ C]{Fe_2O_3\ \text{as cat.}} C_6H_5—CH{=}CH_2 + H_2$$

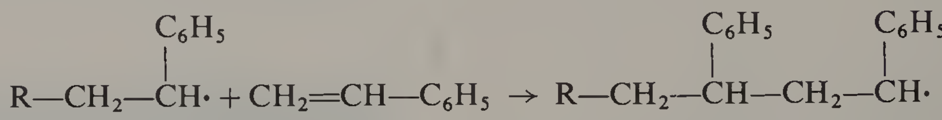
The method by which phenylethene is polymerised is typical of that for a number of other monomers. It is treated with a compound, an **initiator**, which readily decomposes to form free radicals, for example di(benzoyl) peroxide on being heated:

$$\mathrm{C_6H_5{-}CO{-}O{-}O{-}CO{-}C_6H_5 \rightarrow 2C_6H_5{-}CO{-}O\cdot}$$

One of the resulting radicals, R·, adds to the alkene, giving a new radical,

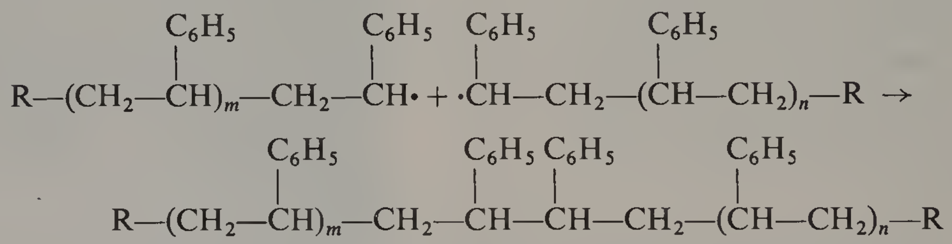
$$\mathrm{R\cdot + CH_2{=}CH{-}C_6H_5 \rightarrow R{-}CH_2{-}\dot{C}H{-}C_6H_5}$$

which in turn adds to another molecule of phenylethene:



$$\mathrm{R{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H\cdot + CH_2{=}CH{-}C_6H_5 \rightarrow R{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H\cdot}$$

Further additions of this sort occur, giving long-chain radicals, but occasionally the chain is interrupted and polymerisation stopped by the chance collision of two radicals:



$$\mathrm{R{-}(CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H)_m{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H\cdot + \cdot\overset{\overset{C_6H_5}{|}}{C}H{-}CH_2{-}(\overset{\overset{C_6H_5}{|}}{C}H{-}CH_2)_n{-}R \rightarrow}$$

$$\mathrm{R{-}(CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H)_m{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}H{-}\overset{\overset{C_6H_5}{|}}{C}H{-}CH_2{-}(\overset{\overset{C_6H_5}{|}}{C}H{-}CH_2)_n{-}R}$$

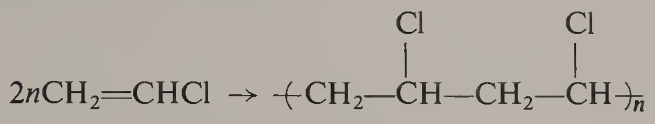
Collisions between radicals are very effective at yielding final products, but the concentration of radicals in the solution is very small, and it is much more likely that one radical will meet a molecule of phenylethene than another radical; in this way, long chains are built up. Note that the length that the growing polymer chain will have reached by the time that collision with another radical brings the growth to an end will vary from one chain to another, since it depends on chance collisions in the solution; therefore, the polymer does not have an exact formula weight, and formula-weight measurements give an average for all the chains. Note also that the phenyl groups occur at regular intervals in the chain except when two chains couple together in the example above. The regularity arises because the growing radical tends to add to the $\mathrm{CH_2}$ group of phenylethene and not to the $\mathrm{CH(C_6H_5)}$ group.

The groups at each end of a polymer depend on the nature of the initiator. For simplicity, the end groups are often omitted in representing the polymers.

The main uses of poly(phenylethene) are in making light-weight packaging materials and a wide variety of household goods such as egg boxes and the lining material for refrigerators.

Poly(chloroethene) (polyvinyl chloride, PVC)

Chloroethene is manufactured from ethene (p. 85) and from ethyne (p. 95), with the former route now becoming the more important. It is converted into poly(chloroethene) by heating in an inert solvent with di(benzoyl) peroxide to initiate polymerisation:



$$2n\mathrm{CH_2{=}CHCl} \rightarrow \left(\mathrm{CH_2{-}\underset{|}{\overset{Cl}{C}}H{-}CH_2{-}\overset{Cl}{C}H}\right)_n$$

PVC is a very tough polymer, and a plasticiser is added to soften it; esters of benzene-1,2-dicarboxylic acid are used for this purpose, sometimes accounting for up to 50 per cent of the total weight. PVC is easy to colour, it is resistant to weathering, fire and chemicals, and it is also a good electrical insulator. It is used as the insulator for cables and in the manufacture of artificial leather (e.g. car upholstery), household goods such as curtains and table cloths, gramophone records and floor coverings.

A more rigid type of PVC is used for guttering and water down-pipes, used frequently in houses.

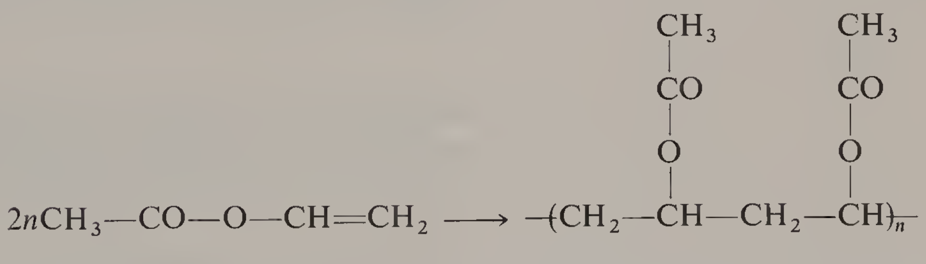
Poly(ethenyl ethanoate)

Ethenyl ethanoate is manufactured by passing a mixture of ethene, ethanoic acid vapour and oxygen over heated palladium(II) and copper(II) chlorides:

$$\mathrm{CH_3CO_2H + CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow{cat.} CH_3CO{-}O{-}CH{=}CH_2 + H_2O}$$

This is related to the Wacker process for ethanal (12.4).

Ethenyl ethanoate is polymerised in the same way as phenylethene:

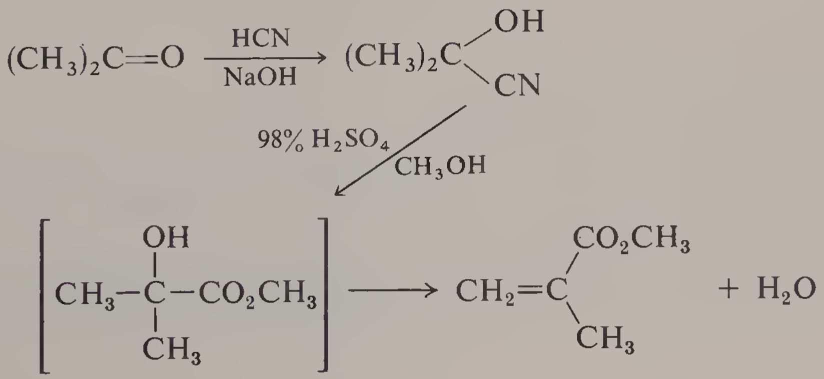


$$2n\mathrm{CH_3{-}CO{-}O{-}CH{=}CH_2} \longrightarrow \left(\mathrm{CH_2{-}\overset{O-CO-CH_3}{C}H{-}CH_2{-}\overset{O-CO-CH_3}{C}H}\right)_n$$

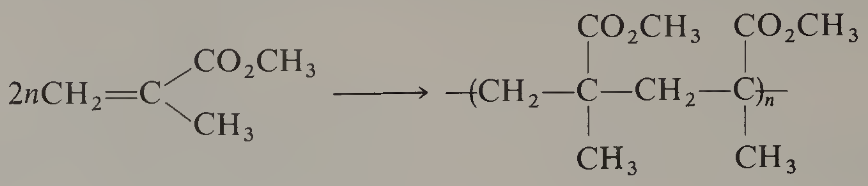
Poly(ethenyl ethanoate) is employed mainly as the essential constituent in plastic emulsion paints. Other uses are as "chewing gum base" and, in solution in propanone, to greaseproof paper.

Polyacrylic esters

Methyl 2-methylpropenoate is manufactured from propanone by addition of hydrogen cyanide in the presence of alkali to give the cyanohydrin (p. 174) followed by reaction with methanol in the presence of sulphuric acid:



Its polymer is formed in the same way as poly(phenylethene) and is sold under the name of "Perspex" (blocks and sheets) and "Diakon" (powders):



$$2n\mathrm{CH_2{=}C(CO_2CH_3)(CH_3)} \longrightarrow -\!\!\left(\mathrm{CH_2{-}\underset{CH_3}{\overset{CO_2CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CO_2CH_3}{C}}}\right)_{\!n}\!\!-$$

The plastics are light, strong and transparent. Sheets are used where transparency is important (packaging, aeroplane windows, lenses, corrugated roof lights).

Polyoxymethylene

Polyoxymethylene is formed by the polymerisation of methanal; gaseous methanal is passed into an inert solvent (a hydrocarbon) which contains an amine as catalyst:

$$2n\mathrm{CH_2{=}O} + \mathrm{H_2O} \rightarrow \mathrm{HO{-}(CH_2{-}O{-}CH_2{-}O)}_n\mathrm{{-}H}$$

To prevent depolymerisation, the —OH groups at the end of each chain are esterified.

The plastic can be readily moulded, and is very hard, resistant to chemicals and remarkably resistant to abrasion. For example, a shaft running at 110 m.p.h. against a steel gear was found to have no wear after 10 000 miles. However, it tends to decompose above about 100°C.

Poly(tetrafluoroethene) (PTFE)

PTFE is made by heating tetrafluoroethene (p. 132) under pressure in the presence of ammonium peroxosulphate as catalyst:

$$2n\mathrm{CF_2{=}CF_2} \xrightarrow{\mathrm{(NH_4)_2S_2O_8}\text{ as cat.}} -\!\!\left(\mathrm{CF_2{-}CF_2{-}CF_2{-}CF_2}\right)_{\!n}\!\!-$$

The polymer is exceptionally resistant to chemical attack. It also has a high softening point (above 320°C). These properties make it suitable for making seals and gaskets which are subject to heavy wear at high temperatures. Its 'anti-stick' properties make it useful as a surface coating for cooking equipment.

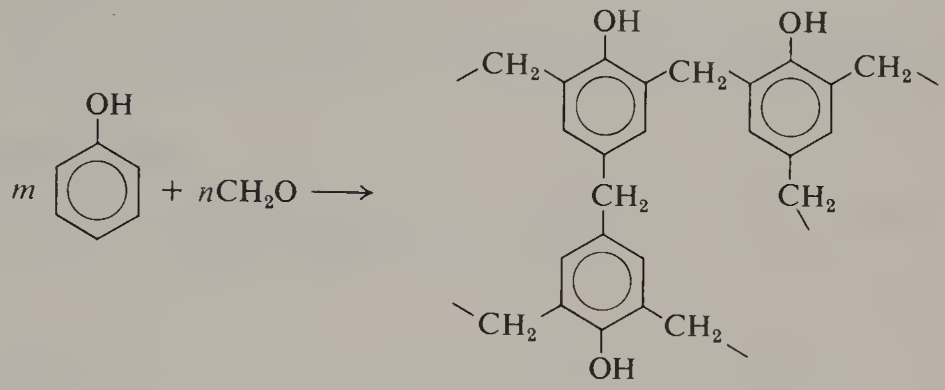
The anti-stick properties of PTFE are probably due to its structure, which is a helix, with the fluorine atoms on the surface of an inner chain of carbon atoms. There is a very smooth surface, and molecules can readily flow over it.

Thermosetting plastics

These plastics contain three-dimensional networks of bonds and are moulded during the polymerisation stage of their manufacture. Unlike thermosoftening plastics, they cannot be remoulded.

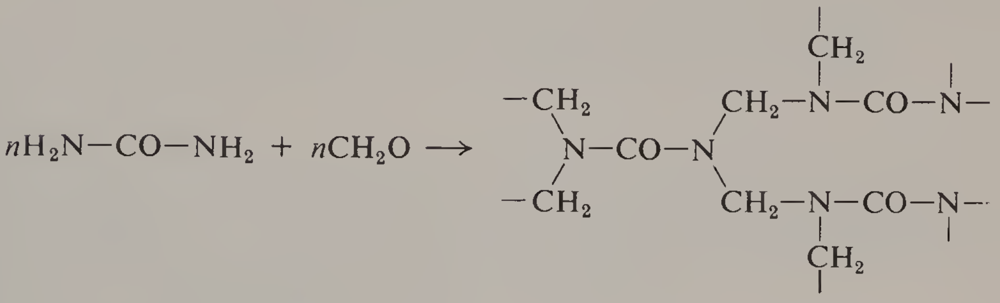
Phenol-methanal plastics (Bakelite)

In 1910, Baekeland patented a process for producing resins from phenol and methanal which are now known as Bakelite. The resins are moulded, together with a filler (such as wood shavings) and a pigment, to form a wide range of articles. The electrical resistance of Bakelite makes it especially useful for electric plugs, switches and tools.

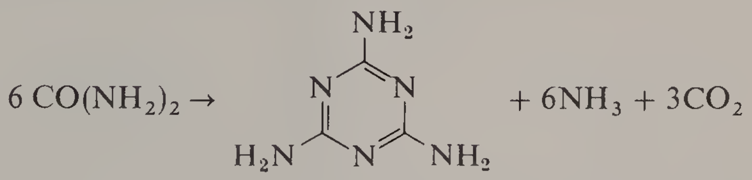


Carbamide-methanal and melamine-methanal plastics

Carbamide and methanal, when heated in a dilute solution of acid, give a resin:



Melamine can be used instead of carbamide to make a resin. Melamine is manufactured from carbamide:

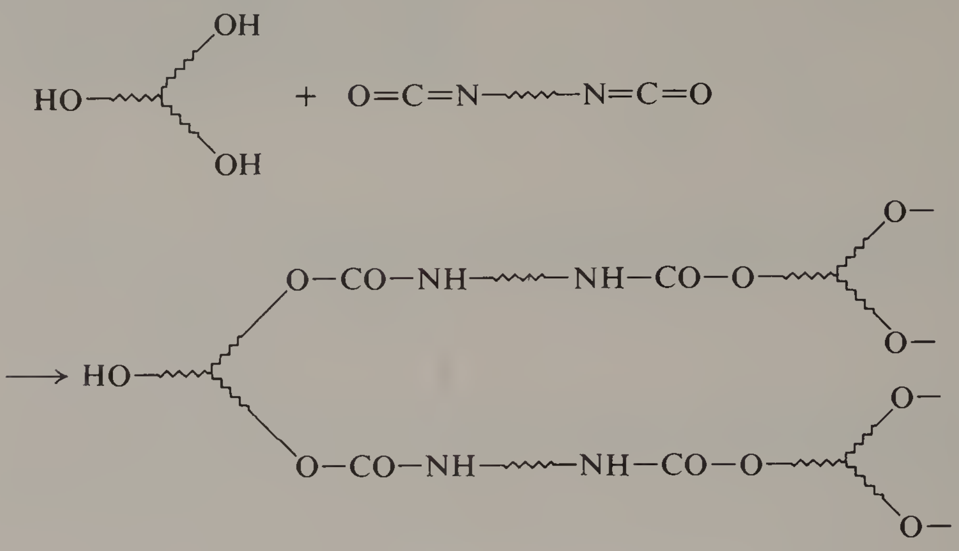


Both carbamide-methanal and melamine-methanal polymers absorb dyes easily, and the powders can be moulded under pressure to form tableware (e.g. Melaware), trays and many household utensils. They are used, in solution, to strengthen paper and to improve the shrink resistance of cotton, wool and rayon. Both are used as ion-exchange resins to demineralise water, as the free NH_2 groups combine with the acidic groups in the water.

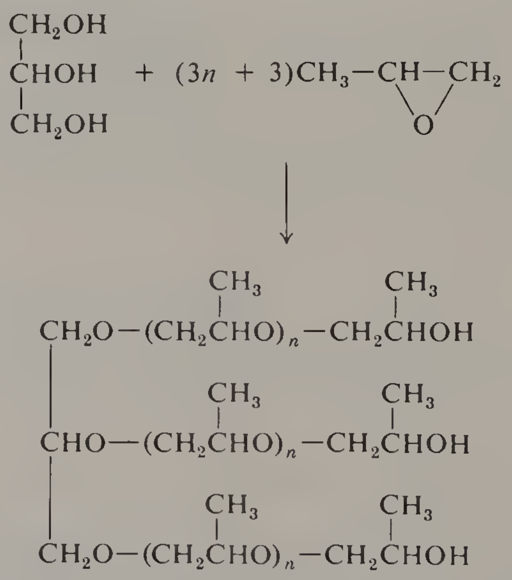
Carbamide-methanal polymers find an importance in the production of chipboard and in cavity-wall insulation.

