

- 7.27 Predict the products of electrolysis in each of the following:
- An aqueous solution of AgNO_3 with silver electrodes
 - An aqueous solution AgNO_3 with platinum electrodes
 - A dilute solution of H_2SO_4 with platinum electrodes
 - An aqueous solution of CuCl_2 with platinum electrodes.
- 7.28 Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.
- 7.29 Given the standard electrode potentials,
 $\text{K}^+/\text{K} = -2.93\text{V}$, $\text{Ag}^+/\text{Ag} = 0.80\text{V}$,
 $\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$
 $\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$. $\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$
 arrange these metals in their increasing order of reducing power.
- 7.30 Depict the galvanic cell in which the reaction $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$ takes place, Further show:
- which of the electrode is negatively charged,
 - the carriers of the current in the cell, and
 - individual reaction at each electrode.



11083CH12

UNIT 8

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Objectives

After studying this unit, you will be able to

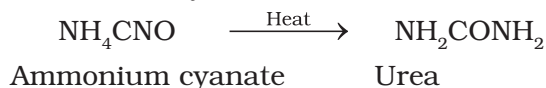
- understand reasons for tetravalence of carbon and shapes of organic molecules;
- write structures of organic molecules in various ways;
- classify the organic compounds;
- name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;
- understand 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.

8.1 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.

8.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

8.2.1 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.

8.2.2 Some Characteristic Features of π Bonds

In a π (π) 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 8.1

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

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

Problem 8.2

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 8.3

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) $\text{HC}\equiv\text{N}$.

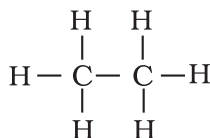
Solution

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

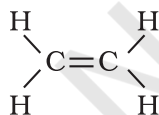
8.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

8.3.1 Complete, Condensed and Bond-line Structural Formulas

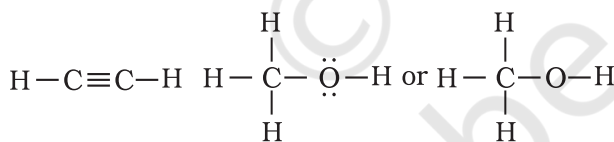
Structures of organic compounds are represented in several ways. The *Lewis structure* or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond 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*.



Ethane



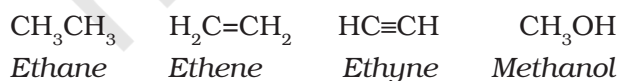
Ethene



Ethyne

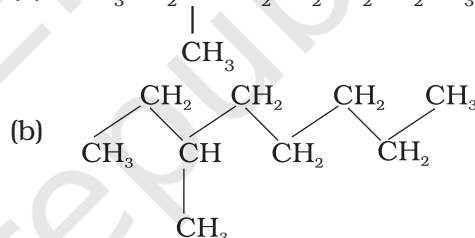
Methanol

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:

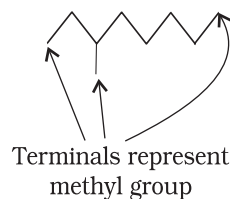


Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3(CH_2)_6CH_3$. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this *bond-line structural* representation of organic compounds, carbon and hydrogen 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 ($-CH_3$) 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:

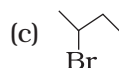
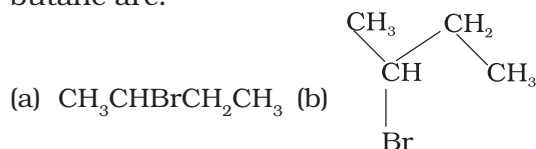
(i) 3-Methyloctane can be represented in various forms as:



