



ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Objectives

After studying this unit, you will be able to:

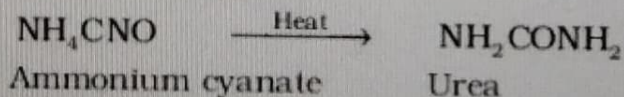
- understand reasons for tetravalence of carbon and shapes of organic molecules;
- write structures of organic molecules in various ways;
- classify the organic compounds;
- name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;
- understand the concept of organic reaction mechanism;
- explain the influence of electronic displacements on structure and reactivity of organic compounds;
- recognise the types of organic reactions;
- learn the techniques of purification of organic compounds;
- write the chemical reactions involved in the qualitative analysis of organic compounds;
- understand the principles involved in quantitative analysis of organic compounds.

In the previous unit you have learnt that the element carbon has the unique property called **catenation** due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called **organic chemistry**. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds.

12.1 GENERAL INTRODUCTION

Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic compounds appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.



The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory.

The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape.

12.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

12.2.1 The Shapes of Carbon Compounds

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure in Unit 4. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of s and p orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp^3 , sp^2 and sp hybrid orbitals by carbon atoms in the respective molecules.

Hybridisation influences the bond length and bond enthalpy (strength) in compounds. The sp hybrid orbital contains more s character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp^3 hybrid orbital. The sp^2 hybrid orbital is intermediate in s character between sp and sp^3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the s character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an sp hybrid orbital with 50% s character is more electronegative than that possessing sp^2 or sp^3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units.

12.2.2 Some Characteristic Features of π Bonds

In a π (pi) bond formation, parallel orientation of the two p orbitals on adjacent atoms is necessary for a proper sideways overlap.

Thus, in $\text{H}_2\text{C}=\text{CH}_2$ molecule all the atoms must be in the same plane. The p orbitals are mutually parallel and both the p orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of p orbitals and, therefore, such rotation about carbon-carbon double bond ($\text{C}=\text{C}$) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.

Problem 12.1

How many σ and π bonds are present in each of the following molecules?

(a) $\text{HC}\equiv\text{CCH}=\text{CHCH}_3$ (b) $\text{CH}_2=\text{C}=\text{CHCH}_3$

Solution

(a) $\sigma_{\text{C-C}}: 4; \sigma_{\text{C-H}}: 6; \pi_{\text{C=C}}: 1; \pi_{\text{C}\equiv\text{C}}: 2$

(b) $\sigma_{\text{C-C}}: 3; \sigma_{\text{C-H}}: 6; \pi_{\text{C=C}}: 2$

Problem 12.2

What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl , (b) $(\text{CH}_3)_2\text{CO}$, (c) CH_3CN ,

(d) HCONH_2 , (e) $\text{CH}_3\text{CH}=\text{CHCN}$

Solution

(a) sp^3 , (b) sp^3 , sp^2 , (c) sp^3 , sp , (d) sp^2 , (e) sp^3 , sp^2 , sp^2 , sp

Problem 12.3

Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

(a) $\text{H}_2\text{C}=\text{O}$, (b) CH_3F , (c) $\text{HC}\equiv\text{N}$.

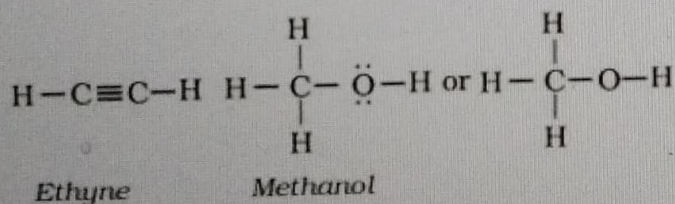
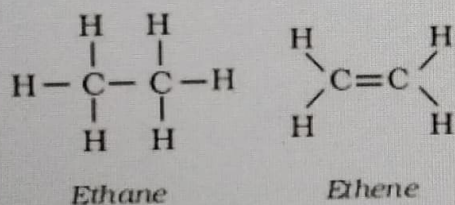
Solution

(a) sp^2 hybridised carbon, trigonal planar; (b) sp^3 hybridised carbon, tetrahedral; (c) sp hybridised carbon, linear.