Polyurethanes

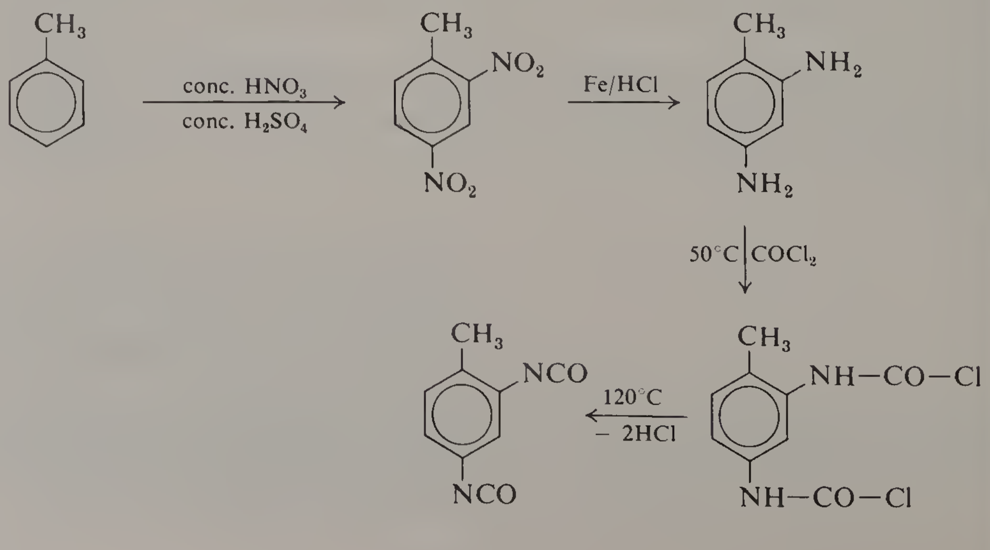
Polyurethane resins are made by polymerisation of a mixture of a di-isocyanate and a molecule containing three hydroxyl groups (a triol):



A triol often used is made from propane-1,2,3-triol and epoxypropane:



The di-isocyanate is made from methylbenzene:



The polymers can be made into the well-known foam-polyurethane plastics by treatment with water. This converts some of the terminal isocyanate groups into amino groups,

$$-N{=}C{=}O + H_2O \rightarrow -NH_2 + CO_2$$

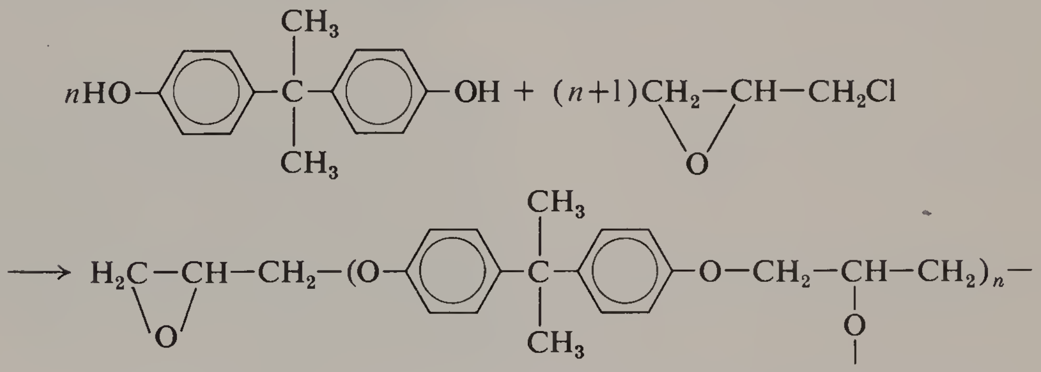
these react with other isocyanate groups to extend the polymer chain,

$$-NH_2 + O{=}C{=}N- \rightarrow -NH-CO-NH-$$

and the carbon dioxide liberated in the first step is embedded in the polymer and causes the characteristic 'foam', as used in making cushion pillows and padding. Polyurethane fibres (such as Lycra) are used in stretch fabrics.

Epoxy resins

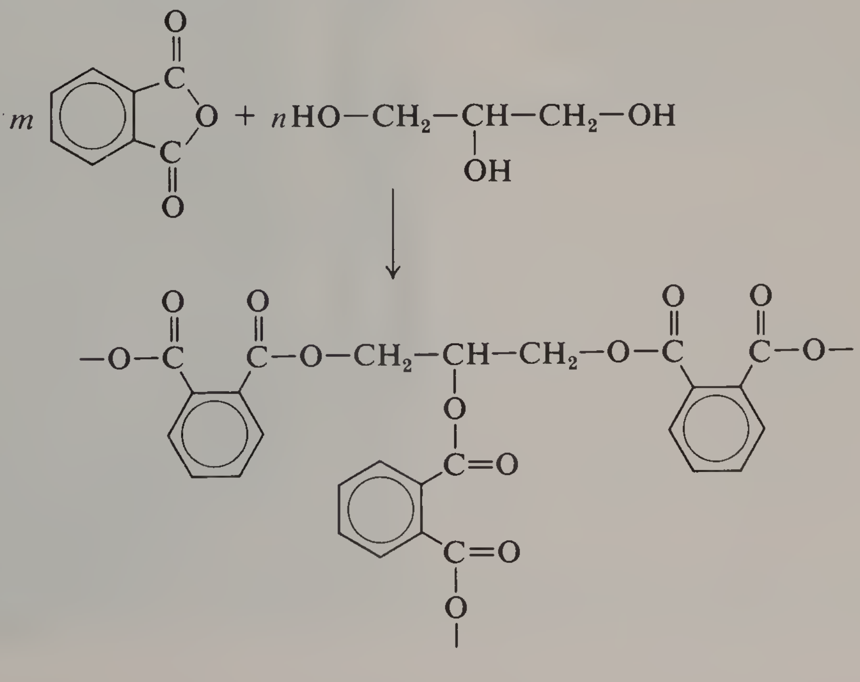
The epoxy resins are made from the epoxide derived from 3-chloropropene and substituted phenols, for example:



The value of *n* can be controlled so as to give a range of resins varying from viscous liquids to solids with high melting points. The resins are used as adhesives (e.g. Araldite), surface coatings and electrical insulators.

Glyptal resins

The glyptals are polyesters formed from propane-1,2,3-triol (**glycerol**) and benzene-1,2-dicarboxylic (**phthal**ic) anhydride. Each of the three hydroxyl groups in glycerol forms an ester linkage with the anhydride, giving a three-dimensional, thermosetting polymer:



21.3
Synthetic fibres

Natural fibres include carbohydrates such as cotton (which contains more than 90 per cent of cellulose) and proteins such as wool; the former are obtained from plants and the latter from animals. Synthetic linear polymers can also be made into fibres, and the following are important examples.

Nylon

Nylon was the first synthetic fibre to be prepared by polymerisation. It was discovered by Carothers in the U.S.A. in 1935 and first manufactured in 1940.

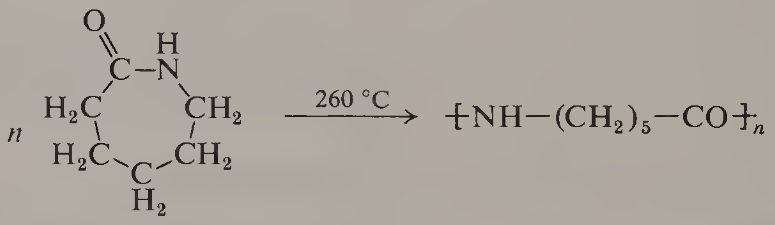
The nylon made by Carothers is now called **nylon-6.6** because it is made from two components each of which contains six carbon atoms. The components are hexanedioic acid and 1,6-diaminohexane (p. 320), which are heated together to give the polymer:

$$n\mathrm{HO_2C{-}(CH_2)_4{-}CO_2H} + n\mathrm{H_2N{-}(CH_2)_6{-}NH_2} \rightarrow$$
$$\mathrm{HO{+}CO{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH{+}_{\!n}H} + (2n-1)\mathrm{H_2O}$$

There are other forms of nylon, each of which contain the peptide link —CO—NH— as in the naturally occurring protein fibres such as wool.

Nylon-6.10, prepared from decanedioic acid [$\mathrm{HO_2C{-}(CH_2)_8{-}CO_2H}$] and 1,6-diaminohexane, has similar properties to nylon-6.6. Its preparation from decanedioyl chloride is described on p. 341.

Nylon-6 is softer and has a lower melting point than either nylon-6.6 or nylon-6.10. It is prepared from caprolactam, whose manufacture has been discussed (p. 321):



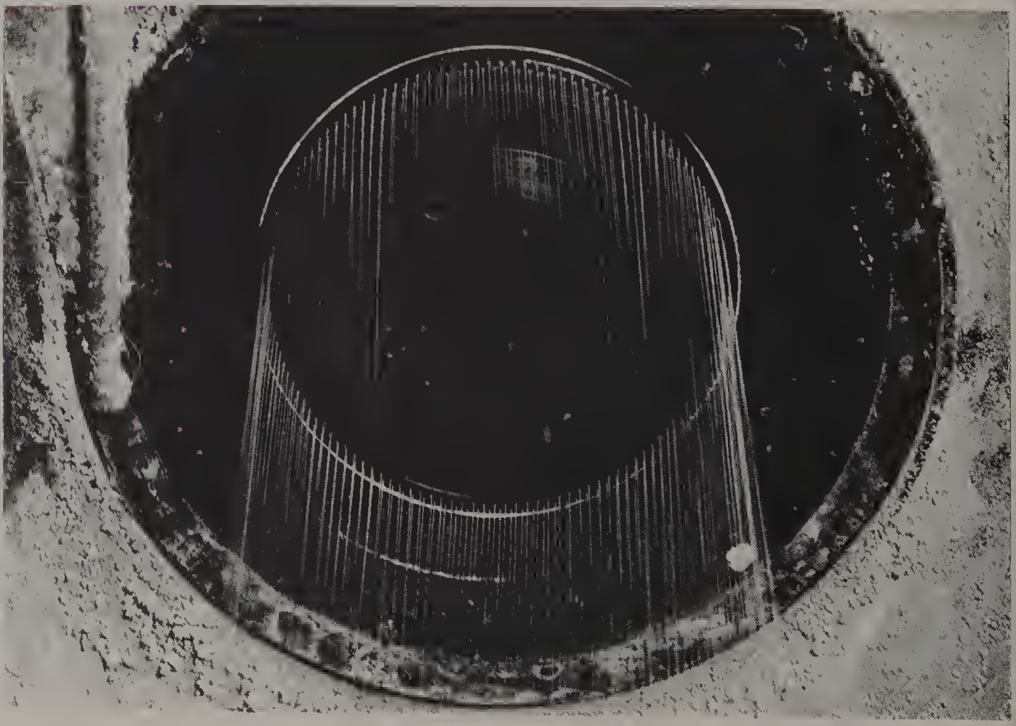
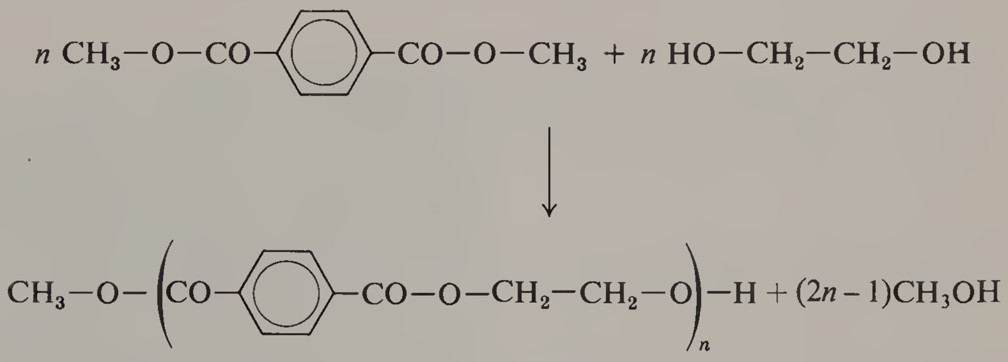


Plate 21.2. Molten terylene being forced through a metal disc. The filaments are then stretched to give them greater strength (Imperial Chemical Industries PLC)

The method for making the crude nylon polymer into fibres is to melt it and then force it through fine jets. It can be bleached with a dilute solution of peroxoethanoic acid. The finer threads are woven for clothing and the thicker ones are used for articles such as brushes, tarpaulins and tyre cord.

Polyester fibres

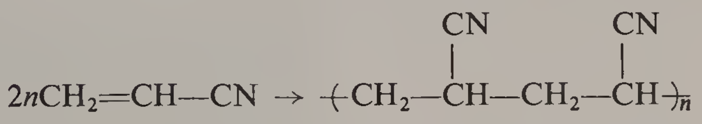
Polyester fibres are formed by condensation of polyhydric alcohols and polybasic acids. A particularly important one is **Terylene** (called **Dacron** in the U.S.A.) which is manufactured by the polymerisation of the dimethyl ester of benzene-1,4-dicarboxylic acid (p. 319) and ethane-1,2-diol (p. 152):



The molten polymer is extruded to form fibres which are used for making material for clothes. It has the useful property of being able to form permanent creases for trousers and skirts.

Propenenitrile fibres

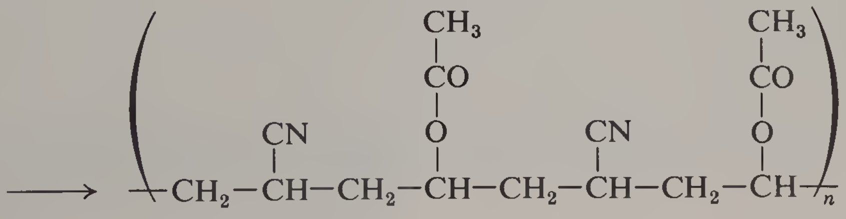
Propenenitrile is mainly manufactured from propene (p. 317). It is polymerised to form a fibre which is sold under the name **Orlon** for making clothes:



$$2nCH_2{=}CH{-}CN \rightarrow \left(CH_2{-}\overset{\overset{CN}{|}}{CH}{-}CH_2{-}\overset{\overset{CN}{|}}{CH} \right)_n$$

Propenenitrile is also made into a **copolymer** by polymerisation together with ethenyl ethanoate. The copolymer contains a more or less regular alternation of the individual monomers:

$$2n\, CH_2{=}CH{-}CN \;+\; 2n\, CH_2{=}CH{-}O{-}CO{-}CH_3$$



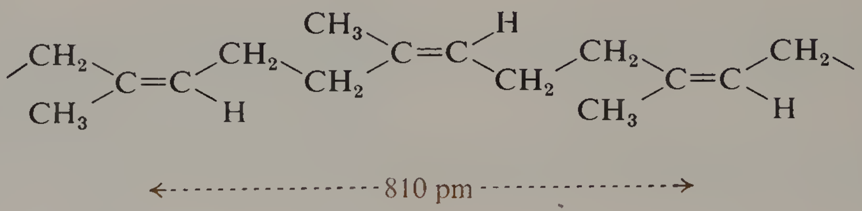
$$\longrightarrow \left(CH_2{-}\overset{\overset{CN}{|}}{CH}{-}CH_2{-}\overset{\overset{\overset{\overset{\overset{CH_3}{|}}{CO}}{|}}{O}}{|}}{CH}{-}CH_2{-}\overset{\overset{CN}{|}}{CH}{-}CH_2{-}\overset{\overset{\overset{\overset{\overset{CH_3}{|}}{CO}}{|}}{O}}{|}}{CH} \right)_n$$

The copolymer is used as a fibre for making materials under the name **Acrilan**.

21.4
Synthetic rubbers

Natural rubber is obtained from **latex**, which is an emulsion of rubber particles in water found in the bark of many tropical and sub-tropical trees. The latex slowly extrudes from the bark when the tree is cut, and it is coagulated by the addition of ethanoic acid.

Rubber has the structure



and can be regarded as a polymer of 2-methylbuta-1,3-diene, $CH_2{=}C(CH_3){-}CH{=}CH_2$. In its crude form, it is not a strong enough or elastic enough material for use, but these properties are improved by heating it with a few per cent of sulphur (**vulcanisation**). The exact mechanism of vulcanisation is not known, but it probably consists of the introduction of links between neighbouring chains of the polymer, corresponding to introducing the rungs into a ladder.

Synthetic rubbers mostly resemble natural rubber in having a series of double bonds in their polymer chain. For this reason, buta-1,3-diene is usually used in their manufacture; when it is incorporated into a polymer, one of the two double bonds is retained.

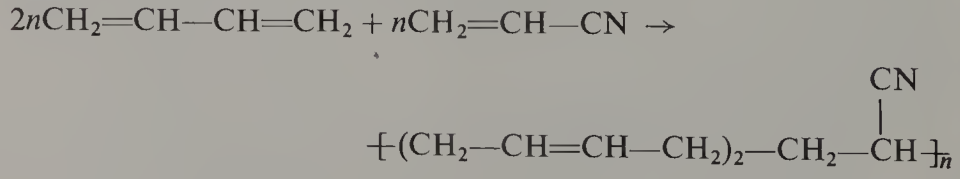
Buta-1,3-diene is made by the dehydrogenation of butane and butenes. They are passed over a catalyst consisting of aluminium and chromium(III) oxides at 600°C, for example:

$$CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[600^\circ C]{Al_2O_3 + Cr_2O_3 \text{ as cat.}} CH_2{=}CH{-}CH{=}CH_2 + H_2$$

The most widely used synthetic rubbers are made by the co-polymerisation of buta-1,3-diene with another monomer, phenylethene (p. 329).

The polymer, known as SBR, is used in the manufacture of car tyres, hoses, shoes soles and waterproof boots; it is vulcanised with sulphur and carbon black is added to strengthen it.

Copolymerisation of buta-1,3-diene with propenenitrile gives **nitrile rubber**:

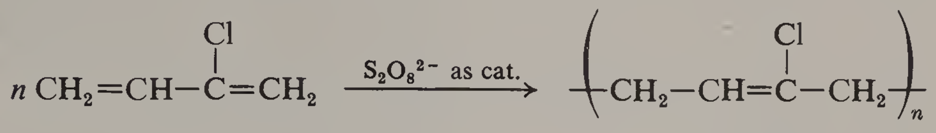


$$2nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}CH{-}CN \rightarrow \left[(CH_2{-}CH{=}CH{-}CH_2)_2{-}CH_2{-}\underset{\substack{|\\ CN}}{CH}\right]_n$$

Nitrile rubber is very resistant to chemicals and so is used in oil seals and gaskets and for making flexible fuel and storage tanks.

Another rubber, known as ABS, is made by copolymerising propenenitrile (30 per cent), buta-1,3-diene (20 per cent) and phenylethene (50 per cent), and is used in car bodies.

