

ELBS

Modern Organic Chemistry

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

Fourth Edition

LOW-PRICED EDITION

Modern Organic Chemistry

Fourth Edition

**R. O. C. Norman, MA, DSc, C Chem,
FRSC, FRS**

Professor of Chemistry, University of York

**D. J. Waddington, BSc, ARCS, DIC,
PhD**

Formerly Head of the Science Department, Wellington College.
Professor of Chemical Education, University of York

ELBS

**English Language Book Society
and
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

ELBS edition first published 1977
Reprinted 1978, 1980
ELBS edition of the fourth edition 1984

© R O C Norman and D J Waddington 1972, 1981, 1983

All rights reserved. No part of this publication
may be reproduced, stored in a retrieval
system, or transmitted in any form or by any
means, electronic, mechanical, photocopying,
recording or otherwise, without the prior
permission of Bell & Hyman Limited.

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 2365 4

Produced in Great Britain by Blantyre Printing & Binding Ltd.,
London and Glasgow

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.

Contents

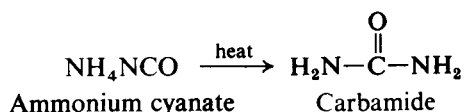
	<i>Page</i>
Preface	vii
Acknowledgements	ix
CHAPTER	
1 Introduction to Organic Chemistry	1
2 Preparation and Purification of Organic Compounds	12
3 Determination of the Structure of an Organic Compound	33
4 Bonding in Organic Compounds	50
5 Alkanes	69
6 Alkenes	79
7 Alkynes	94
8 Aromatic Compounds	99
9 Halogen Compounds	116
10 Alcohols and Phenols	143
11 Ethers	166
12 Aldehydes and Ketones	171
13 Carboxylic Acids	189
14 Derivatives of Carboxylic Acids	211
15 Isomerism	235
16 Amines	251
17 Nitro Compounds	274
18 Naturally Occurring Compounds	281
19 Petroleum	301
20 The Petrochemical Industry	314
21 Polymers	327
22 Looking to the Future	345
APPENDIX	
I Summary of Industrial Processes	348
II Questions	353
III Apparatus and Chemicals	373
IV Suppliers of Apparatus and Chemicals	376
V Teaching Aids and Materials	377
VI Physical Constants	379
INDEX	381

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:



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.

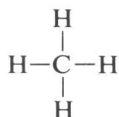
Today, the distinction between organic and inorganic chemistry is an arbitrary one. Organic chemistry is regarded as the chemistry of compounds of carbon other than its oxides, the metallic carbonates and related compounds.

1.2 Bonding

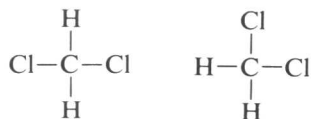
The bonds which carbon forms are covalent: that is, each bond is formed by the sharing of two electrons, one of which is provided by the carbon atom and one by the other atom. Carbon has four electrons available for sharing, so that it forms four bonds; a fuller description is given later (Chapter 4). 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, CH₄, 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