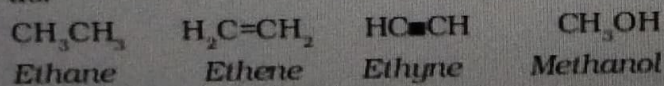
12.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

12.3.1 Complete, Condensed and Bond-line Structural Formulas

Structures of organic compounds are represented in several ways. The *Lewis structure* or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (-). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lone-pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called *complete structural formulas*.

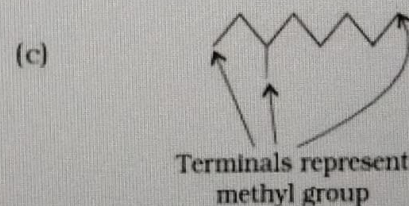
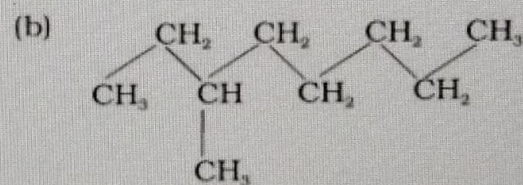
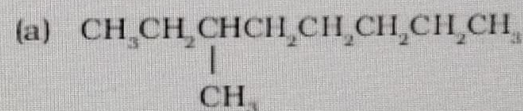


These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a *condensed structural formula*. Thus, ethane, ethene, ethyne and methanol can be written as:

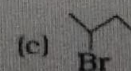
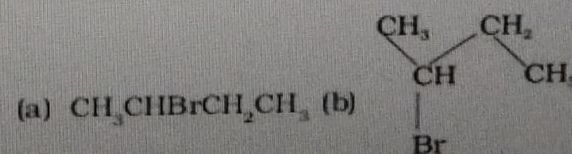


Similarly, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ can be further condensed to $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this *bond-line structural* representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a *zig-zag* fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl ($-\text{CH}_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows:

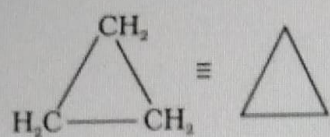
(i) 3-Methyloctane can be represented in various forms as:



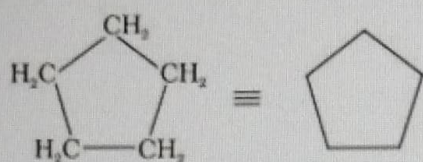
(ii) Various ways of representing 2-bromobutane are:



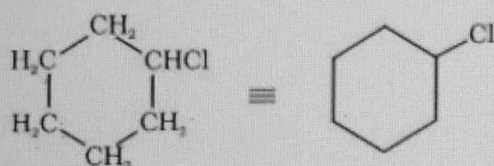
In cyclic compounds, the bond-line formulas may be given as follows:



Cyclopropane



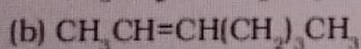
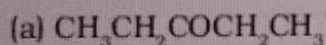
Cyclopentane



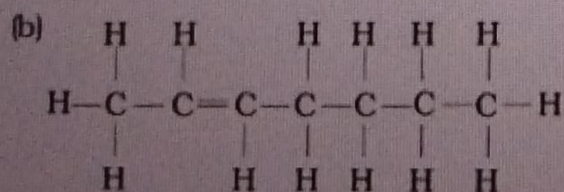
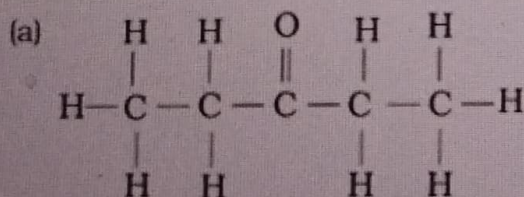
chlorocyclohexane

Problem 12.4

Expand each of the following condensed formulas into their complete structural formulas.

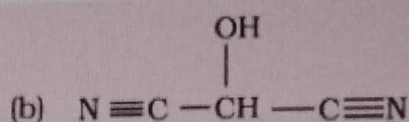
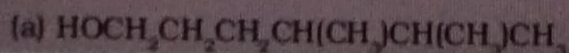


Solution



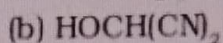
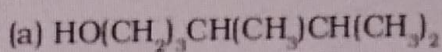
Problem 12.5

For each of the following compounds, write a condensed formula and also their bond-line formula.