Derivatives of buta-1,3-diene are often used to make rubbers of special qualities. One, known as **Neoprene rubber**, is resistant to organic solvents and is strong. It is used to make hoses and gaskets where oil resistance is needed. Neoprene is made from 2-chlorobuta-1,3-diene (chloroprene):



$$n\,CH_2{=}CH{-}\overset{\overset{\large Cl}{|}}{C}{=}CH_2 \xrightarrow{S_2O_8^{2-}\text{ as cat.}} \left({-}CH_2{-}CH{=}\overset{\overset{\large Cl}{|}}{C}{-}CH_2{-} \right)_n$$

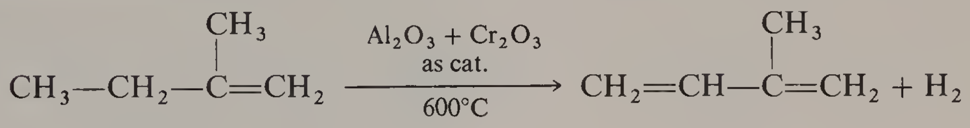
Neoprene

2-Chlorobuta-1,3-diene is made from buta-1,3-diene:

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{Cl_2} CH_2{=}CH{-}CHCl{-}CH_2Cl \xrightarrow{-HCl} CH_2{=}CH{-}CCl{=}CH_2$$

Polymerisation of 2-methylbuta-1,3-diene with a Ziegler catalyst gives a polymer which has very similar properties to natural rubber. The catalyst (triethylaluminium and titanium(IV) chloride) produces a regular molecular pattern similar to that of natural rubber, the distance being 810 pm between each recurring unit (p. 338).

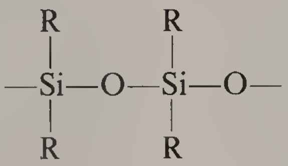
Competition between natural rubber and man-made poly(2-methylbuta-1,3-diene) (polyisoprene) is one of economics. In recent years, rubber trees have been bred which give a very high yield of latex, while 2-methylbuta-1,3-diene is still expensive to make. 2-Methylbuta-1,3-diene at present is generally manufactured by the dehydrogenation of 2-methylbutane, which is present in naphtha (p. 315), or 2-methylbut-1-ene and 2-methylbut-2-ene, which are formed during the cracking of naphtha (p. 318). For example:



$$CH_3{-}CH_2{-}\overset{\overset{\large CH_3}{|}}{C}{=}CH_2 \xrightarrow[600^\circ C]{Al_2O_3 + Cr_2O_3 \text{ as cat.}} CH_2{=}CH{-}\overset{\overset{\large CH_3}{|}}{C}{=}CH_2 + H_2$$

21.5
Silicones

Silicones are polymers with alternating silicon and oxygen atoms and alkyl or aryl groups attached to the silicon atoms:



$${-}\underset{\underset{\large R}{|}}{\overset{\overset{\large R}{|}}{Si}}{-}O{-}\underset{\underset{\large R}{|}}{\overset{\overset{\large R}{|}}{Si}}{-}O{-}$$

This —Si—O— framework gives the polymers stability towards heat, as in silica, while the nature of the organic groups determines other properties such as solubility in organic solvents, water-repellency and flexibility. For example, phenyl groups give more flexible polymers than alkyl groups.

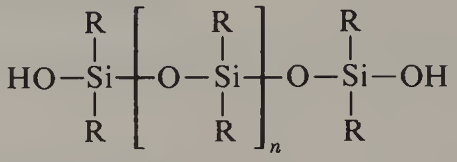
Silicones are manufactured from chlorosilanes, e.g. R_2SiCl_2 and $RSiCl_3$, where R is an alkyl or aryl group. The chlorosilanes are made in a variety of ways. For example, if chloromethane is passed through heated silicon, with copper as catalyst, a volatile mixture of chlorosilanes distils over, which can be purified by fractionation. For example:

$$Si + 2CH_3Cl \xrightarrow[300^\circ C]{\text{Cu as cat.}} (CH_3)_2SiCl_2$$

The dichlorosilanes are hydrolysed to form dialkylsilanediols, $R_2Si(OH)_2$, which polymerise spontaneously to form long linear chains. Cross-linking can be effected at a later stage by addition of an organic peroxide, to yield silicone rubbers.

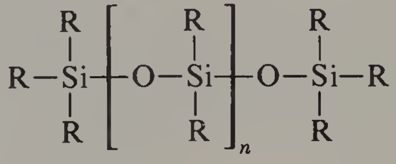
Silicones can be sub-divided into three classes: (a) silicone fluids, (b) silicone rubbers, (c) silicone resins. Their physical form depends on the structure of the polymer.

(a) **Silicone fluids** are long-chain polymers of the alkylsilanediol, which are very stable. They have the structure:



$$HO-\underset{R}{\overset{R}{Si}}\left[-O-\underset{R}{\overset{R}{Si}}-\right]_n O-\underset{R}{\overset{R}{Si}}-OH$$

or



$$R-\underset{R}{\overset{R}{Si}}\left[-O-\underset{R}{\overset{R}{Si}}-\right]_n O-\underset{R}{\overset{R}{Si}}-R$$

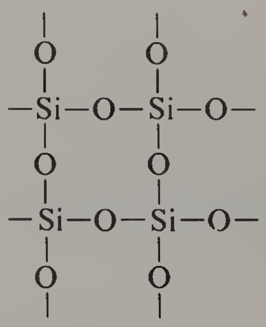
Those with short chains are oils, which have a more or less constant viscosity over a wide temperature range (−50 to +200°C). They also have very low vapour pressures. Thus, fluids with phenyl groups attached to the silicon atom are used as oils for vacuum pumps. Fillers are added to silicone fluids to form heavy greases used when changes in viscosity or a high vapour pressure are undesirable.

The fluids are also used in polishes (a mixture of wax and a silicone fluid dissolved in an organic solvent), in paints and for water-proofing fabrics, paper and leather. They also have anti-foaming properties and have been used sometimes to suppress the foaming of detergents in sewage disposal plants, although the fluids are very expensive.

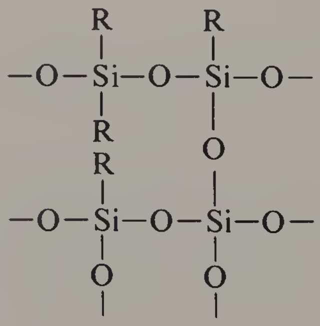
(b) **Silicone rubbers** are made by introducing some cross-linking into long chain linear polymers. Thus the structure is somewhat similar to natural rubber. The cross-linking is effected by addition of catalysts (e.g. di(benzoyl) peroxide).

Although their strength at normal temperatures is inferior to that of natural rubber, silicone rubbers are more stable at low temperatures (−70°C) and at high temperatures (200–300°C) and are generally more resistant to chemical attack. They are thus used for specialised purposes when ordinary rubber would be useless.

(c) **Silicone resins** have a three-dimensional structure similar to that of silica:



Silica



Silicone resin

Note that the structure is three-dimensional and that the atoms are tetrahedrally arranged about the silicon atoms. The resins are usually applied as a solution in an organic solvent, and are used as an electrical insulating varnish or for application to surfaces where water repellency is desired. They are also used to give an 'anti-stick' surface to materials coming into contact with 'sticky' materials such as dough and other foodstuffs.

Thus the word 'silicones' is a general term used for long-chain polymers (fluids), two-dimensional structures (rubbers) and three-dimensional macromolecules (resins). Silicones have several distinctive and valuable properties: (i) constancy of physical properties over a wide temperature range, (ii) water-repellency, (iii) electrical insulation, (iv) 'anti-stick', (v) 'anti-foam'.

21.6
Practical work

1. Preparation of poly(phenylethene)

Mix thoroughly 5 cm^3 of phenylethene and 0·3 g of di(dodecanoyl) peroxide in a test-tube. Place the test-tube in a beaker of boiling water for about 15 minutes, and then cool.

The solid formed, poly(phenylethene), can be dissolved in methylbenzene and then precipitated from this solution by adding ethanol.

2. Preparation of a polyacrylic ester

Fill a test-tube about 1/3 full of small Perspex chips and heat them, collecting the distillate, which is methyl 2-methylpropenoate, in a test-tube surrounded by cold water (Fig. 21.2).

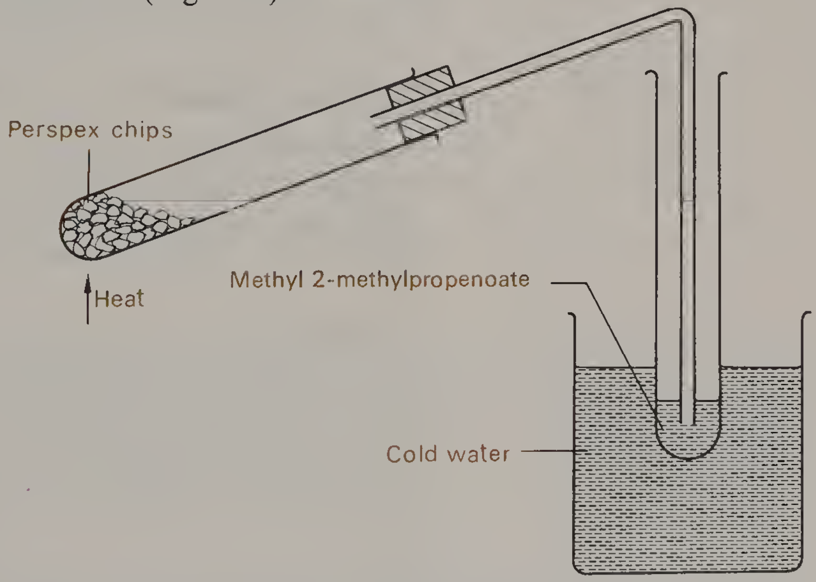


FIG. 21.2. *Preparation of methyl 2-methylpropenoate from Perspex*

To 5 cm^3 of the monomer in a test-tube, add about 0·1 g of di(dodecanoyl) peroxide and shake the mixture until the catalyst has dissolved. Stopper the tube and place it in a beaker of water. Bring the water to the boil (take care, as the stopper may be expelled with considerable force). The liquid will polymerise after about 10 minutes.

The monomer may be discoloured (owing to oxidation during its preparation).

3. Preparation of nylon-6.10

In a 250 cm^3 beaker, dissolve 1·5 cm^3 of decanedioyl chloride in 50 cm^3 of tetrachloromethane. In a second beaker make up a solution of 2·2 g of

1,6-diaminohexane and 4 g of sodium carbonate in 50 cm^3 of water.

Add the aqueous solution of 1,6-diaminohexane from a pipette, *with a pipette bulb*, making sure that there is a minimum of mixing of the two layers.

Then, using a wire loop, draw a thread of nylon from the liquid interface. A glass rod can also be used, with the advantage that the nylon fibre can be wrapped around it as the fibre is drawn from the interface.

4. Preparation of nylon-6.6

Nylon-6.6 can be prepared with hexanedioyl chloride in place of decanedioyl chloride.

5. Properties of nylon-6

Warm, *very gently* over a small bunsen flame, about 1 g of nylon-6 pellets in a test-tube. Draw some fibres from the melt, using a thin wire.

(a) Test the fibres for strength and elasticity by pulling them.
(b) Examine a fibre using a polaroid, before and after stretching.

6. Preparation of a phenol-methanal resin

To 10 cm^3 of formalin in an 'old' boiling-tube (which can be thrown away after being used), add about 4 g of phenol. Then add about 1 cm^3 of *concentrated* sulphuric acid dropwise, with stirring. Keep the mixture for two or three days, when the condensation polymerisation should have taken place and the solid resin formed.

7. Preparation of a carbamide-methanal resin

Place about 0·5 g of carbamide in a test-tube, and add about 1 cm^3 of *concentrated* hydrochloric acid and 5 cm^3 of water. Add 1 cm^3 of formalin and shake the mixture. Allow the mixture to stand and a white powder is deposited. This is a thermosetting plastic.

8. Preparation of an epoxy resin

To 10 cm^3 of Epikote 815 in a small tin, add, with stirring, about 1·5 cm^3 of bis-(2-aminoethyl)amine. After about 30 minutes, a hard mass of epoxy resin is formed. Observe whether heat is evolved during the reaction.

Bis-(2-aminoethyl)amine has a harmful vapour and safety glasses should be worn.

9. Preparation of a polyurethane foam

To about 5 cm^3 of a triol (Caradol GXR 13) in a small tin or old beaker, add 10 cm^3 of a di-isocyanate (Caradate 30). Mix the two liquids together with a spatula for about 15 seconds. Clean the spatula at once. The foam is expanded by the carbon dioxide produced during the reaction, because some water, already added to the triol by the manufacturer, reacts with some of the isocyanate groups.

10. Preparation and properties of a silicone

Put a few drops of dichlorodimethylsilane (**CARE**) in a shallow dish.

Allow the vapour of the chlorosilane (**CARE**) to come into contact with a filter paper, by placing the paper on top of the dish for a few minutes.

Although the paper may appear to be dry, there is a considerable number of layers of water molecules adsorbed on to the surface. These react with the dichlorodimethylsilane vapour to form diols, which then polymerise to yield a silicone.

Then pour water gently on to the treated paper, and contrast its water-repelling properties with the properties of an untreated filter paper.

21.7
Further reading

'Technology of Plastics'. *Penguin Technology Survey 1967*. N. Denton, ed. A. Garratt. Penguin Books Ltd.

21.8
Film and Videotapes

The Polyolefins (F) Shell Film Library.
Catalysis (V) I.C.I.
Polymers (V) I.C.I.

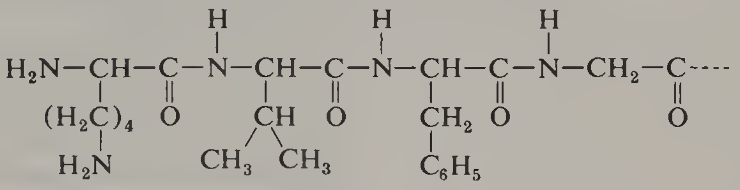
21.9
Questions

1 Give an account of the preparation, structure, properties and uses of high polymers. (O(S))

2 Explain using suitable examples the principles of addition and condensation polymerisation.

What is the effect of chain-length and cross-linking on the physical properties of polymers? (L(X,S))

3 The structure drawn below is that of one end of a molecule of a compound, the total molecular weight of which is of the order of 10^4.



$$\mathrm{H_2N{-}\underset{\underset{H_2N}{|}}{\underset{(H_2C)_4}{\underset{|}{CH}}}{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}\underset{CH_3\ \ CH_3}{\underset{CH}{\underset{|}{CH}}}{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}\underset{C_6H_5}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}CH_2{-}\underset{O}{\underset{\|}{C}}{\cdots}}$$

(a) Name two classes of compound to which the large molecule could belong.

(b) If the compound were hydrolysed by boiling with hydrochloric acid, four smaller molecules would be formed from that part of the structure shown above. Draw the structural formula of each of these molecules.

(c) To what general class of compound do these smaller molecules belong? (L(Nuffield))

4 Give (a) **two** general methods for increasing the length of a carbon chain and (b) **two** general methods for diminishing the length of a carbon chain. Illustrate by means of specific examples, with accompanying formulae, names and reagents.

How is poly(ethene) made? Give **two** reasons for its widespread use as a container material. Show by reference to the respective chemical structures how poly(ethene) differs from the polyester Terylene. (JMB)

5 Name (a) **one** commercial plastic formed by addition polymerisation, (b) **one** commercial plastic formed by condensation polymerisation, (c) **one** naturally occurring polymer. Give the monomers from which these three polymers are formed and give an account of the new chemical bonds formed in polymerisation and of the conditions necessary for the formation of the polymers named in (a) and (b).

What features of molecular structure should be present in polymers which are required to be (i) elastic, (ii) rigid? (C(T))

6 Explain the meaning of (i) addition polymerisation, (ii) condensation polymerisation. Give one large-scale use of each of these processes. What is the effect of 'cross-linking' on the physical properties of a polymer?

Write the structural formulae for two different polymers you might expect to be formed from glycine, ($H_2N.CH_2.CO.OH$). (C(T))

7 What is meant by a 'condensation reaction'? Illustrate your answer with examples drawn from the chemistry of aldehydes and ketones. Explain why the condensation reaction between $HO.OC(CH_2)_4CO.OH$ and $H_2N.(CH_2)_6.NH_2$ is of commercial importance. Comment on the relative merits of various methods which you could employ to determine the molecular weight of the product of this reaction. (W(S))

8 (a) Define what is meant by each of the following terms:
- (i) a random copolymer,
- (ii) an alternating copolymer,
- (iii) a block copolymer.

(b) (i) Define what is meant by the *glass transition temperature*, T_g.
- (ii) State three structural factors which determine this temperature.
- (iii) Is T_g for poly(ethanediyl benzene-1, 4-dicarboxylate) (Terylene) higher or lower than that for nylon 6?
- (iv) Give a reason for your answer in (iii).
- (v) How do you account for the fact that pleats in a polyester (Terylene) garment are not removed during washing of the garment?

(JMB Syllabus A)

9 (a) Give the structural formula of hexanedioic (*adipic*) acid.
- (b) Give the structural formula of 1,6-diaminohexane.
- (c) What feature of the molecules in (a) and (b) enable them to be used to make polymeric material?
- (d) Indicate by means of equations how the compounds in (a) and (b) interact to form a polymer.
- (e) What is the name of the chemical group formed in (d)?
- (f) Give the structural formula of the repeating unit of this polymer.
- (g) What is the common name of this polymer?
- (h) What type of polymerisation process did you show in (d)?
- (j) How is the material made in (d) converted into a fibre?
- (k) What determines the strength of a fibre?
- (l) Which particular physical property of the fibre in (j) makes it especially suitable for use in ropes and ladies' stockings?

(JMB Syllabus A)

10 (a) What are the chemical structures of (i) nylon 6, (ii) polyester (Terylene) and (iii) poly(propene)?
- (b) In what major chemical respect does silk or wool differ from nylon 66?
- (c) Why does wool absorb moisture more readily than nylon?
- (d) Describe briefly what is meant by *melt-spinning*.
- (e) What is the effect of the process known as *drawing*?

(JMB Syllabus A)

11 (a) What do you understand by the term *thermoset* as used to describe polymers?
- (b) Describe very briefly the experimental conditions for the production of (i) phenol-methanal (phenol-formaldehyde) resins and (ii) urea-methanal (urea-formaldehyde) resins.
- (c) State one major use for each of the resins in (b).
- (d) In what two respects is urea-methanal superior to phenol-methanal?
- (e) How is carbamide (urea) made on the industrial scale?

(JMB Syllabus A)

Chapter 22

Looking to the future

Organic chemistry is a constantly evolving subject. As we remarked in the Preface, industrial methods for the production of organic compounds have changed profoundly since we prepared the first edition of this book some ten years ago; moreover, the basic principles of the subject have also developed significantly. What may happen in the next decade? We shall draw attention to some likely lines of development.