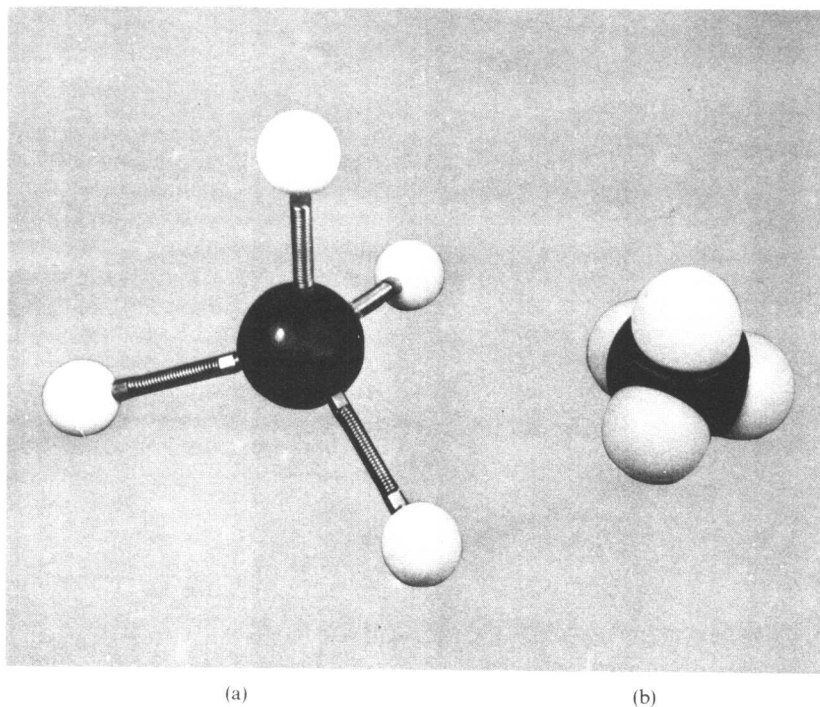


However, two-dimensional representations can be misleading and care must be exercised in their use. For instance, it might appear that there would be two compounds with the formula CH_2Cl_2 :



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

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

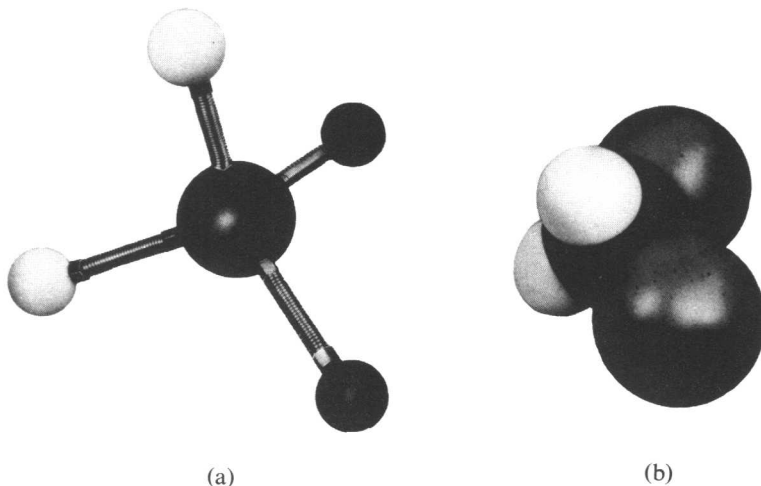


It is useful to have a simple set of molecular models to consider problems like this; they can provide a quick means of translating the planar representations on paper into the more realistic three-dimensional structures.

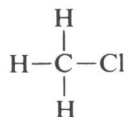
The simplest models are called **ball and spring**. The balls are coloured differently to represent different atoms, and have holes drilled in them corresponding to the number of bonds they can form. The balls are joined

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.

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).

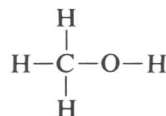


A carbon atom can be attached to monovalent atoms other than hydrogen. For example, one chlorine atom can replace one hydrogen atom to give chloromethane (also called methyl chloride):

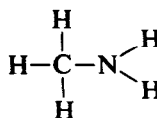


Again for simplicity, some or all of the bonds are usually omitted in representing these compounds, so that chloromethane is written as $\text{CH}_3\text{—Cl}$ or CH_3Cl . Replacement of more than one of the hydrogen atoms by chlorine atoms gives the compounds dichloromethane (CH_2Cl_2), trichloromethane (CHCl_3) and tetrachloromethane (CCl_4).

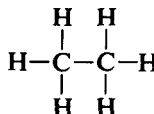
Carbon can be bonded to a divalent atom, as in methanol, CH_3OH :



to a trivalent atom, as in methylamine, CH_3NH_2 :



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

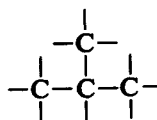


Notice that ethane can be written as above or as C_2H_6 , but not as CH_3 ; although the formula CH_3 describes the *relative* numbers of each kind of atom correctly, it does not give adequate information about the total number of atoms in the molecule. For this purpose, the **molecular formula** must 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 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 kJ mol^{-1} for its rupture, the energy of the C—C bond is calculated to be 345 kJ mol^{-1} . This is a very high value as compared with those for other elements joined by single bonds (e.g. 163 kJ mol^{-1} for N—N and 146 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.