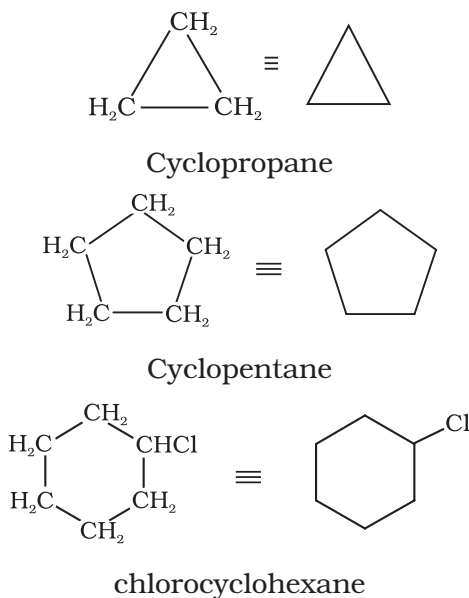
(c)



(ii) Various ways of representing 2-bromo butane are:



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

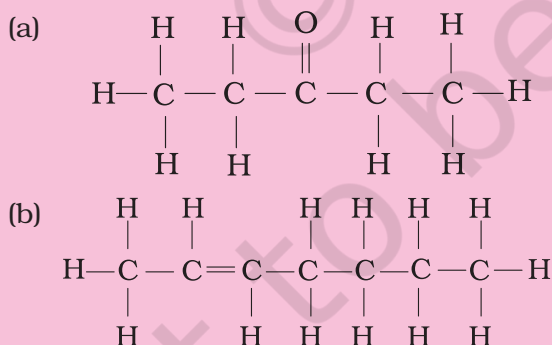


Problem 8.4

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

- (a) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
 (b) $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$

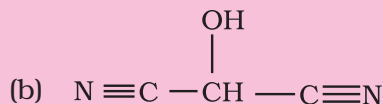
Solution



Problem 8.5

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

- (a) $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_3$

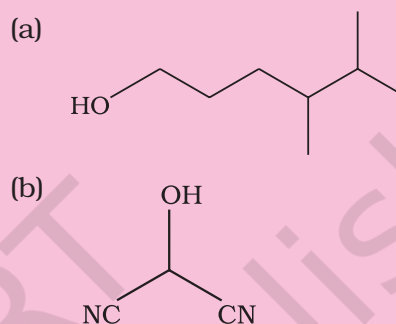


Solution

Condensed formula:

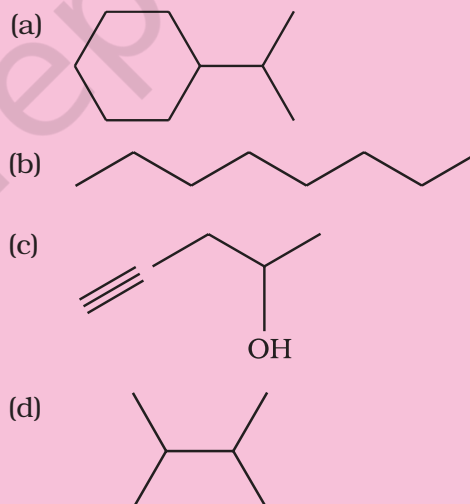
- (a) $\text{HO}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$
 (b) $\text{HOCH}(\text{CN})_2$

Bond-line formula:

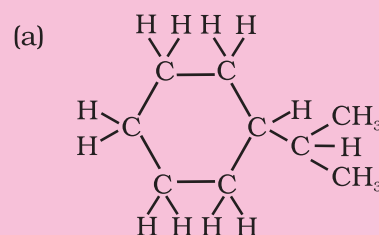


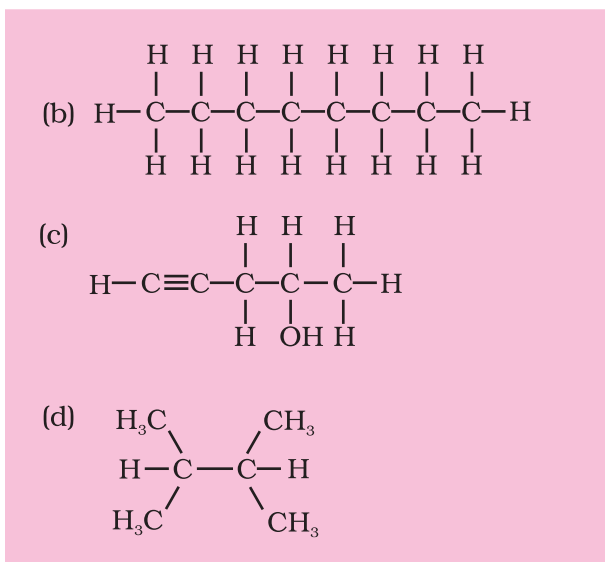
Problem 8.6

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



Solution





8.3.2 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 (—) and dashed (-----) 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. 8.1