One is biotechnology, which has been practised for centuries in the production, for example, of cheese, beer and wines, and which is now taking off in new directions. It is organic chemistry that is effected by the enzymes in micro-organisms instead of by the more usual reagents and catalysts of the laboratory. Enzymes invariably act far more rapidly than laboratory catalysts, and they are highly specific in the reactions they bring about.

A recent example is the manufacture of protein mainly from methanol and ammonia, with small amounts of other materials such as sodium and potassium ions. The bacterium that effects this conversion reproduces with such rapidity that a few dm^3 of its culture yield 40 tonnes of protein in 36 hours. The product is marketed as "Pruteen", and is just as nutritious as the more familiar protein from animals since it contains all the necessary amino-acids.

Genetic engineering is a form of biotechnology of immense potential. It is based on using specific hydrolytic (bond-breaking) and condensation (bond-making) methods, usually involving enzymes, to insert a section of a DNA molecule into an organism that does not normally possess it. In this way, a gene is introduced that causes the organism to synthesise a type of protein unnatural to it. For example, one development is the introduction of the gene that codes for human insulin into a bacterium: the bacteria reproduce rapidly to provide a supply of human insulin which can augment the pig and cow insulin used in the treatment of diabetes, and indeed may prove to have advantages over them.

Secondly, new speciality polymers will be developed. One—"superglue"—is already well established; it is based on a disubstituted alkene monomer which polymerises when it is exposed to the air to give a polymer with very strong adhesive qualities. Others will be developed for medical prostheses and implants to replace parts of the cardiovascular system, for which they have the advantages of easy fabrication, high strength per unit mass and chemical inertness, so that there is minimum response from neighbouring tissues. Still other polymers will probably be obtained, in the longer term, which have catalytic properties similar to those of enzymes, so that fast and efficient production methods can be developed; one has only to recall the high pressures and high temperatures required for many of the processes in Chapter 20 to realise the cost advantage of employing a catalyst which could operate at much lower pressures and temperatures—ideally under normal atmospheric conditions.

Thirdly, methods will be explored for making petrol, or its equivalent, from sources other than oil. One is already well developed and is operated in South Africa: the gasification of coal brought about with air and steam.

The process can be considered in terms of these simple equations:

$$C + O_2 \rightarrow CO_2$$
$$C + H_2O \rightarrow CO + H_2$$
$$C + CO_2 \rightarrow 2CO$$

The second and third reactions are endothermic, and the heat to bring them about is provided by the (exothermic) first reaction. The mixture of carbon monoxide and hydrogen—synthesis gas—is then converted, with a zeolite catalyst, into a mixture of alkanes and aromatics which is suitable as petrol.

Other approaches for the production of fuel already include the fermentation of sugar or starch to give ethanol. This is being successfully used in Brazil, where cane and cassava are the crops employed; the principal fuels for cars there are either ethanol or conventional petrol to which ethanol is added. This innovation will gather momentum in other countries.

The digestion of cellulose to give methane is another way in which chemists will rely on the use of natural products to generate petrol and other important industrial chemicals.

It is, incidentally, notable that these processes correspond to converting biomass into energy, whereas the Pruteen plant essentially brings about the opposite, since the methanol and ammonia required as feedstocks are manufactured by energy-consuming methods. This reflects the flexibility of organic chemistry, an aspect that gives the industry based on it an advantage over many other industries: one can choose either to build large molecules up from small ones or degrade large molecules to smaller ones. Which one chooses to do depends on factors such as location (Brazil is ideal for the rapid growth of biomass, South Africa is rich in coal and so on), and the prevailing needs, and so economics, of the time.

It is worth noting the central place taken by synthesis gas in this discussion. We saw earlier that it is formed from various fractions of oil and from natural gas (Chapter 20). In this tailpiece, we have described how it can also be formed from coal and from biomass. When oil and natural gas become more expensive as supplies dwindle, the chemical industry, for many of its large-bulk materials, will switch to these other sources.

Fourthly, new and often complex organic compounds will be synthesised or obtained from natural sources which could have important biological properties, as drugs, herbicides and so on. Particular attention will be given to tailor-making compounds for specific uses, for example, developing methods for insect control to which only one chosen species of insect is susceptible.

Finally, there are bound to be significant developments in elucidating *how* organic reactions occur. In this book, we have often described the present theory of how a particular reaction is thought to occur—its mechanism—but there has been no space to give the detailed evidence. Nonetheless, this is an important branch of organic chemistry and one in which scientists have applied considerable ingenuity.

One particularly fascinating line related to this is opening up: the attempt to understand how molecules vital to life were first synthesised. In this pre-life stage, the earth's atmosphere contained mainly methane, ammonia and water, with small amounts of phosphine and hydrogen sulphide. Various sources of energy were available that could have induced reactions between them: ultraviolet light, electrical discharges, radioactive emanations from the crust of the earth and heat from volcanoes. Laboratory experiments have shown that, when a mixture of methane, ammonia and water vapour is subjected to an electrical discharge, several of the biologically important amino-acids are produced, and these observations have provided a clue and a starting point. Now attempts are in progress to find how other small molecules may have been made, and to find, too, how these combined to form the large biomolecules like proteins on which life depends.

It has sometimes been said that the researches of the 'pure' chemist in areas such as reaction mechanism and synthesis have no relevance to the important applications of chemistry. Nothing could be further from the truth. For example, if we can understand *how* a particular compound acts as a pain-killing drug, we may be in a better position to design improved drugs for we should know what the key functional groups and their relationships are. When Kipping, in Britain in the 1930s, began his studies of organic compounds of silicon, preparing as many as he could, seemingly for the sake of it, who could have predicted the wide industrial applications his work was to have? Some of his compounds turned out to yield polymers with valuable properties, and so laid the basis for the manufacture of silicones.

Whether the predictions we have made in our tailpiece prove to be right or wrong, we have no doubt that the next decades will provide developments in organic chemistry that are both fascinating and important.

Appendix I

Summary of industrial processes

Charts 1–4 summarise the uses of four major organic starting materials: methane, ethene, propene and benzene.

CHART 1 *Uses of methane*

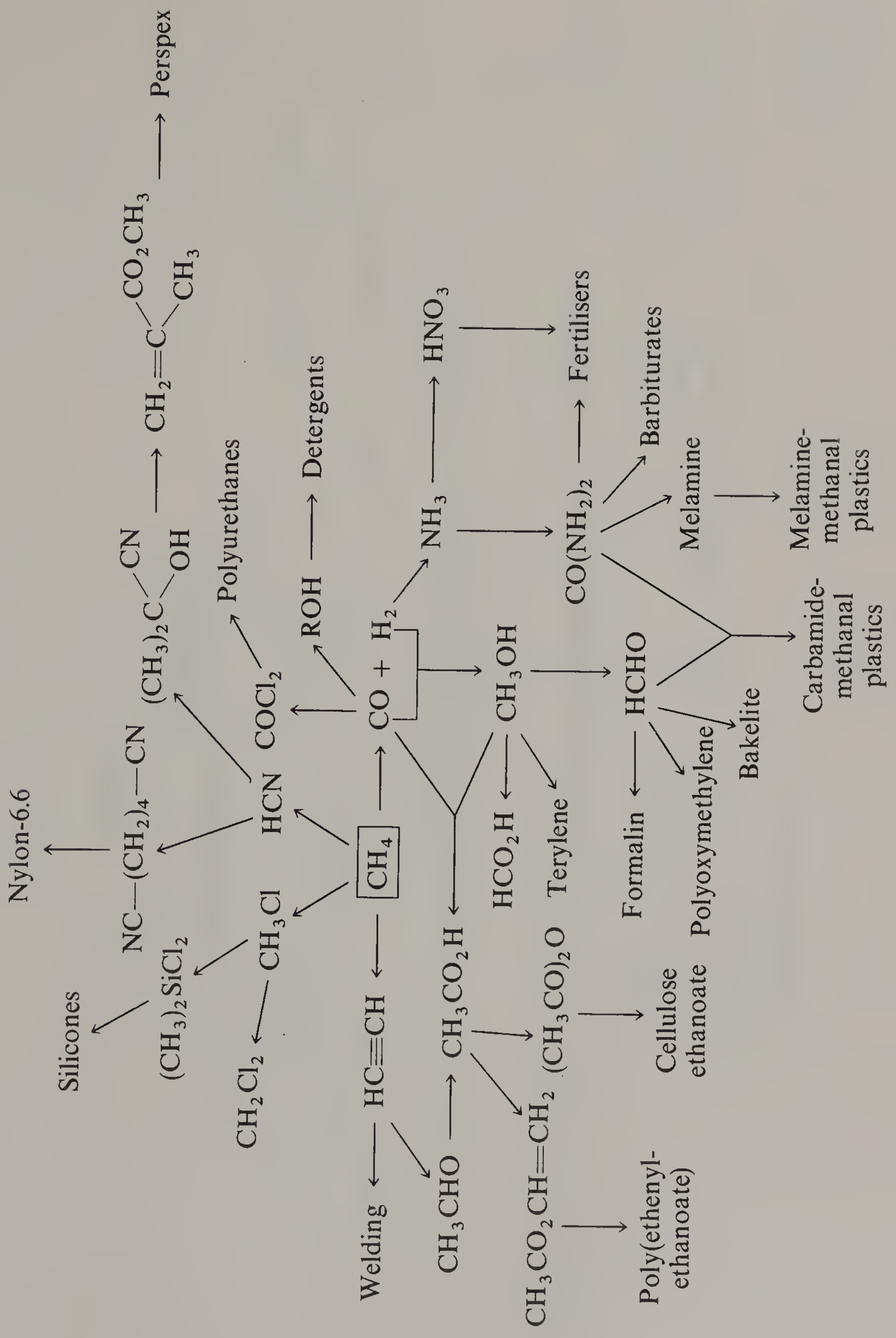


CHART 2 *Uses of ethene*

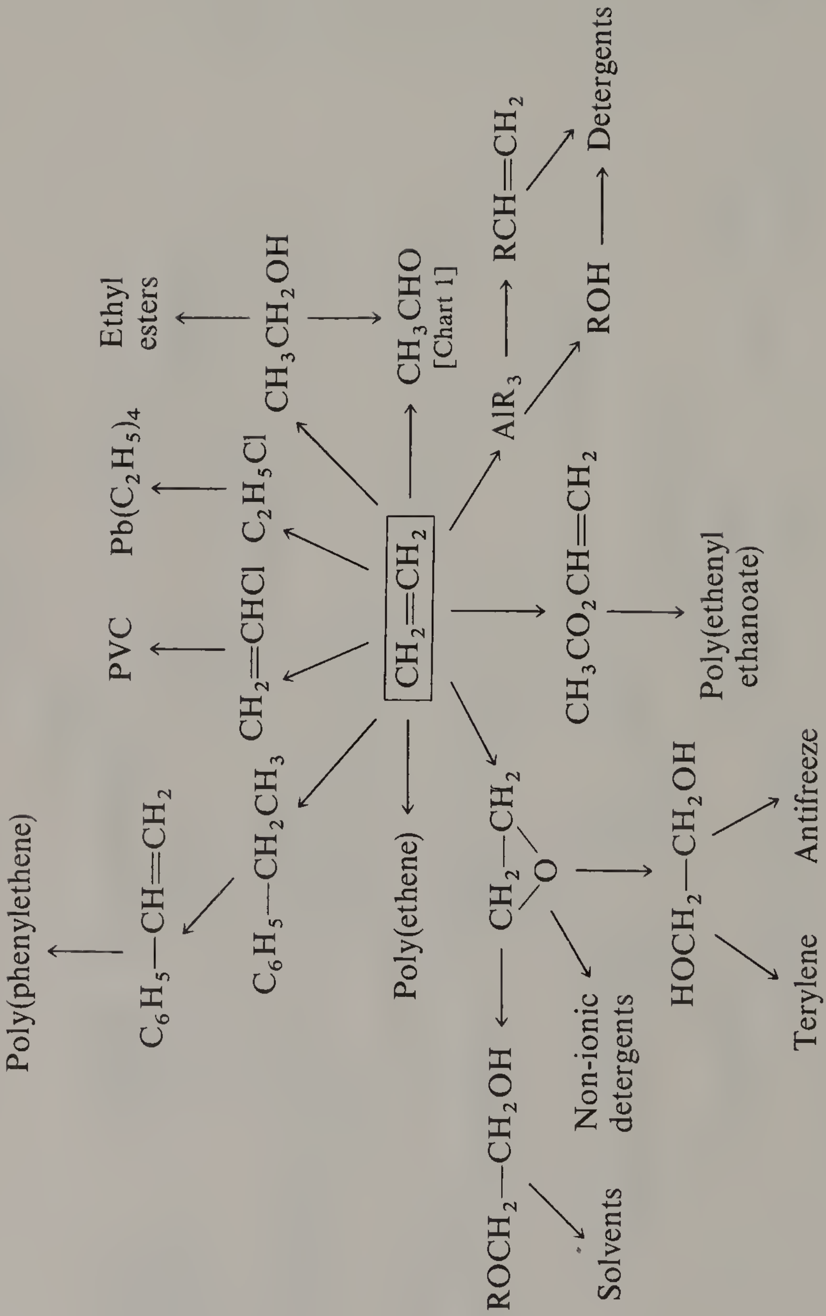


CHART 3 *Uses of propene*

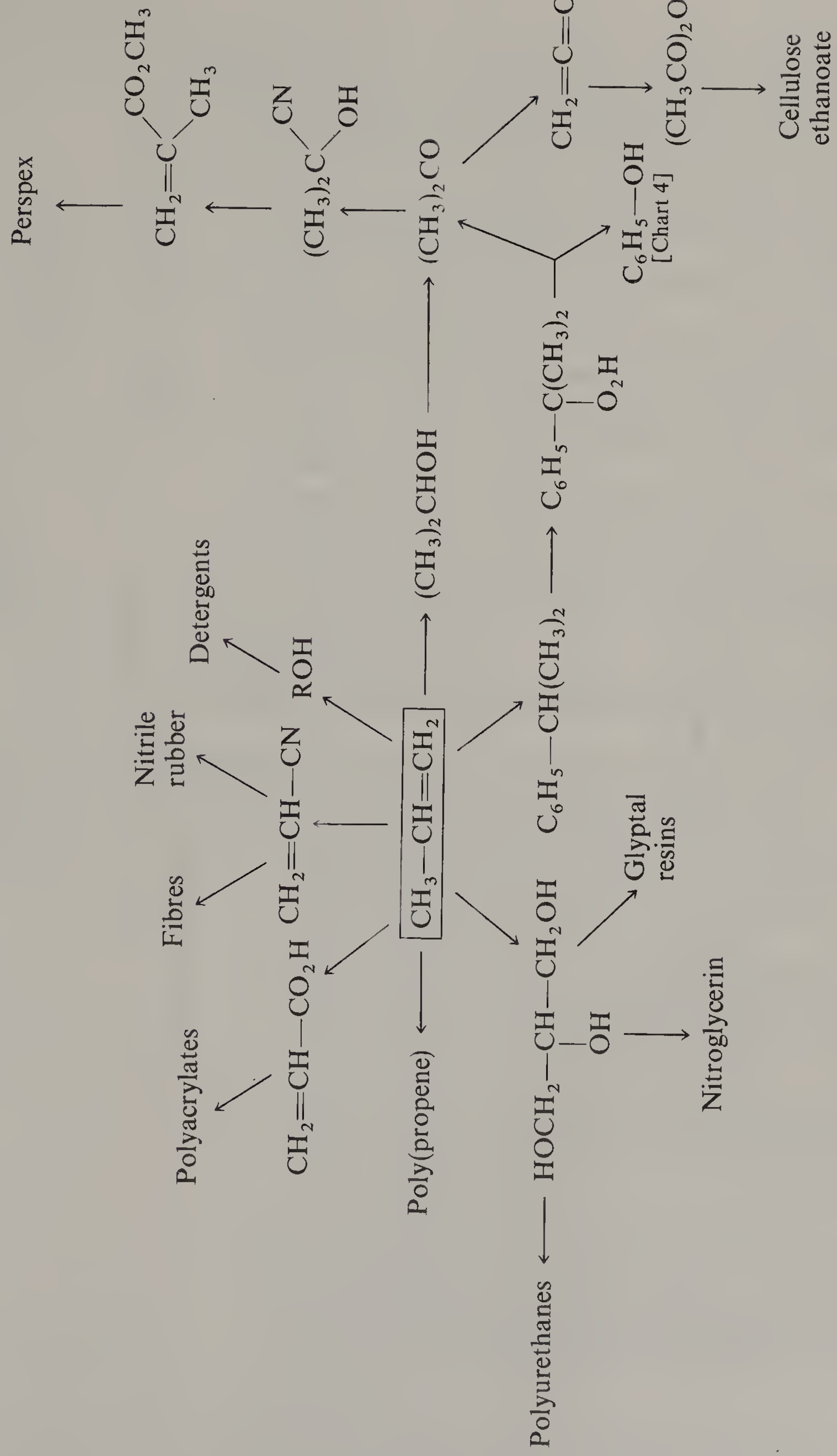
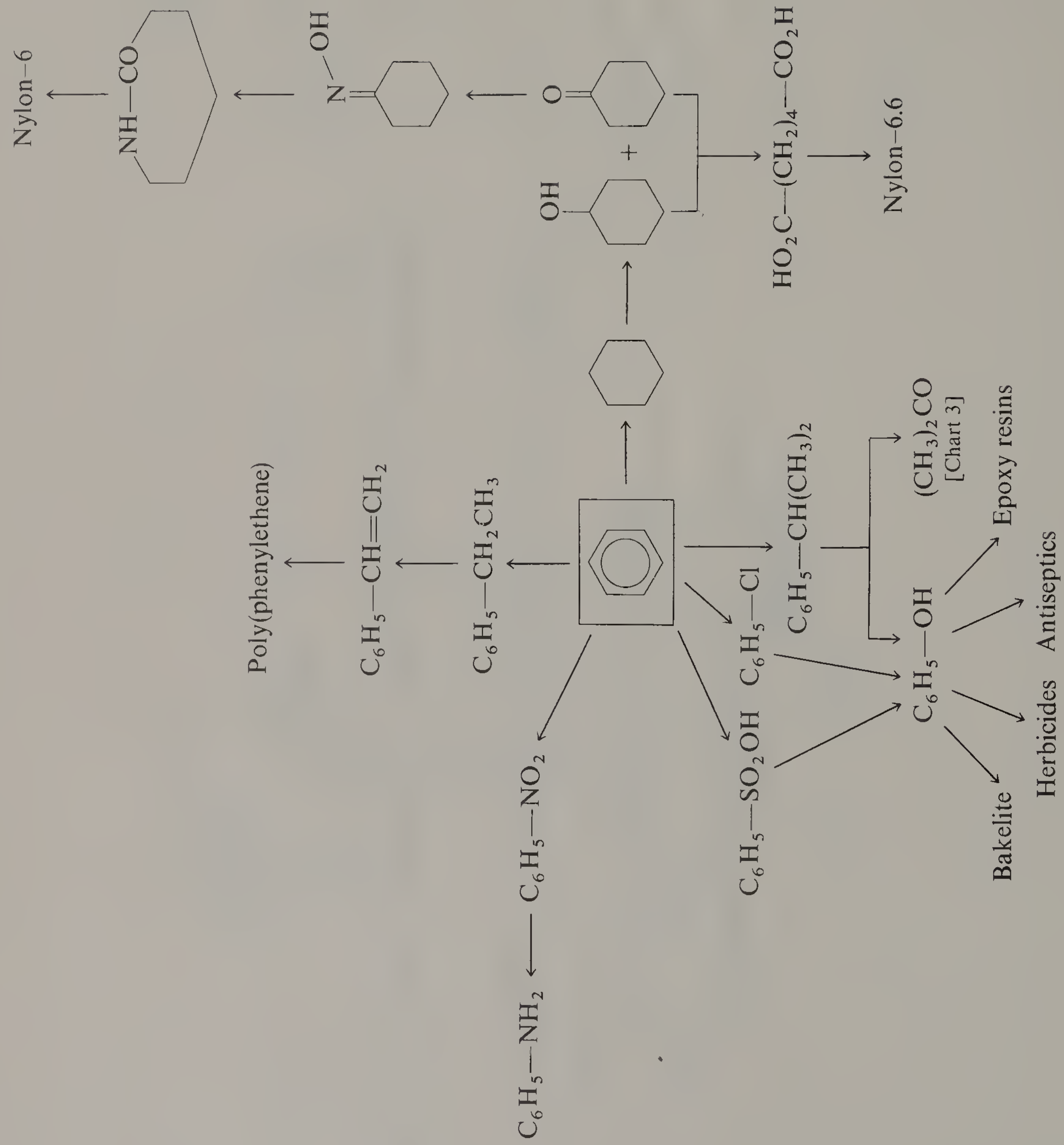