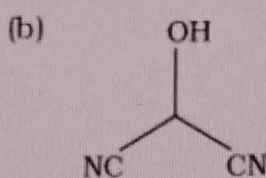
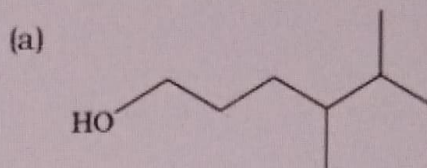


Solution

Condensed formula:

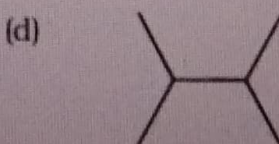
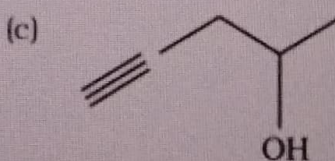


Bond-line formula:

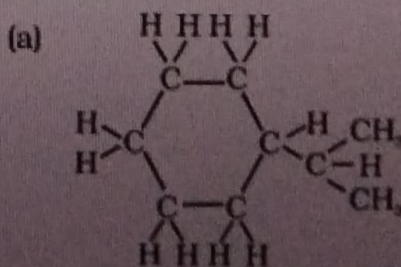


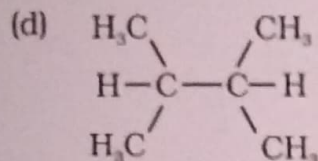
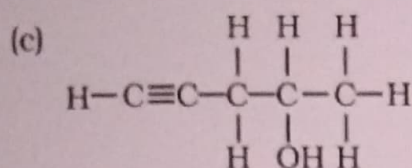
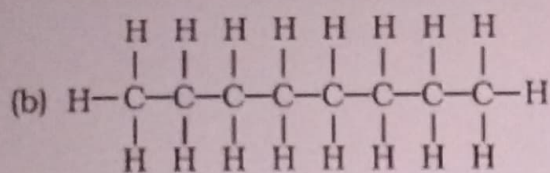
Problem 12.6

Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen



Solution





12.3.2 Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid (\blacktriangleleft) and dashed (\cdots) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line ($-$). 3-D representation of methane molecule on paper has been shown in Fig. 12.1.

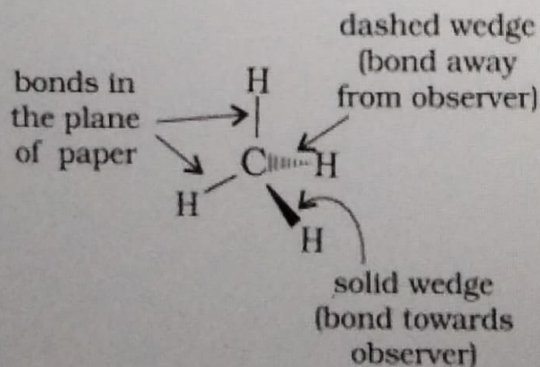
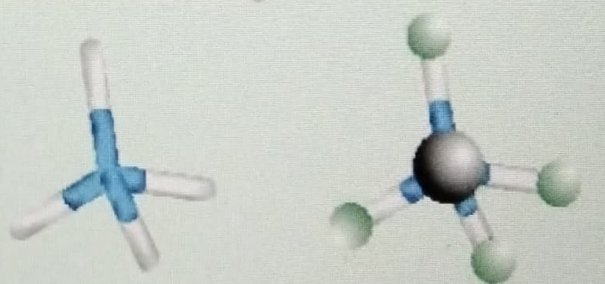


Fig. 12.1 Wedge-and-dash representation of CH_4

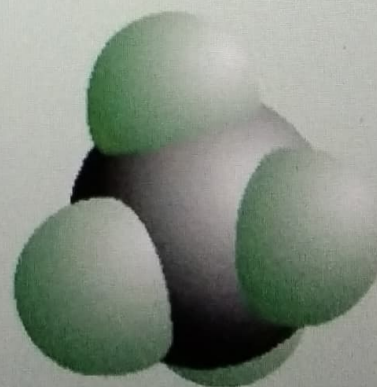
Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model*, (2) *Ball-and-stick model*, and (3) *Space filling model*. In the *framework model* only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of atoms. In the *ball-and-stick model*, both the atoms and the bonds are shown. Balls represent atoms and the stick denotes a bond. Compounds containing $\text{C}=\text{C}$ (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as *ball-and-spring model*. The *space-filling model* emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modelling.