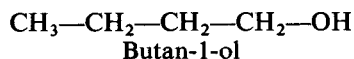
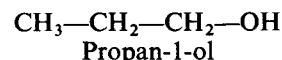
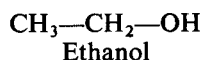
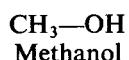


There are also compounds in which some of the bonds between carbon atoms are double or triple bonds (1.5) or in which the atoms form rings (1.6). All these possibilities increase still further the number of carbon compounds which can be formed.

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 $\text{C}_n\text{H}_{2n+2}$. 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,



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

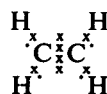
Several homologous series can be considered to be derived from the alkanes, $\text{C}_n\text{H}_{2n+2}$, a hydrogen atom being replaced by a functional group. The group formed from the alkane, $\text{C}_n\text{H}_{2n+1}$, is known as the **alkyl group**, and is often represented by the letter R.

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

<i>Alkane</i> $\text{C}_n\text{H}_{2n+2}(\text{RH})$	<i>Alkyl group</i> $\text{C}_n\text{H}_{2n+1}(\text{R})$
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

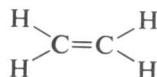
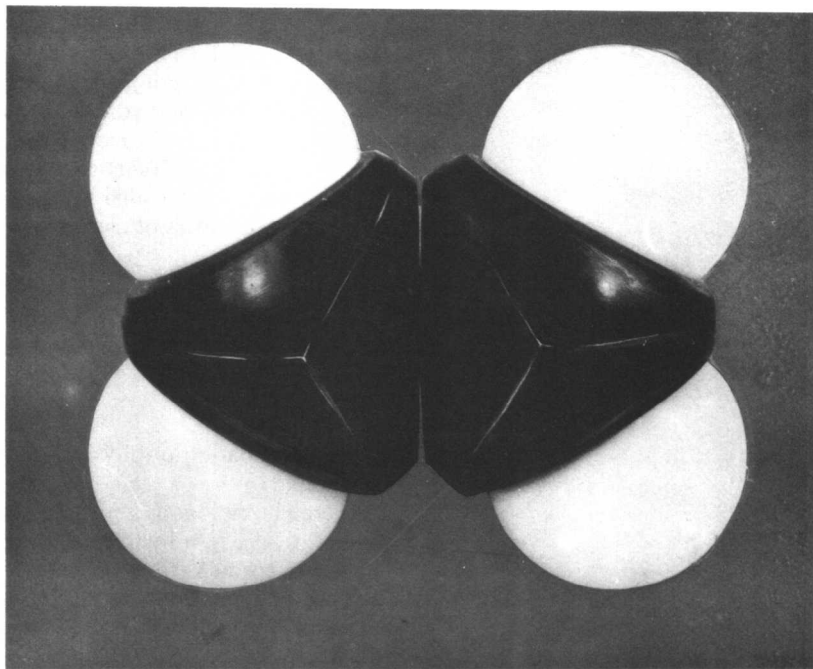
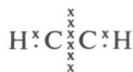


Plate 1.3. A space-filling
molecular model of ethene



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



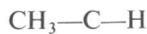
The carbon and hydrogen atoms lie in a straight line (Plate 1.4) and the molecule is described as *linear*. A simple representation is