CHART 4 *Uses of benzene*



Questions

1 Suggest the identity of compounds *A*, *B* and *C* from the following data, and explain the reactions which are described.

A is a crystalline solid. When a little water is added to *A* two liquid layers are formed; addition of more water gives a homogeneous aqueous solution. This liquid

- (i) has no reaction with sodium carbonate solution but indicators show that it has a pH value of less than 7;
- (ii) gives a purple coloration on the addition of a few drops of iron(III) chloride solution;
- (iii) gives a white precipitate on the addition of bromine water.

B is a white crystalline solid which, on heating with an excess of soda-lime, evolves a gas producing an alkaline solution in water. An aqueous solution of *B*

- (i) deposits a white crystalline precipitate on the addition of concentrated nitric acid;
- (ii) evolves carbon dioxide and nitrogen on the addition of sodium nitrite solution followed by dilute hydrochloric acid;
- (iii) evolves nitrogen on the addition of alkaline sodium hypochlorite solution.

C is a gas which dissolves in water to give a strongly alkaline solution. This solution, when neutralised by hydrochloric acid, gives a white crystalline compound on evaporation.

When *C* is burnt it produces twice its own volume of carbon dioxide, the gas volumes being measured at the same temperature and pressure. (C(T))

2 Identify the following compounds, explaining your reasoning and writing equations where possible for the reactions which are described.

- (a) A colourless solid, *A*, dissolves in water to give a neutral solution. When heated with aqueous sodium hydroxide an alkaline gas is expelled and the residual solution effervesces when it is treated with an excess of a dilute acid. A white crystalline precipitate is formed when an aqueous solution of *A* is treated with concentrated nitric acid.
- (b) A liquid *B* is miscible with water in all proportions to give solutions with a pH of less than 7. When *B* is warmed with concentrated sulphuric acid a gas is given off which burns with a blue flame. *B* reduces hot alkaline permanganate and ammoniacal silver nitrate.
- (c) A colourless liquid *C*, boiling at 184°C, is sparingly soluble in warm water to which it gives a feebly alkaline reaction. When it is treated with sodium nitrite, in the presence of an excess of dilute hydrochloric acid at 5°C, it yields a solution which reacts with an alkaline solution of phenol to give an orange yellow precipitate.
- (d) *D* is a blue solid which gives off an inflammable vapour and leaves a bright metallic residue when it is heated in a test tube. It dissolves in water to give a light blue solution which (i) turns to a deep blue colour with an excess of ammonia, and (ii) gives a reddish brown colour with a few drops of iron(III) chloride solution. When *D* is heated with concentrated sulphuric acid a sharp smell is produced, but if alcohol is also present a sweet fruity odour results.
- (e) *E* is a white solid which is almost insoluble in cold water but dissolves quite readily in hot water to give an acidic solution. When it is heated with soda-lime it gives off a vapour which burns with a luminous and smoky flame and is 39 times denser than hydrogen under the same conditions. (O)

3 Identify the organic compounds described below and where possible write equations to represent the reactions which occur.

(a) A colourless solid, *A*, has a characteristic smell. Its aqueous solution is very feebly acidic and gives a white precipitate with bromine water and a violet coloration with aqueous iron(III) chloride. It reacts with phosphorus pentachloride to give a derivative with a vapour density of 56·3.

(b) A white solid, *B*, has a high melting point and dissolves in water to give a neutral solution. It forms salts with acids and bases and yields a gas when heated with soda-lime which is alkaline to litmus paper but, unlike ammonia, burns in air.

(c) A colourless oil, *C*, has a very characteristic smell. On exposure to the air it slowly forms a colourless solid which dissolves very sparingly in cold water to give an acidic solution. *C* reduces ammoniacal silver nitrate but not Fehling's solution, and reacts with phenylhydrazine to give a crystalline derivative.

(d) A colourless fuming liquid, *D*, reacts violently with water to give two acids in equal molar proportions. Its vapour density is 39.

(c) A white solid, *E*, dissolves in water to give a solution which is acidic and which decolorises a hot acidified solution of potassium permanganate. When heated with concentrated sulphuric acid it is completely decomposed without blackening and yields a mixture of gases, one of which turns lime water milky and one of which burns with a blue flame. (O)

4 Suggest, with reasons, the identity of the organic compounds *A*, *B* and *C*.

(i) A colourless liquid hydrocarbon *A* has no reaction with bromine in the dark until iron powder is added, when a colourless gas, fuming in moist air, is evolved.

When *A* is heated under reflux with alkaline potassium permanganate, and then an excess of sulphur dioxide is bubbled through the mixture, colourless crystals separate on cooling.

(ii) A colourless liquid *B* reacts violently with water to give a strongly acidic solution. A portion of this solution on treatment with dilute nitric acid and silver nitrate solution gives a white precipitate. A further portion, after neutralisation with ammonia, reacts with 'neutral' iron(III) chloride (ferric chloride) solution to give a deep red brown solution. This solution gives a brown precipitate when boiled.

1·00 g of *B* was allowed to react with an excess of water. The resulting solution required 21·6 cm^3 of 1M (1N) sodium hydroxide for an end point with phenolphthalein indicator.

(iii) A colourless crystalline compound *C* gives an acidic solution in water. This solution gives a white precipitate on treatment with calcium chloride solution.

When treated with hot concentrated sulphuric acid, *C* reacts to evolve a gas which burns with a blue flame together with a gas which gives a white precipitate with lime water. (C(T))

5 An optically inactive acid *A*, $C_5H_8O_5$, on being heated lost CO_2 to give an acid *B*, $C_4H_8O_3$, capable of being resolved.

On action of sulphuric acid, *B* gave an acid *C* whose ethyl ester gave *D* on the action of hydrogen and platinum.

D, with conc. ammonia gave *E*, C_4H_9ON, which with bromine and potassium hydroxide solution gave *F*, C_3H_9N. *F* with nitrous acid gave *G*.

G on mild oxidation gave *H*. Both *G* and *H* gave the iodoform reaction. Elucidate the reaction scheme and suggest a synthesis of *C*.

6 Explain the following observations, and identify **all** the compounds mentioned.

(a) Three isomeric compounds of formula (C_3H_9N) react differently with nitrous acid.

(b) Compound *J* ($C_4H_{10}O$) gives a mixture of three compounds *K*, *L*, *M* (C_4H_8) when passed over alumina at 300°C. Compound *N* ($C_4H_{10}O$) gives only one product *P* (C_4H_8) under the same conditions. Comment on the types of isomerism shown by compounds *K*, *L*, *M* and *P*. (C(N, S))

7 A compound *A* contains C, 66·4 per cent; H, 5·5 per cent; and Cl, 28·1 per cent. Show how these figures are used to derive the empirical formula C_7H_7Cl.

When *A* is treated with aqueous potassium hydroxide it is converted into a hydroxy compound *B*. Mild oxidation of *B* gives a compound which yields a white precipitate with hydroxylamine ($H_2N.OH$). Further oxidation of *B* gives a white crystalline solid *C* which liberates carbon dioxide from aqueous sodium carbonate. Benzene is obtained on heating *C* with soda-lime.

From these data deduce the structure of *A* and by means of equations trace the course of the above reactions.

How may *A* be synthesised from the parent hydrocarbon? (JMB)

8 Suggest a possible structural formula for each of the compounds *A* to *D* inclusive and explain the reactions involved, giving equations where possible:

A, molecular formula $C_3H_6O_2$, gives an effervescence with sodium hydrogen carbonate solution and reacts with phosphorus pentachloride to give a compound which contains 38·4 per cent by weight of chlorine.

B, *empirical* formula CH_2Br, on refluxing with aqueous sodium hydroxide gives a compound which reacts with sodium to give hydrogen, one mole of the compound giving one mole of hydrogen.

C, molecular formula $C_4H_{10}O$, is readily oxidised to give a compound C_4H_8O which can be further oxidised to give a compound $C_4H_8O_2$.

D, molecular formula C_7H_7Cl, on refluxing with aqueous sodium hydroxide and subsequent mild oxidation gives a compound C_7H_6O, which readily undergoes further oxidation to give a compound $C_7H_6O_2$. (L(X))

9 Account for the following observations, and identify the compounds *G*–*S*.

(a) The chlorine in compound *G* (C_7H_7Cl) is readily displaced by treatment with dilute aqueous sodium hydroxide. The chlorine in the isomeric compound *H* is unaffected by this treatment.

(b) Compound *J* ($C_4H_{10}O$) gives a mixture of three compounds *K*, *L*, *M* (C_4H_8) when passed over alumina at 300°C. Compound *N* ($C_4H_{10}O$) gives only one product *P* (C_4H_8) under the same conditions. Comment on the types of isomerism shown by the compounds *K*, *L*, *M* and *P*.

(c) If compound *Q* is treated first with bromine and then with ethanoyl chloride, compound *R* ($C_8H_6Br_3NO$) is obtained. If *Q* is treated first with ethanoyl chloride and then with bromine, compound *S* (C_8H_8BrNO) is the product. (C(T, S))

10 Give the structures of *A*, *B* and *C* in the following:

(i) Compound *A*, C_7H_8O, which is soluble in aqueous sodium hydroxide, is no more soluble in aqueous sodium carbonate than it is in water. If forms $C_7H_5OBr_3$ with bromine.

(ii) Compound *B*, $C_6H_4Br_2$, which is unaffected by boiling with aqueous sodium hydroxide, gives two isomers of formula $C_6H_3Br_2NO_2$ with a mixture of concentrated nitric and sulphuric acids.

(iii) Compound *C*, $C_8H_6O_4$, dissolves in aqueous sodium carbonate but not in cold water. When heated, the compound is converted into $C_8H_4O_3$. (O Schol.)

11 A compound *A*, $C_{13}H_{10}BrNO$, which is sparingly soluble in cold water, dissolved on boiling with concentrated hydrochloric acid. When cooled the resulting solution deposited a solid *B*, $C_7H_6O_2$, which displaced carbon dioxide from sodium carbonate solution. Basification of the solution which remained yielded a solid *C*, which contained C, 41·9 per cent; H, 3·5 per cent; Br, 46·5 per cent and N, 8·1 per cent. Treatment of an ice-cold solution of *C* in hydrobromic acid with sodium nitrite followed by copper(I) bromide gives compound *D*. The reaction of *D* with fuming nitric acid and concentrated sulphuric acid gives only one compound *E*.

Suggest possible structures for the compounds *A*, *B*, *C*, *D* and *E*. (O Schol.)

12 Treatment of 2-bromobutane ($CH_3.CHBr.CH_2.CH_3$) with hot, alcoholic potassium hydroxide gives a mixture of three isomeric butenes, *C*, *D*, and *E*. Reaction with trioxygen and then water of the minor product, *C*, gives methanal and another aldehyde in equimolar amounts. Both *D* and *E* give the same single product, *F*, with trioxygen and then water.

Write down the structures of the compounds *C*, *D*, and *E*. Describe the type of isomerism shown by *D* and *E*, and explain how it arises.

What reactions would you carry out to identify *F*?

Draw clear, structural diagrams to represent the two molecular species obtained when either *D* or *E* is treated with hydrogen chloride. How would these species differ in properties? What difficulties would be encountered in their separation? (C(T,S))

13 How, by a chemical test, would you distinguish

(i) between $CH_3.C_6H_4.NH_2$ and $C_6H_5.CH_2.NH_2$;
(ii) between $CH_3.C_6H_4.OH$ and $C_6H_5.CH_2.OH$;
(iii) between $CH_3.C_6H_4.Cl$ and $C_6H_5.CH_2.Cl$;
(iv) between C_6H_6 (benzene) and C_6H_{12} (hexene)?

In each case, indicate which member of the pair is identified and give the reaction, if any, of the other compound with the reagent used. (C(T))

14 Describe **two** chemical tests which you would carry out in each case to distinguish between the following pairs of substances:

(a) ethene and ethyne;
(b) methylamine and ammonia;
(c) ethanal and propanone;
(d) ammonium ethanoate and ethanamide;
(e) methanoic acid and ethanoic acid.

Wherever possible give equations for the reactions. (O)

15 Describe, with equations, a chemical test you would employ to distinguish between members of each of the following pairs of compounds:

(a) ethyl ethanoate and ethyl benzoate;
(b) chlorobenzene and (chloromethyl)benzene;
(c) ammonium ethanoate and ethanamide;
(d) ethanoyl chloride and chloroethanoic acid;
(e) propanone and pentan-3-one. (W)

16 (a) Give **one** *chemical* test in **each** case to distinguish

(i) between benzoic acid and phenol;
(ii) between benzaldehyde and phenylethanone;
(iii) between nitrobenzene and phenylamine.

(b) Outline the essential practical steps that you would take to obtain pure samples of both substances from a mixture of phenol and phenylamine. (C(T))

17 For each of the following pairs of compounds describe one *simple* chemical test that would distinguish between its members. State exactly what you would do and what you would expect to see and write equations for all the reactions you describe.

(a) Propanone and methanol;
(b) phenol and benzoic acid;
(c) carbamide and ammonium ethanoate;
(d) hexane ($CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$) and benzene;
(e) propene ($CH_3.CH{=}CH_2$) and propyne ($CH_3C{\equiv}CH$);
(f) stearin (a fat) and casein (a protein). (JMB)

18 Describe **one** chemical test in **each** case to distinguish:

(a) between methanoic acid and ethanedioic acid;
(b) between phenol and benzenesulphonic acid;
(c) between propanone and ethanal;
(d) between methylbenzene and benzene;
(e) between trichloromethane and 1,2-dichloroethane. (C(N))

19 Describe how you would distinguish between the following pairs of isomers by **two** simple chemical tests in **each** case. Give equations for the reactions involved.

(a) $CH_2{=}CH.CH{=}CH_2$ and $CH_3.CH_2.C{\equiv}CH$;
(b) $CH_3.CH_2.CH_2.OH$ and $(CH_3)_2CH.OH$;
(c) o-$CH_3.C_6H_4.NH_2$ and $C_6H_5.CH_2.NH_2$;
(d) $HO.CH_2.CO.NH_2$ and $NH_2.CH_2.COOH$. (C(S))

20 With the aid of a **named** example in each case, outline, giving conditions and reagents, how you would bring about the following change of functional group in *aliphatic* compounds:

(a) $—CH_2OH$ to $—CO.OH$;
(b) $—CO.Cl$ to $—CHO$;
(c) $—NH_2$ to $—OH$;
(d) $—CN$ to $—CO.OH$;
(e) $—CO.OH$ to $—CN$.

Name the product formed in each case. (W)

21 Describe briefly how you would carry out the following conversions, giving essential conditions for the reactions but no details of the apparatus:

(a) $CH_3I \rightarrow C_2H_5NH_2$;
(b) $C_6H_5CH_3 \rightarrow C_6H_5CHO$;
(c) $C_6H_6 \rightarrow C_6H_5NH_2$;
(d) $CH_3COOH \rightarrow CH_3NH_2$. (O)

22 Give conditions and equations to show how the following conversions may be made:

(a) ethylamine to ethanol;
(b) ethanoyl chloride to ethanal;
(c) ethanamide to methylamine;
(d) ethanonitrile to ethanoic acid;
(e) ethanoic acid to aminoethanoic acid. (W)

23 Indicate the steps by which you would carry out the following conversions:

(a) C to CH_3COOH;
(b) **either** D_2O to CD_4
or CH_3COOH to CH_2NH_2COOH;
(c) $(COOH)_2$ to $HCOOH$;
(d) $C_6H_5NO_2$ to C_6H_6. (O(S))

24 Indicate the steps by which you would bring about **four** of the following conversions:

(a) CH_3COOH to $C_2H_5NH_2$;
(b) C_6H_6 to $C_6H_5NH.NH_2$;
(c) CH_3OH to $CH_3.CO.CH_3$;
(d) C_2H_5OH to $CH_3.CHOH.COOH$;
(e) C_2H_5OH to $H_2N.CH_2.CH_2.CH_2.CH_2.NH_2$.