Framework model

Ball and stick model

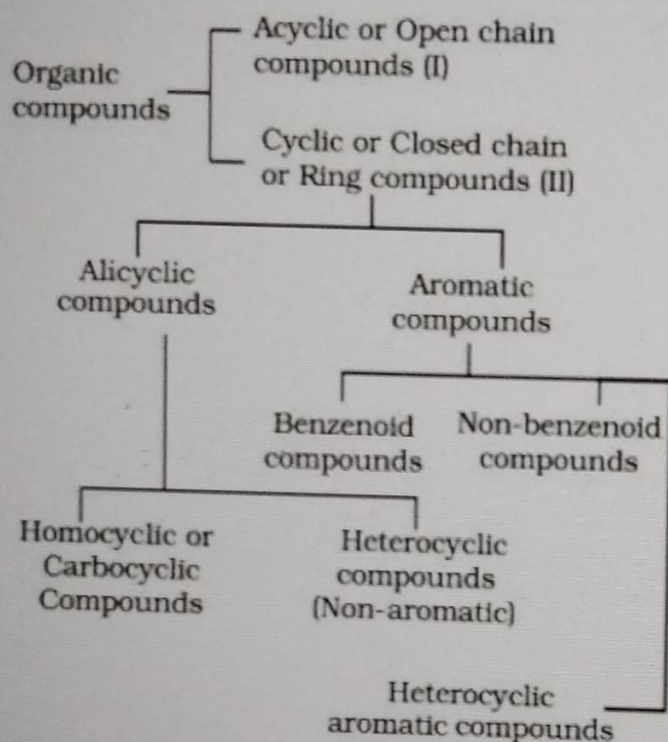


Space filling model

Fig. 12.2

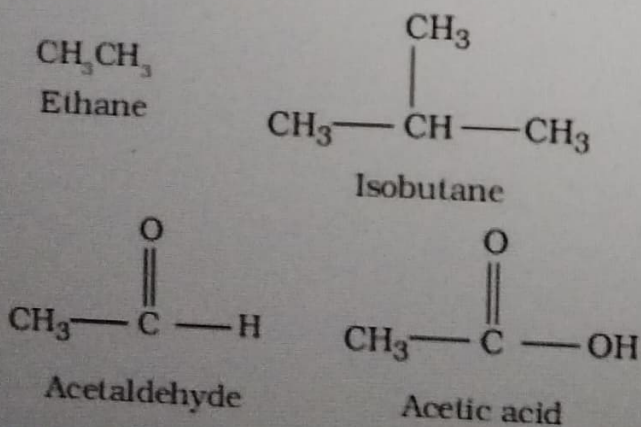
12.4 CLASSIFICATION OF ORGANIC COMPOUNDS

The existing large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:



I. Acyclic or open chain compounds

These compounds are also called as **aliphatic** compounds and consist of straight or branched chain compounds, for example:

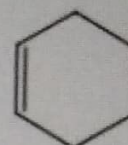
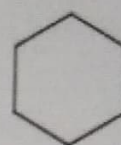
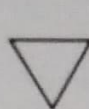


II Cyclic or closed chain or ring compounds

(a) Alicyclic compounds

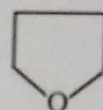
Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring

(homocyclic).



Cyclopropane Cyclohexane Cyclohexene

Sometimes atoms other than carbon are also present in the ring (heterocyclic). Tetrahydrofuran given below is an example of this type of compound:



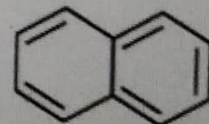
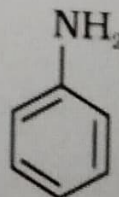
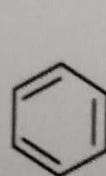
Tetrahydrofuran

These exhibit some of the properties similar to those of aliphatic compounds.

(b) Aromatic compounds

Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 13. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic compounds may also have heteroatom in the ring. Such compounds are called heterocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds

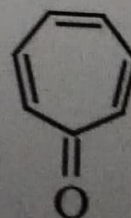


Benzene

Aniline

Naphthalene

Non-benzenoid compound



Tropone