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



Ethanenitrile



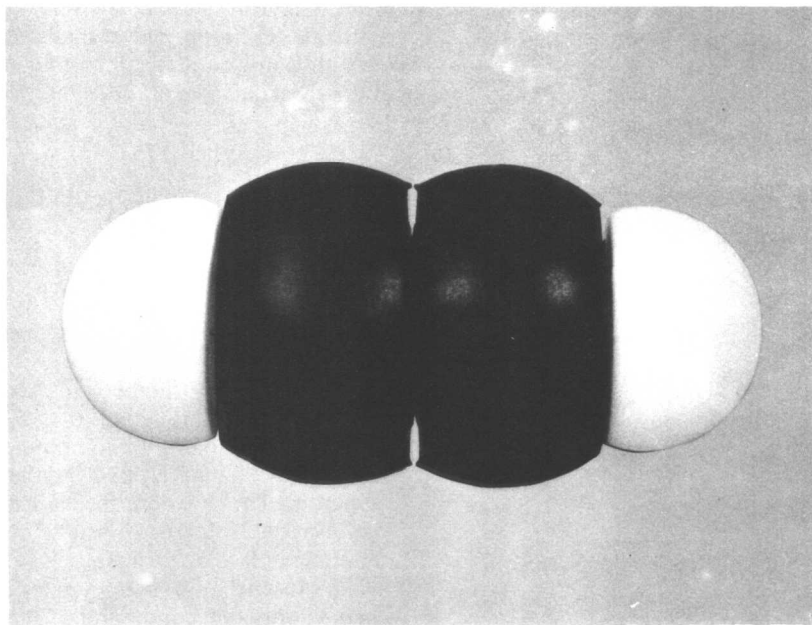
Ethanal



Ethanoic acid

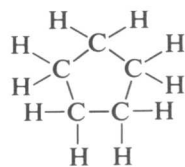
The groups $\text{C}\equiv\text{N}$, $\text{C}=\text{O}$ and CO_2H are called the nitrile, carbonyl and carboxylic acid groups, respectively.

Plate 1.4. A space-filling molecular model of ethyne



1.6 Aliphatic, alicyclic and aromatic compounds

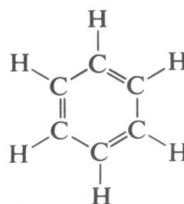
The compounds we have mentioned so far have had carbon atoms joined in straight chains or branched chains, and these are described as **aliphatic**. There are also compounds in which some of the atoms form a ring, e.g.



Cyclopentane

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

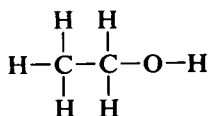
There is a special class of ring compound of which benzene is the parent:



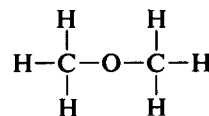
A large number of compounds contain the same carbon ring but have atoms or groups other than hydrogen attached to it. For example, writing benzene as C_6H_6 , chlorobenzene is C_6H_5-Cl . Compounds of this nature were originally termed **aromatic** because some of them have pleasant smells (Greek: *aroma*, 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 :



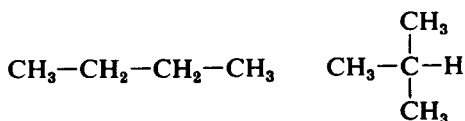
Ethanol



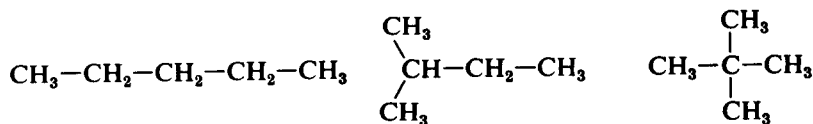
Dimethyl ether

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.

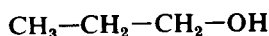
The existence of a large number of isomers is illustrated by the alkanes. There is only one compound of molecular formula CH_4 (methane), C_2H_6 (ethane) or C_3H_8 (propane). There are two of molecular formula C_4H_{10} :



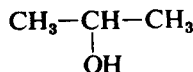
and three of molecular formula C_5H_{12} :



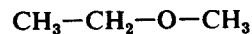
Because carbon atoms can be joined in straight and in branched chains, the number of possible isomers increases very rapidly as the number of carbon atoms increases; for example, there are 5 isomers with molecular formula C_6H_{14} and 18 with molecular formula C_8H_{18} . When other atoms are introduced, 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:



Propan-1-ol



Propan-2-ol

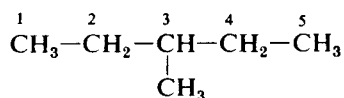


Ethyl methyl ether

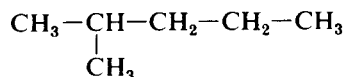
1.8 Nomenclature of carbon compounds

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,



is termed 3-methylpentane. The compound



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 $\text{C}=\text{C}$ 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.



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

The unsaturated compounds with a $\text{C}\equiv\text{C}$ triple bond, which are often described as acetylenes after the simplest member of the series, acetylene itself ($\text{CH}\equiv\text{CH}$), 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