Give equations for the reactions which take place. (O(S))

25 Write down **one** reaction scheme for each of the following conversions, indicating reagents and conditions for each step:

(a) ethyne → ethanoyl chloride;
(b) phenylamine → phenyl benzoate;
(c) ethanol → chloroethanoic acid;
(d) benzene → phenylmethanol;
(e) propan-2-ol → 2-aminopropane. (O and C(S))

26 Write down **one** reaction scheme for each of the following conversions:

(a) ethyne → ethanoic acid;
(b) benzene → 2-nitrophenol;
(c) ethanal → ethylamine;
(d) diethyl propanedioate → propanonitrile;
(e) nitrobenzene → benzoic acid. (O and C(S))

27 Write formulae to show the structures of the products and comment briefly on the reactions between the substances mentioned for **five** of the following cases:

(a) ethanol and sulphuric acid;
(b) ethanol and sodium hypochlorite;
(c) benzene and fuming sulphuric acid;
(d) propanone and sodium hydrogen sulphite;
(e) phenylamine, hydrochloric acid and sodium nitrite at 0°C;
(f) phenol and ethanoic anhydride. (O Schol.)

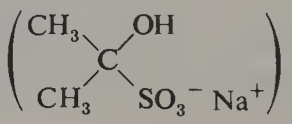
28 How, and under what conditions, does sodium hydroxide react with

(i) 1,2-dibromoethane;
(ii) ethanal;
(iii) benzaldehyde;
(iv) carbamide;
(v) ethyl ethanoate?

What chemical test will distinguish between ethanamide and carbamide? (C(T))

29 How, and under what conditions, does sodium hydroxide react with the following compounds:

(a) chlorobenzene;
(b) chloroethanoic acid;
(c) carbamide;
(d) tristearin (a fat);
(e) sodium 2-hydroxypropane-2-sulphonate



$$\left((CH_3)_2C(OH)SO_3^-\ Na^+\right)$$

(O and C)

30 Describe, with the aid of an illustrative example in each case together with any necessary conditions, **one** use of each of the following reagents in organic chemistry:

(a) phosphorus pentachloride;
(b) phosphorus pentoxide;
(c) trioxygen;
(d) lithium aluminium hydride;
(e) hydrogen. (W)

31 Give an account of the uses in organic chemistry of:

(a) sodium;
(b) silver nitrate;
(c) benzoyl chloride;
(d) copper(II) sulphate;
(e) phosphorus pentachloride;
(f) nitric acid. (C Entrance)

32 Discuss the use of the following in the synthesis of organic compounds:

(a) sulphuric acid;
(b) nitric acid;
(c) sodium;
(d) aluminium chloride. (O(S))

33 How and under what conditions does sulphuric acid react with the following compounds:

(a) propanone;
(b) propene;
(c) phenylamine;
(d) 2-hydroxypropanoic acid;
(e) *N*-phenylethanamide? (O and C(S))

34 How, and under what conditions, does sulphuric acid react with:

(i) ethanamide;
(ii) phenol;
(iii) ethanedioic acid;
(iv) ethanol;
(v) phenylamine? (C(T))

35 Describe the reactions which can take place between sulphuric acid and each of the following substances: ethyne, ethanol, ethanal and benzene.

Give the conditions under which the reactions take place. (O)

36 What is the action of reducing agents on the following compounds:

(a) ethyne;
(b) ethanoyl chloride;
(c) benzenediazonium chloride;
(d) phenol;
(e) bromoethane?

State the reducing agents and the conditions necessary in each case. (O and C(S))

37 By means of specific examples, illustrate the uses of the following as oxidising agents in organic chemistry: potassium permanganate, potassium dichromate, trioxygen, ammoniacal silver nitrate.

How would you convert compound (a), below, into compounds (b) and (c)?

(a) $CH_3.CHOH.CH_2.CH_2.CH{=}CH_2$

(b) $CH_3.CO.CH_2.CH_2.CO_2H$

(c) $HO.CO.CH_2.CH_2.CH{=}CH_2$. (O Schol.)

38 By means of equations and brief notes on conditions of temperature and concentration, indicate the various ways in which sulphuric acid can react with the following compounds:

(a) ethanol;
(b) ethene;
(c) benzene;
(d) glycine;
(e) carbamide.

How and under what conditions does sodium hydroxide react with (i) the products from ethene and (ii) the products from benzene? (JMB)

39 Explain concisely the meaning of each of the following in organic chemistry, illustrating your answer with one example in each case:

(a) ethanoylation;
(b) unsaturation;
(c) nitration;
(d) polymerisation;
(e) sulphonation. (AEB)

40 Explain, with the aid of appropriate reactions and necessary conditions in each case, the significance of the following terms: *dehydration*, *decarboxylation*, *alkylation*, *acylation*, *condensation*. (W)

41 Explain and illustrate with an appropriate example, each of the following terms:

(i) alkane;
(ii) alkene;
(iii) ethanoylation;
(iv) saponification;
(v) polymerisation;
(vi) Cannizzaro reaction. (AEB)

42 Explain carefully the following terms illustrating each by one example of your own choice:

(a) photochemical chlorination;
(b) reaction with trioxygen;
(c) hydrogenation;
(d) ‘cracking’ of alkanes;
(e) saponification.

Describe very briefly the commercial application of any **three** of these processes. (JMB)

43 Describe, with the necessary conditions, the hydrolysis of **five** named compounds each selected from a different homologous series. (W)

44 Explain, and illustrate with **one** example in each case, the meaning of **five** of the following: unsaturation, polymerisation, homologous series, saponification, nitration, ethanoylation. (O)

45 Indicate, giving one example in each case, what you understand by the following terms: nucleophile, electrophile, free radical, homolysis, and heterolysis.
Give the mechanisms of THREE of the following reactions:
(a) 1-chlorobutane with aqueous sodium hydroxide;

(b) benzene with a mixture of concentrated nitric and sulphuric acids;
(c) methane with chlorine;
(d) 2-iodo-2-methylpropane with aqueous sodium hydroxide. (L)

46 'The carbonyl group, $>C{=}O$, modifies the properties of the group to which it is attached.' Comment on this statement by comparing:

(a) ethanoic acid with ethanol in (i) the degree to which ionisation occurs in water, (ii) the reaction with phosphorus pentachloride;
(b) the action of cold dilute acids on ethanamide and ethylamine;
(c) the action of cold water on ethanoyl chloride and chloroethane.

Show how the properties of the carbonyl group are modified by comparing the behaviour of propanone and ethanoic acid towards 2,4-dinitrophenylhydrazine, and interpret the result in terms of electronic theory. (SUJB)

47 Carbon compounds are often classified according to the functional groups they contain. Examples of such groups are given below:

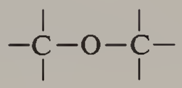
(i) $>C{=}C<$

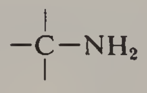
(ii) $-C{\equiv}C-$

(iii) $-CH_2-OH$

(iv) $>C{=}O$

(v) ${}_{H}{>}C{=}O$

(vi)

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

(vii)

$-\overset{|}{\underset{|}{C}}-NH_2$

(a) Name the *class* of compound you associate with each functional group.
(b) Give *one* named example from each class and write its structural formula.
(c) Give one typical reaction for each of the seven compounds you have chosen in part (b).

Write an equation for each reaction. (L(X))

48 In what types of organic compounds do the following functional groups occur: (ii) —COCl, (ii) $—NH_2$, (iii) —COOH, (iv) —O—, (v) $—CONH_2$?

Describe **two** reactions characteristic of each group. (AEB)

49 For each of the following pairs of compounds give:

(a) **one** reaction in which the specified group behaves similarly in both;
(b) **two** reactions in which the specified group behaves differently in each.

(i) the $>C{=}O$ group in $CH_3.CH_2.CHO$ and $CH_3.CH_2.CO.CH_3$;
(ii) the $—NH_2$ group in $CH_3.CH_2.CH_2.NH_2$ and $C_6H_5.CO.NH_2$;
(ii) the —Br atom in $CH_3.CH_2.Br$ and $C_6H_5.Br$.

Give brief *practical* details of chemical tests for distinguishing between any **two pairs** of the components in (i), (ii), and (iii).
(The results of negative tests must be made clear.) (SUJB)

50 'A benzene ring influences the chemical behaviour of functional groups attached to it.' Illustrate and discuss with suitable examples. (O Schol.)

51 (a) For each of parts (i) to (x) below ONLY ONE of the alternatives *A*, *B*, *C*, *D*, *E* is correct. Answer each part by giving the appropriate letter.

A $CH_3.CH_2.NH_2$ *B* $CH_3.CO.NH_2$ *C* $C_6H_5NO_2$
D $C_6H_5.NH_2$ *E* $C_6H_5N_2Cl$

(i) Which is a strong electrolyte?
(ii) Which dissolves in dilute hydrochloric acid, but not in water?
(iii) Which is insoluble in water, acid and alkali?
(iv) Which is a colourless liquid at 20°C when pure?
(v) Which has the highest vapour pressure at 15°C?
(vi) Which is explosive when pure?
(vii) Which yields a product with one less carbon atom when treated with bromine and potassium hydroxide solution?
(viii) Which is the most ready to combine with a proton?
(ix) Which gives ammonia on warming with aqueous sodium hydroxide solution?
(x) Which evolves nitrogen on treatment with nitrous acid at 5°C?

(b) How and under what conditions does ethanamide (acetamide) react with
(i) bromine and sodium hydroxide
(ii) dilute hydrochloric acid? (SUJB)

52 For each of the following, give the name and structural formula of one organic compound which contains the type of linkage mentioned:

(a) a triple bond between carbon and carbon;
(b) a triple bond between carbon and nitrogen;
(c) a triple bond between nitrogen and nitrogen;
(d) a double bond between carbon and oxygen;
(e) a double bond between carbon and nitrogen;
(f) a double bond between nitrogen and oxygen.

Specify the reagents and conditions necessary to reduce the substances you mention giving the appropriate equations and naming the products. (*Note*. The reagents should be different in each case.)

Describe one other characteristic reaction of each of the compounds with triple bonds. (JMB(S))

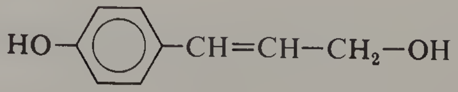
53 A compound *X* is shown to have the following structure

$$OHC.CH_2.CH{=}CH.CH_2.CONH_2$$

How would you expect *X* to behave towards the following reagents under varying conditions:

(a) sodium hydroxide;
(b) phosphorus pentachloride;
(c) potassium permanganate;
(d) bromine;
(e) sodium and ethanol? (L)

54 From your knowledge of the reactions of particular groups predict the reactions of the compound



with:

(a) bromine water;
(b) hydrogen and finely divided nickel;
(c) sodium hydroxide;
(d) ethanoic acid;
(e) dilute, alkaline potassium permanganate. (C(T))

55 Name the organic compounds produced, write their structural formulae, and state the conditions under which they are formed when:

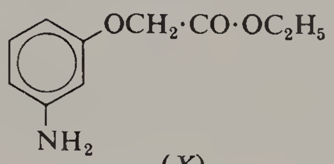
(a) phenol, ethanamide, and ethyne are each treated with bromine;

(b) phenylamine, ethanol and propene are each treated with hydrogen bromide.

(W)

56 (a) Monochlorination of benzene in the presence of iron(III) chloride (ferric chloride), and treatment of the product with a mixture of concentrated nitric and sulphuric acids gives two isomers of formula $C_6H_4ClNO_2$. Write structures for these isomers, and suggest a method by which a third isomer could be prepared from benzene.

(b) A compound is believed to have structure *X*.



(*X*)

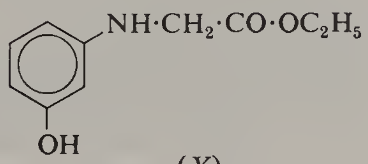
By what chemical reactions would you show the presence of:

(i) the benzene ring;

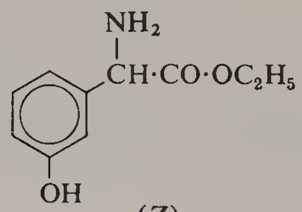
(ii) the amino group;

(iii) the ester group?

By what reactions would you distinguish between isomers *X*, *Y* and *Z*?



(*Y*)

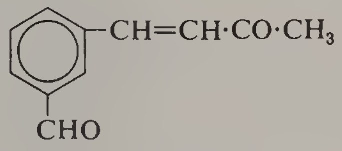


(*Z*)

(C(T, S))

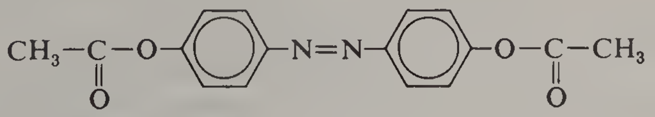
57 This question involves practical procedures in the chemistry of carbon compounds. Where you have direct experience describe the practical details as fully as you can, otherwise give an account of the reagents and conditions which you think would be appropriate.

(a) Suppose you were given a substance reputed to have the following formula:



Describe how you would attempt to confirm its formula. You should assume that the constituent elements and the molecular weight of the compound are known.

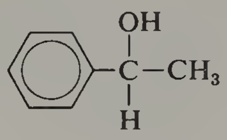
(b) Describe how you would attempt to prepare a substance of the following formula:



Assume that the only starting material containing the benzene ring which you are allowed is phenol. You are allowed to use any other material which you would normally expect to find in a school laboratory. (L(Nuffield,S))

58 Using your knowledge of simpler substances, set out the differences which you could expect to find in the properties and reactions of the compounds in the following pairs of substances:

(a)



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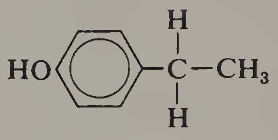
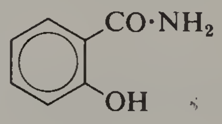
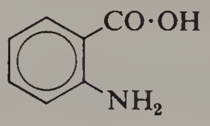


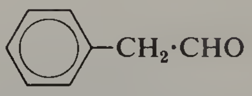
(b) (i)



and (ii)



(c)



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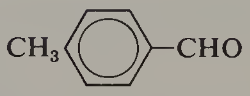


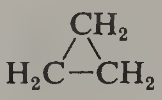
Starting from methyl-2-nitrobenzene, outline a possible synthesis of amine, (b) (ii), and show how this, in turn, could be converted into the hydroxy-derivative (b) (i). (JMB(S))

59 An understanding of the 'nature of the chemical bond' allows one to explain some of the properties of known compounds and make predictions about the properties of unknown ones.

Discuss the chemical bonding in the following compounds and explain how chemical properties of each depend on the types of bonds they contain:

CH_4, $CH_2{=}CH{-}CH{=}CH_2$, $(CH_3)_3N$, CH_3CHO.

What predictions would you make about the properties of cyclopropane,



(C Schol.)

60 How, and under what conditions, do the following pairs of substances react:

(a) propene and hydrogen iodide;
(b) ethanol and sulphuric acid;
(c) nitrobenzene and nitric acid;
(d) chlorine and ethanoic acid?

Explain the underlying chemical principles in (a) and (c).

What light does reaction (d) throw on the structure of ethanoic acid? (AEB)

61 Give names and structural formulae for the isomers of compounds having molecular formulae (a) $C_2H_4Br_2$, (b) C_4H_9I.

State what happens when each of the isomers you name reacts with potassium hydroxide, mentioning any essential conditions of reaction. In the cases of any hydroxy compounds formed, what happens to these on oxidation?

Outline how the isomers of $C_2H_4Br_2$ may be prepared. (AEB(S))

62 Suggest reasons why

(i) ethers do not react with sodium, but dissolve in concentrated acids and possess lower boiling points than the isomeric alcohols;

(ii) methanoic acid shows reducing and acidic properties, but ethanoic acid shows only acidic properties;

(iii) the compounds represented by $CH_3.CHOH.COOH$ may or may not be optically active;

(iv) nitrous acid gives an alcohol on reaction with a primary aliphatic amine but not with a primary aromatic amine. (AEB(S))

63 Discuss the following statements:

(a) Benzoic acid is soluble in aqueous sodium hydrogen carbonate whereas phenol is not.

(b) The carbon–oxygen bond lengths in dimethyl ether are 1·43 Å; in propanone the carbon–oxygen bond length is 1·24 Å, and in carbon monoxide it is 1·13 Å.

(c) The addition of bromine to ethene is a very fast reaction, whereas the addition of bromine to propenonitrile ($CH_2{=}CH{-}CN$) proceeds slowly.

(d) Ethyne has a pK_a of 26 and forms salts with sodium, copper and Grignard reagents. Ethene does not form salts with these reagents. (C Schol).

64 Explain:

(a) The carbon–carbon bond lengths in the benzene nucleus are all identical.

(b) Nitric acid alone has no reaction with benzene but a reaction occurs if concentrated sulphuric acid is present.

(c) Propanone, but not methyl ethanoate, forms a phenylhydrazone.

(d) Chloroethanoic acid is stronger than bromoethanoic acid and both are stronger than ethanoic acid itself.

(e) Hydrogen bromide reacts with propene to give two isomeric derivatives with one isomer in much the greater proportion. (S(S))

65 Give a classified account of the addition of simple molecules to unsaturated linkages in organic compounds. Your account should include, if possible, any suggested mechanisms to explain the additions. (L(S))

66 (a) Friedel—Crafts reactions involve a halogen carrier.

(i) Give **two** examples of such carriers and explain how they work.

(ii) Give **three** different types of reactions in which the halogen carrier is used to bring about substitution in the benzene nucleus.

(iii) State the conditions required in order to obtain good quantitative yields of product in Friedel—Crafts reactions.

(b) The halogenation of alkanes takes place in the presence of ultraviolet radiation.

(i) What type of reaction is this?

(ii) What part does the radiation play?

(iii) What are the products of the chlorination of ethane using this process?

(c) Give the name **or** structure of the major organic product formed when 2-chloropropane reacts with

(i) sodium hydroxide in alcoholic solution,

(ii) silver ethanoate in alcoholic solution,

(iii) dry silver oxide. (AEB(I))

67 Comment on **four** of the following observations:

(a) Treatment of *trans*-butenedioic acid with dilute potassium permanganate solution gives (±)2,3-dihydroxybutanedioic acid.

(b) Bromobenzene is stable to dilute aqueous sodium hydroxide solution whilst 1-bromobutane is hydrolysed.

(c) Reaction of 1-chloropropane with benzene and aluminium chloride gives (1-methylethyl)benzene.

(d) When a limited amount of hydrogen is passed into benzene containing a nickel catalyst a mixture of cyclohexane and benzene is obtained, but no intermediate products can be isolated.

(e) When propanone is dissolved in heavy water containing sodium carbonate in solution hexadeuteropropanone is formed. (O Schol.)

68 Explain **three** of the following observations:

(a) On treatment with hot chromic acid ethanal and propanone both yield the same compound which is soluble in sodium carbonate solution with the evolution of carbon dioxide; but with cold chromic acid only ethanal yields such a compound.

(b) Both ethanol and propanone yield trichloromethane when they are heated with aqueous sodium hypochlorite.

(c) A compound, BrCH═CHBr, on being heated yields another compound of the same molecular formula.

(d) Optically inactive 2-hydroxypropanoic acid reacts with a laevorotatory base to give a mixture of two salts which can be separated by fractional crystallisation. (O Schol.)

69 Comment on **three** of the following:

(a) The pK_a values for propanoic, ethanoic, and fluoroethanoic acids are 4·88, 4·80 and 2·66, respectively.

(b) When treated with deuterium oxide containing a trace of sodium hydroxide, pentan-3-one incorporates four atoms of deuterium per molecule.

(c) Optically active butan-2-ol ($CH_3.CH_2.CHOH.CH_3$) retains its optical activity indefinitely in aqueous solution, but racemises rapidly in aqueous sulphuric acid. The alcohol undergoes no chemical change in aqueous sodium bromide solution, but is rapidly converted into 2-bromobutane upon addition of sulphuric acid to the solution.

(d) In addition of bromine to alkenes, the following order of reactivity is observed:

$$CH_2 = CH_2 < CH_3.CH = CH_2 < (CH_3)_2C = CH_2.$$

(e) The heats of combustion of cyclopropane, cyclobutane, cyclopentane, and cyclohexane are 500, 656, 793·5, and 944 kcal/mole, respectively. (O Schol.)

70 Comment on **four** of the following observations:

(a) Phenylamine dissolves in dilute hydrochloric acid solution to a much greater extent than it dissolves in water.

(b) While benzaldehyde reacts smoothly with boiling sodium hydroxide solution to give phenylmethanol, $C_6H_5CH_2OH$, and sodium benzoate, ethanal is polymerised by cold sodium hydroxide solution.

(c) Phenol dissolves in sodium hydroxide solution but not in sodium carbonate solution.

(d) Benzene tends to undergo substitution reactions (with bromine for example) rather than addition reactions.

(e) Phenol is brominated much more rapidly than benzene. (C Schol.)

71 Write balanced equations for the reactions which occur, name the organic products formed, and state what would be observed when:

(a) benzoyl chloride is added slowly to cooled concentrated aqueous ammonia, and the product is isolated and distilled with phosphorus pentoxide;

(b) benzene is added slowly to a mixture of fuming nitric acid and concentrated sulphuric acid, and the resulting mixture is poured into water;

(c) propan-2-ol is mixed with a little potassium iodide solution and a solution of sodium hypochlorite is added;

(d) ethanamide is treated with bromine, followed by dilute potassium hydroxide solution, and the resulting mixture is run into hot concentrated potassium hydroxide solution;

(e) benzaldehyde is shaken with concentrated potassium hydroxide solution and, after standing overnight, water is added. The mixture is then extracted with ether and the aqueous solution is acidified. (JMB)

72 You are given unlabelled bottles of the following substances: propan-2-ol (isopropanol), methanoic acid, benzoyl chloride, methanal, phenylamine, ethanonitrile.

In each case give a *single* positive chemical test (six texts in all) which would enable the bottle to be labelled correctly. (O and C)

73 For each of the following cases give the structural formula of a compound which fulfils the stated conditions:

(a) an aldehyde, $C_5H_{10}O$, which shows optical activity;
(b) a compound, $C_6H_5NO_3$, which is volatile in steam;
(c) a hydrocarbon, C_4H_6, which gives a silver derivative;
(d) an amine, C_3H_9N, which cannot be ethanoylated;
(e) a dibasic acid which on heating gives a compound, $C_5H_{10}O_2$, which could show optical activity;
(f) an aliphatic aldehyde, $C_5H_{10}O$, which is not polymerised by alkali;
(g) an aldehyde, C_8H_8O, which polymerises with alkali. (O and C(S))

74 Explain what impurities are likely to be present in crude samples of iodoethane, benzoic acid, ethyl ethanoate, and phenylamine prepared in the laboratory. Describe, in each case, how such impurities may be removed and what criterion of purity you would employ for the final product.

A yield of 13·04 g of phenylamine was obtained from 21·30 g of nitrobenzene. Calculate the percentage of the theoretical yield for the reaction. (W)

75 Crude *N*-phenylethanamide is purified by washing successively with water, aqueous sodium hydrogen carbonate, dilute hydrochloric acid and water. Explain the purpose of each wash.

Why is it incorrect to attempt to dry (a) ethanol with calcium chloride, (b) ethanoic acid with potassium carbonate, (c) iodoethane with sodium? What alternative procedure would you adopt to dry ethanol, ethanoic acid and iodoethane?

What principle underlies the use of a mixed melting point as a criterion of purity? (W)

76 (a) Mention, with brief comment, **one** example of each of the following:

(i) A pure compound which cannot be adequately represented by a single structural formula.
(ii) A reversible isomeric change.
(iii) A reaction which is catalysed by acids and by bases.

(b) Predict the outcome of the following experiments:

(i) 2-Methylpropene ($Me_2C{=}CH_2$) is treated with concentrated sulphuric acid and then with water.
(ii) A mixture of 1 mole of ethyl benzoate and 1 mole of ethyl 2,4,6-trimethylbenzoate is heated with water containing 1 mole of potassium hydroxide.
(iii) Phenyl ethyl ether is treated with concentrated hydriodic acid. (C Schol.)

77 Explain **five** of the following observations:

(a) Glycine, $C_2H_5O_2N$, is soluble in water and insoluble in ether.
(b) Ethanal and methanal react differently with aqueous sodium hydroxide.
(c) From a mixture of ethene and ethyne, ethene may easily be separated.

(d) A ketone, $C_5H_{10}O$, is known which does not give the iodoform reaction.
(e) The reaction between iodoethane and silver cyanide yields two *isomeric* compounds.
(f) A compound, C_2H_3ClO, reacts violently with ethanol, evolving an acidic gas. (O and C)

78 Explain:
(a) The function of sulphuric acid in the nitration of benzene.
(b) The ease with which phenol is nitrated compared with benzene.
(c) The increase in acid strength as the hydrogen atoms of the methyl group in ethanoic acid are successively replaced by chlorine atoms.
(d) The low yield of ethanal when a mixture of calcium methanoate and ethanoate is heated.
(e) The reluctance of bromine to add on to ethene if the walls of the vessel containing the gases are covered with inert wax. (SUJB(S))

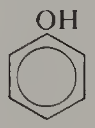
79 Suggest explanations for the following observations:
(a) The apparent molecular weight of ethanoic acid calculated from physical measurements was found to be 55 using a solution of the acid in water and 120 using a solution of the same concentration in benzene.
(b) A solution of 2-hydroxypropanoic acid isolated from a natural source rotated polarised light to the right, whereas a solution of 2-hydroxypropanoic acid synthesised from ethanal did not rotate polarised light.
(c) Phenylethene, $C_6H_5.CH{:}CH_2$, changed into a hard, transparent solid on standing in air. (C(S))

80 Describe briefly how you would obtain **one** constituent in a pure condition from **each** of the following mixtures (a chemical method is required in **each** case):
(a) phenol and benzenesulphonic acid;
(b) ethanol and propanone;
(c) ethanoic acid and methanoic acid;
(d) phenylamine and chlorobenzene;
(e) benzene and methylbenzene. (C(N))

81 By using *simple laboratory procedures* indicate how you would obtain a pure specimen of the compound with the first structure from each of the following mixtures:

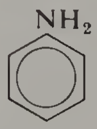
(a) $CH_3.CH_2.CH_2.CH_3$ $\quad$ $CH_3.CH_2.CH{=}CH_2$ $\quad$ $CH_3.C{\equiv}C.CH_3$

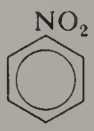
(b)



(c) $CH_3{\cdot}CO{\cdot}CH_3$ $\quad$ $CH_3{\cdot}CH_2{\cdot}OH$

(d)





Physical methods alone will not be accepted and all chemical reactions must be fully explained. (SUJB(S))

82 Describe and explain how you would obtain a sample of the first named substance from **each** of the following mixtures:

(a) ethanol and water;
(b) phenol and ethanoic acid;
(c) ethane and ethene;
(d) chloroethane and ethylamine. (C(N))

83 Give one example in each case of a reaction involving

(a) homolytic fission of a C—H bond;
(b) heterolytic fission of a C—halogen bond;
(c) formation of a C—C bond.

Suggest a possible mechanism for each reaction that you mention.

(O Schol.)

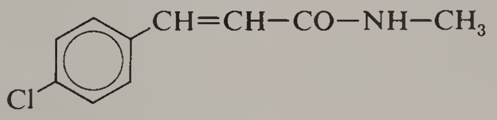
84 Write short notes on the types of reactions which establish new carbon–carbon bonds. (C Schol.)

85 (i) In **two** of the following cases, write formulae to illustrate reactions in which

(a) a new carbon–carbon bond is made;
(b) a new carbon–nitrogen bond is made;
(c) an existing carbon–oxygen bond is broken.

[Give two or three examples in each case, with the names of the substances, the reagents and the essential conditions. *No* further account is required.]

(ii) Show which bonds in the following molecule could be broken (a) by oxidation, and (b) by hydrolysis. Write the formulae of the products.



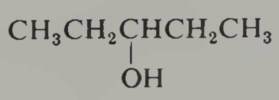
(O Schol.)

86 Give a well-ordered account of methods of forming carbon–carbon bonds in organic chemistry.

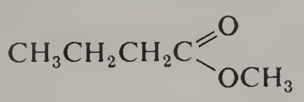
What would you expect the yield of propane to be in the Wurtz reaction between sodium and an equimolar mixture of iodomethane and iodoethane?

(O Schol.)

87 Suggest syntheses for **five** of the following compounds, starting from readily available chemicals containing not more than 3 carbon atoms for aliphatic compounds, or 6 carbon atoms for aromatic compounds:

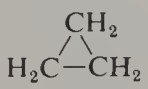


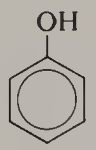
$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$

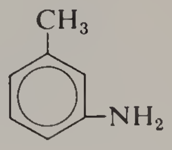


$CH_3CH_2CH_2C(=O)OCH_3$

$CH_3CH=CHCH_3$







$CH_3(CH_2)_2CH_2OCH_2(CH_2)_2CH_3$ (C Schol.)

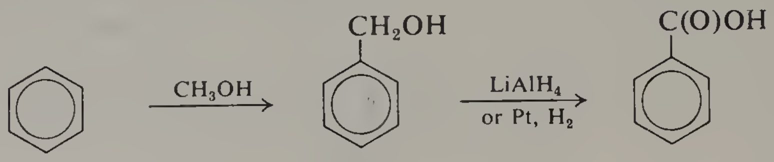
88 Answer **three** of the following. On an examination paper, a student offered the suggestions given below for carrying out a series of conversions of organic compounds. Point out the errors made by this student, and where the method was not correct, offer suggestions by which the desired conversion *could* be carried out:

(a) $CH_3CH_2OH \xrightarrow{NaCl} CH_3CH_2Cl \xrightarrow[\text{(ii) HCHO}]{\text{(i) Mg, ether}} CH_3CH_2CHO$;

(b) $CH_3CH_2C(O)CH_3 \xrightarrow{NaOH} CH_3CH_2C(O)OH \xrightarrow[NaOH]{CH_3OH}$
$CH_3CH_2C(O)OCH_3$;

(c) $CH_3CH{=}CH_2 \xrightarrow{H_2O} CH_3CH(OH)CH_3 \xrightarrow{NaOH}$
$CH_3CH(ONa)CH_3 \xrightarrow{CH_3I} CH_2CH(OCH_3)CH_3$;

(d)

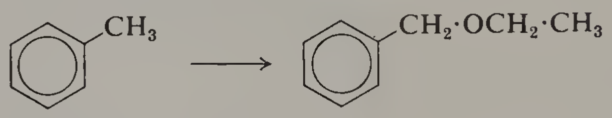


(C Schol.)

89 Write feasible schemes (formulae and reagents, and conditions where relevant) for **four** of the following transformations:

(a) $CH_3.CH_2.OH \rightarrow HC{\equiv}CH$;
(b) $C_6H_6 \rightarrow C_6H_5CN$;
(c) $CH_3.CO.CH_3 \rightarrow CH_3.CH(CO_2H).CH_3$;

(d)



(e) $CH_2{=}CH_2 \rightarrow CH_3.CO.OCH_2.CH_2.OCO.CH_3$;
(f) $NH_3 \rightarrow H_2N.CO.NH.CO.NH_2$. (O Schol.)

90 In each of these questions a statement is followed by five alternative responses. Only one of these alternatives is correct. Indicate your choice of *A*, *B*, *C*, *D* or *E*.

(i) Which one of the following is a polyester?
A 1,2-diaminohexane;
B poly(chloroethene);
C Terylene;
D Nylon 6.6;
E poly(phenylethene).

(ii) Which one of the following statements is necessarily an inaccurate description of the homolytic fission of a chemical bond?
A One of the atoms leaves with both of the electrons forming the bond.
B The fission is promoted by ultraviolet light.
C The fission gives atoms or radicals.
D The fission is assisted by heat.
E The fission can occur in either the gaseous or the liquid phase.

(iii) When equal volumes of ethanoyl chloride and ethanol are mixed and the mixture is then poured into excess cold dilute alkali, which one of the following statements best describes the change which takes place?
A A white precipitate is thrown down.
B A vinegar-like smell is discernible.
C A pleasant fruity smell is discernible.
D A pungent smell of hydrogen chloride is discernible.
E A vigorous effervescence ensues.

(iv) Which one of the following groups of products is formed when methane and chlorine are mixed in the dark?

A chloromethane and hydrogen chloride;
B chloromethane, dichloromethane and hydrogen chloride;
C trichloromethane, tetrachloromethane and hydrogen chloride;
D no products are formed;
E hydrogen chloride and a deposit of carbon.

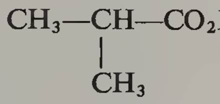
(v) Which one of the compounds having the following structural formulae can be resolved into optical isomers?

A $NH_2.CH_2COOH$;
B $NH_2.CH(CH_3).COOH$;
C $CH_3.CH{=}CH.C_2H_5$;
D $HOOC.CH_2.CH(CH_3).CH_2.COOH$;
E $HO.CH_2.CH_2.C(CH_3)_2.CH_2.NH_2$.

(vi) Which of the following reagents does not react with ethanal?

A NH_3; *B* CN^-; *C* $CH_3.CO_2C_2H_5$;
D BH_4^-; *E* acidified MnO_4^-.

(vii) The compound $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CO_2H$ was produced by oxidation. Which one of the following compounds was the most likely starting material?



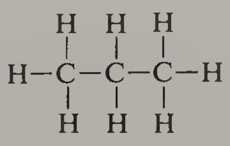
A butan-1-ol;
B 2-methylpropan-1-ol;
C butan-2-ol;
D 2-methylpropan-2-ol;
E propan-2-ol. (JMB (Specimen paper))

91 For each of the following reactions choose from the list *A–E* the most appropriate reaction type.

A nucleophilic addition; *B* electrophilic addition;
C nucleophilic substitution; *D* electrophilic substitution;
E redox

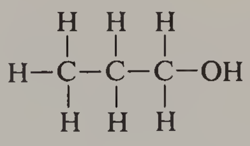
$$C_6H_6 + Br_2 \xrightarrow{AlBr_3} C_6H_5Br$$
$$C_6H_5.CHO \xrightarrow[\text{solution}]{\text{Fehling's}} C_6H_5.COOH$$
$$CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2Br$$
$$C_6H_5.CHO + NaHSO_3 \longrightarrow C_6H_5.CH(OH).SO_3Na$$

The following formulae represent the structure of five organic compounds.



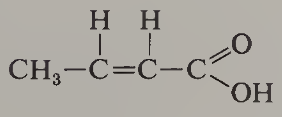
$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H$

A



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

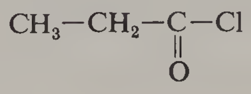
B



C

$C_6H_5NH_2$

D



$CH_3{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}Cl$

E

By using the appropriate letter for the compounds answer the questions which follow and give the equation where indicated.

(a) Which compound will form a salt with mineral acids?

(b) Which compound will react with an organic acid in the presence of a mineral acid to form an ester?

(c) Which compound will decolorise both bromine water and dilute acidified potassium permanganate solution?

(d) Which compound would form an aldehyde on oxidation?

(e) Which compound would you expect to react vigorously with water?

(JMB (Specimen paper))

92 (a) Give the structural formula for each of the following compounds. (The formulae should be abbreviated to the type: $CH_3.CHCl.CH_2.CH_3$).

A sodium hexanoate
B 3-methylpenta-2,4-diene
C 4-bromo-2-methylpentan-1-ol
D 2-methylpentane-1,4-diol

(b) Which one of the compounds would be the most likely starting point for the development of a new polymer?

(c) Which one of the compounds would be most likely to leave a solid residue when it is strongly heated in air?

(d) State briefly how *C* could be converted into *D* (the isolation of the product is not required).

(e) (i) Which one of the compounds is most likely to be a solid at room temperature?

(ii) State briefly the reasons for your answer.

(f) If you were given unlabelled samples of *B*, *C* and *D*, state briefly how you would quickly distinguish between them using the least number of tests and observations. (L(Nuffield))

93 Given samples of D_2O and CD_3OH as the only deuterium-containing compounds, but having available any other organic or inorganic compounds, how would you prepare

CD_3CO_2H, CH_3CO_2D, CH_3CHDCH_2D, $CH_3CHBrCH_2D$, CD_3CH_2OH?

(O and C(S))

94 Compare and contrast the reaction of benzene with concentrated sulphuric acid at 80°C with that of ethene and concentrated sulphuric acid at the same temperature.

How can the formation of a new carbon–sulphur bond in one case, but not in the other, be explained in mechanistic terms, and to what extent do the results justify the inclusion of benzene in a class of hydrocarbons separate from the alkenes?

Dimethyl sulphate, $CH_3O.SO_2.OCH_3$, an ester of sulphuric acid, is a methylating agent. It reacts with sodium ethoxide to give methoxyethane. On the other hand the ester methyl ethanoate does not give methoxyethane on reaction with sodium ethoxide. Both of the esters are hydrolysed by aqueous alkali to methanol. How can these results be explained? O(S)

Appendix III

Apparatus and chemicals

Apparatus with ground-glass joints is described throughout this book. In this way, preparations and reactions can be studied more rapidly than with older apparatus.

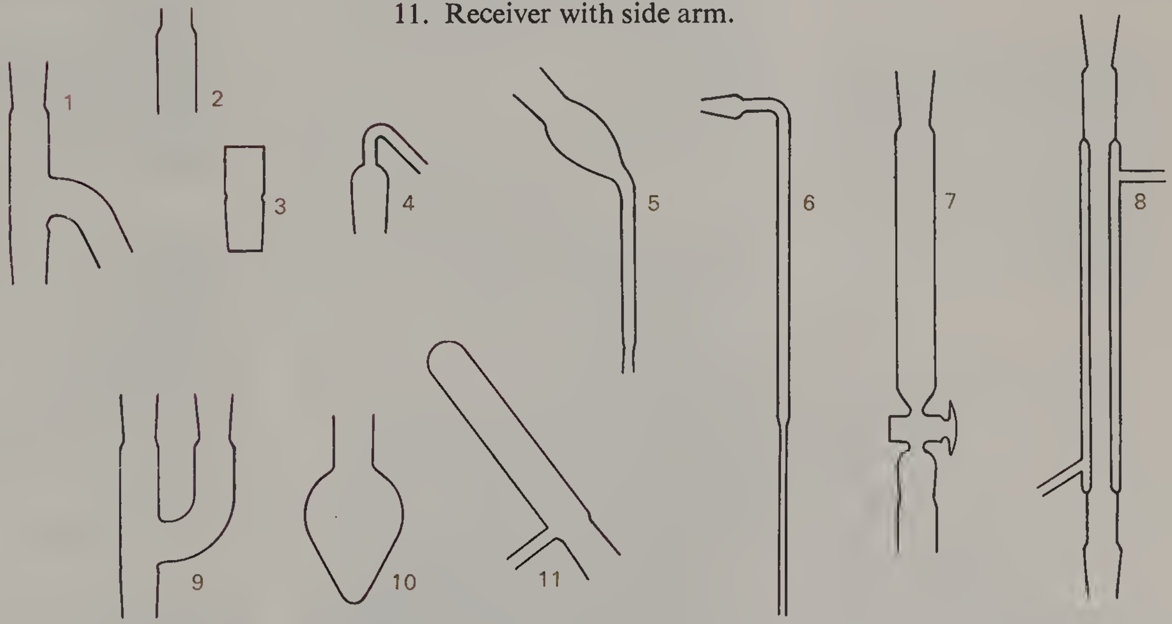
Sensible precautions ensure a long life for the apparatus. The joints must be clean and the flasks must be heated over a gauze, or in a water- or oil-bath, by means of a small flame from a microburner or bunsen burner.

The same apparatus as described in *Organic Chemistry through Experiment* (D. J. Waddington and H. S. Finlay, Bell and Hyman Ltd) is used, namely that produced in conjunction with Philip Harris Ltd. The number of pieces has been reduced to a minimum and the set consists of:

1. Stillhead;
2. Adaptor for thermometer, steam lead or air leak;
3. Stopper;

4 and 5. Adaptors for collection of gases;

6. Steam lead which can also be used as an air leak;
7. Dropping funnel, which can also be used as a separating funnel;
8. Water condenser, which can also be used as an air condenser;
9. Flask head;
10. 50 cm³ pear-shaped flask. A 100 cm³ round-bottomed flask may be used instead;
11. Receiver with side arm.



An air condenser, fractionating column and an air leak (for vacuum distillation) can also be obtained.

Test-tube preparations of gases and liquids are used throughout the book for they can be done quickly, and many of the properties of compounds are studied by experiments using test-tubes and other simple equipment. Standard sized Pyrex test-tubes (150 × 16 mm) and delivery tubes made from soda-glass tubing (4 mm i.d.) are convenient to use. Dropping pipettes may be made from soda-glass tubing (6 mm i.d.) and using cylindrical rubber teats. These should be calibrated in 0·5 cm³ portions with a small dab of paint, the calibration saving much time during experiments.

A list of organic and inorganic reagents is given in this Appendix and a list of suppliers in Appendix IV.

Organic reagents

Alkylbenzene (Appendix IV)

Benzaldehyde
Benzoic acid
Benzoyl chloride
Bis-(2-aminoethyl)amine (diethylene triamine) (Appendix IV)
Bromobenzene
1-Bromobutane
2-Bromobutane
2-Bromo-2-methylpropane
Butan-1-ol
Butenedioic anhydride (maleic anhydride)

Caradate 30 (Appendix IV)
Caradol C2 (Appendix IV)
Carbamide (urea)
Chlorobenzene
2-Chlorobenzoic acid
1-Chlorobutane
2-Chlorobutane
(Chloromethyl)benzene (benzyl chloride)
Cotton wool
Cyclohexane
Cyclohexanol
Cyclohexene

Decanedioyl chloride (sebacoyl chloride) (Appendix IV)
1,6-Diaminohexane
Dichlorodimethylsilane (Appendix IV)
1,1-Dichloroethane
1,2-Dichloroethane
Di(dodecanoyl) peroxide (lauroyl peroxide) (Appendix IV)
Diethyl ether
2,4-Dinitrophenylhydrazine. 1 g in 50 cm³ of methanol to which 2 cm³ of *concentrated* sulphuric acid is added. Filter if necessary
Dodecanol (Appendix IV)

Epikote 815 (Appendix IV)
Ethanal (acetaldehyde)
Ethanamide (acetamide)
Ethanedioic acid (oxalic acid)
Ethane-1,2-diol (ethylene glycol)
Ethanoic acid (acetic acid)
Ethanoic anhydride (acetic anhydride)
Ethanol
Ethanenitrile (acetonitrile)
Ethanoyl chloride
Ethyl benzoate

Formalin, 40 per cent solution of methanal in water
Fructose
Fuchsin

Glucose
Glycine

Hexane (or pentane)
Hexanedioyl chloride (adipyl chloride) (Appendix IV)

1-Iodobutane

Lard (or olive oil)
Light petroleum, b.p. 60–80°C

Malachite green
Methanoic acid (formic acid)
Methanol
Methylamine, 33 per cent solution in water
Methylammonium chloride
Methylbenzene (toluene)
2-Methylbutan-2-ol
Methylene blue
2-Methylpropan-2-ol

Naphthalen-2-ol (β-naphthol)
Ninhydrin
Nitrobenzene
Nitroethane (Appendix IV)
2-Nitrophenol
4-Nitrophenol
Nylon-6, pellets (Appendix IV)

Oil, crude
Olive oil (or lard)

Paraffin oil
Pentane (or hexane)
Pentan-3-one (diethyl ketone)
Pent-1-ene (Appendix IV)
Perspex, chips
Phenol
Phenylamine (aniline)
Phenylethanone (acetophenone)
Phenylethene (styrene) (Appendix IV)
Phenylethyne (phenylacetylene) (Appendix IV)
Phenylhydrazine
Phenylmethanol (benzyl alcohol)

(Phenylmethyl)amine (benzylamine)
Proline
Propane-1,2,3-triol (glycerol)
Propan-2-ol
Propanone (acetone)

Schiff's reagent. 0·1 per cent solution of fuchsin in water through which sulphur dioxide is passed until the solution is colourless
Sodium ethanedioate (sodium oxalate)
Sodium ethanoate (sodium acetate), anhydrous
Sodium methanoate (sodium formate)
Sodium potassium 2,3-dihydroxybutanedioate (sodium potassium tartrate)
Starch, soluble
Sucrose

Tetrachloromethane
Trichloromethane (chloroform)
Triphenylchloromethane (Appendix IV)
Tris-(2-hydroxyethyl)amine (triethanolamine)

Urease (Appendix IV)

Inorganic reagents

Alumina, for chromatography
Aluminium, powder
Aluminium chloride, anhydrous
Ammonia solution, (a) concentrated, (b) 2M solution

Bleaching powder
Bromine, (a) liquid, (b) saturated aqueous solution

Calcium dicarbide
Calcium chloride, anhydrous
Calcium hydroxide, saturated solution (lime-water)
Chlorosulphonic acid
Copper(II) carbonate
Copper (I) chloride
Copper(II) oxide
Copper(II) sulphate, anhydrous

Disodium pentacyanonitrosylferrate(III) (sodium nitroprusside)

Fehling's solution I. 7 g of copper(II) sulphate pentahydrate in 100 cm^3 of water

Fehling's solution II. 12 g of sodium hydroxide and 5 g of sodium potassium 2,3-dihydroxybutanedioate (tartrate) in 100 cm^3 of water

Hydrochloric acid, (a) concentrated, (b) 2M solution

Iodine, (a) solid, (b) 1 per cent solution in 20 per cent solution of potassium iodide
Iron, filings
Iron(III) chloride
Iron(II) sulphate

Lithium tetrahydridoaluminate

Magnesium, turnings for Grignard reactions
Magnesium sulphate, anhydrous
Mercury(II) chloride

Nitric acid, (a) concentrated, (b) 2M solution

Phosphoric acid, concentrated
Phosphorus pentachloride
Platinum, wire (about 28 s.w.g.)
Potassium bromide
Potassium carbonate, anhydrous
Potassium dichromate
Potassium hydroxide, pellets
Potassium manganate(VII)

Rocksil

Silica gel (Appendix IV)
Silver nitrate
Soda-lime
Sodium
Sodium carbonate, anhydrous
Sodium chloride
Sodium dichromate
Sodium hydrogencarbonate
Sodium hydroxide, (a) pellets, (b) 2M solution
Sodium metabisulphite
Sodium nitrate
Sodium nitrite
Sodium sulphate, anhydrous
Sulphur dioxide. Syphon
Sulphuric acid, (a) oleum, (b) concentrated, (c) M solution

Tin, granulated

Zinc, dust

Appendix IV

Suppliers of apparatus and chemicals

Most of the chemicals and apparatus can be obtained from all laboratory suppliers. If the following prove to be difficult to find, they may be obtained from the suppliers below:

	Supplier
Alkylbenzene	4, 6
Bis-(2-aminoethyl)amine (diethylene triamine)	1
Caradate 30	5
or Polyurethane foam, polymer B	2
Caradol GXR13	5
or Polyurethane foam, polymer A	2
Decanedioyl chloride (sebacoyl chloride)	1, 2, 3
Decanedioyl chloride (sebacoyl chloride, 5% in tetrachloromethane)	2, 3
Dodecanol	1, 3
Epikote 815	4
Hexanedioyl chloride (adipoyl chloride)	1, 2, 3
Hexanedioyl chloride (adipoyl chloride in ampoules. 5% in tetrachloromethane)	2, 3
Nitroethane	1, 2
Nylon-6 pellets	1, 2, 3
Nylon tubing, for column chromatography	7
Phenylethene (styrene)	1, 2, 3
Phenylethyne (phenylacetylene)	1
Silica gel G for thin-layer chromatography	1, 2, 3
Triphenylchloromethane	1

Suppliers

(1) B.D.H. Chemicals Ltd., Poole, Dorset, BH12 4NN
(2) Griffin and George Ltd., Ealing Road, Alperton, Wembley, Middlesex, HA0 1HJ or Braeview Place, Nerston, East Kilbride, Glasgow G74 3XJ or Ledson Road, Wythenshawe, Manchester, M23 9NP
(3) Philip Harris Ltd., Lynn Lane, Shenstone, Staffordshire, WS14 0EE
(4) Shell Chemicals U.K. Ltd., Public Relations Department, Downstream Building, Shell Centre, York Road, London SE1 7PG
(5) Strand Glassfibre Ltd., Brentway Trading Estate, Brentford, Middlesex TW8 8ER
(6) Education Section, Unilever PLC, P.O. Box 68. Unilever House, London EC4P 4BQ
(7) Walter Coles and Co. Ltd., Plastic Works, 47/49 Tanner Street, London SE1 3PL

Appendix V

Teaching aids and materials

The following are the addresses of some of the major companies and organisations producing teaching aids and materials, some of which have been specifically mentioned in the text.

Education Liaison Officer
Room 414
British Gas Corporation
326 High Holborn
London WC1V 7PT

BP Educational Services
Britannic House
Moor Lane
London EC2Y 9BU

Education Department
Esso Petroleum Company Limited
Esso House, Victoria Street
London SW1E 5JW

Schools Liaison Officer
I.C.I. Educational Publications
P.O. Box 96
1 Hornchurch Close
Coventry CV1 2QZ

Shell Education Service
Shell U.K. Limited
PO Box 148, Strand
London WC2R 0DX

Unilever Education Section
Unilever PLC
Unilever House, PO Box 68
London EC4P 4BQ

Schools Information Centre on the Chemical Industry
The Polytechnic of North London
Holloway Road
London N7 6DB

Public Relations Department
National Coal Board
Hobart House
Grosvenor Place
London SW1X 7AE

Information Officer
Institute of Petroleum
61 Cavendish Street
London W1M 8AR

Films (F) and videotapes (V) are suggested in the text. Those obtainable free are marked with an asterisk (*).

British Petroleum: application to borrow BP films should be made to the BP Film Library, 15 Beaconsfield Road, London NW10 2LE. Enquiries concerning the purchase of films should be addressed to Films/TV Branch, Information Department, The British Petroleum Company Limited, Britannic House, Moor Lane, London EC2Y 9BU.

Educational Foundation for Visual Aids, National Audio-Visual Aids Library, Paxton Place, Gipsy Road, London SE27 9SS.

Gas Council Film Library, 59 Bryanston Street, London W1A 2AZ.

Guild Organisation Ltd., Woodston House, Oundle Road, Woodston, Peterborough PE2 9PZ.

Shell Film Library, 25 The Burroughs, Hendon, London NW4 4AT.

Unilever films are handled by the National Audio-Visual Aids Library (see above) but special enquiries may be addressed to The Film Librarian, Unilever Films, Unilever House, PO Box 68, London EC4P 4BQ. In Scotland, Unilever films are obtainable from the Scottish Central Film Library, Glasgow G3 7XN.

ICI videotapes may be purchased from Argus Film and Video Library, 15 Beaconsfield Road, London NW10 2LE.

Open University films may be bought from Open University Educational Enterprises Ltd., 12 Cofferidge Close, Stony Stratford, Milton Keynes MK11 1BY, or hired from Guild Organisation Ltd. (see above). Open University videotapes may be bought from Guild Organisation Ltd.

Appendix VI

Physical constants

International relative atomic masses

($^{12}C = 12{\cdot}000000$)

Element	*Relative atomic mass*	*Element*	*Relative atomic mass*
Aluminium	26·9815	Nitrogen	14·0067
Bromine	79·909	Oxygen	15·9994
Calcium	40·08	Phosphorus	30·9738
Carbon	12·01115	Platinum	195·09
Chlorine	35·453	Potassium	39·102
Copper	63·54	Silicon	28·086
Fluorine	18·9984	Silver	107·870
Hydrogen	1·00797	Sodium	22·9898
Iodine	126·9044	Sulphur	32·064
Iron	55·847	Tin	118·69
Lead	207·19	Zinc	65·37
Magnesium	24·312		

Masses of isotopes relative to ^{12}C

^{1}H	1·0078246	^{35}Cl	34·9688531
^{14}N	14·0030738	^{37}Cl	36·9659034
^{16}O	15·9949141	^{79}Br	78·91839
^{31}P	30·973764	^{81}Br	80·91642
^{32}S	31·9720727	^{127}I	126·90466

Some aldehydes and ketones and the 2,4-dinitrophenylhydrazone derivatives

For Experiment 12, Section 12.7, p. 186.

	B.p. (°C) of the aldehyde or ketone	*M.p. (°C) of the 2,4-Dinitrophenylhydrazone*
Methanal	–21	166
Ethanal	21	168
Propanal	49	155
Butanal	75	123
2-Methylpropanal	64	187
Pentanal	104	98
Benzaldehyde	179	237
2-Hydroxybenzaldehyde	197	252
4-Methoxybenzaldehyde	248	254
4-Methylbenzaldehyde	204	233

Propanone	56	128
Butan-2-one	80	115
Pentan-2-one	102	144
Pentan-3-one	102	156
Heptan-4-one	144	75
Phenylethanone	202	250
4-Methylphenylethanone	224	258
Diphenylmethanone	306 (m.p. 49°C)	238

Index

Page numbers in **bold** type refer to experimental work

Now in its fourth edition this well established book is designed for 'A' level students and for many college courses. It will also be useful for the early part of some university courses.

This new edition maintains the structure of earlier editions. The preparations and properties of organic compounds are set out in terms of functional groups and against a background of the principles of bonding, energetics and reaction mechanisms.

However, organic chemistry is a constantly evolving subject and the new edition reflects this, in particular, in introducing

- the newer techniques for the separation and purification of organic compounds
- the newer techniques for the determination of molecular structures
- the latest industrial processes which themselves reflect the response of industry to rising costs of basic feedstocks (oil) and energy, and the use of alternative feedstocks throughout the world (e.g. natural gas in the U.K., biomass in developing countries). These changes have been dramatic and form the basis of two chapters
- a chapter on possible developments in the future, with its emphasis on biotechnology and newer catalysts.

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