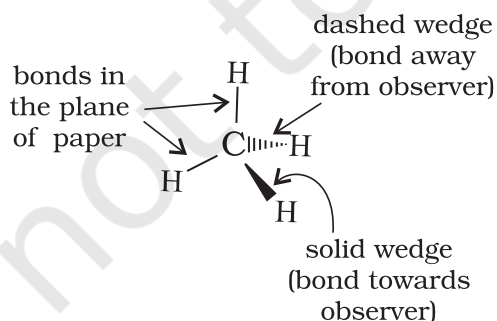
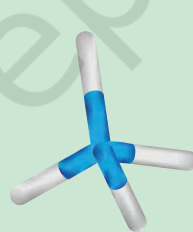


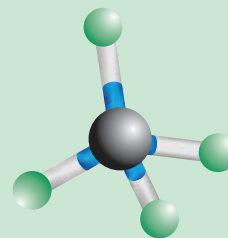
Fig. 8.1 Wedge-and-dash representation of CH_4

Molecular Models

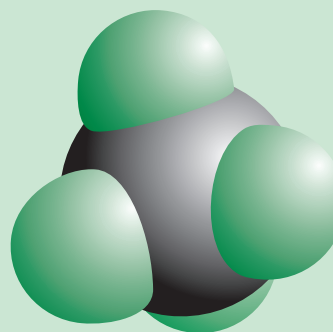
Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model*, (2) *Ball-and-stick 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

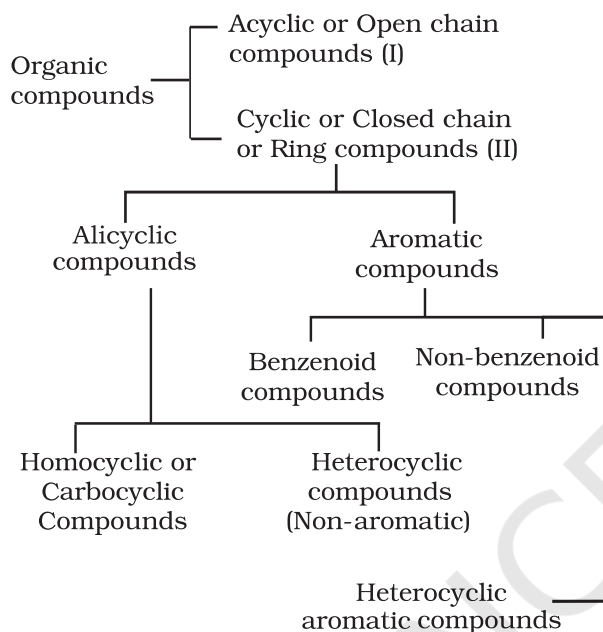


Space filling model

Fig. 8.2

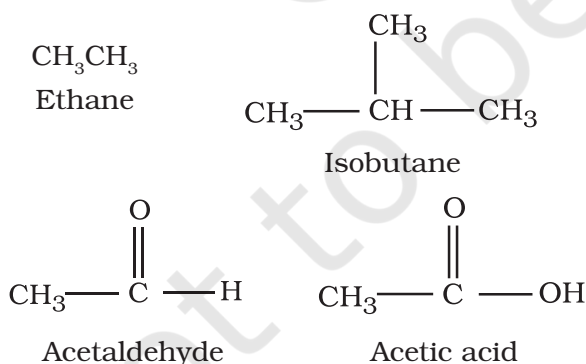
8.4 CLASSIFICATION OF ORGANIC COMPOUNDS

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:

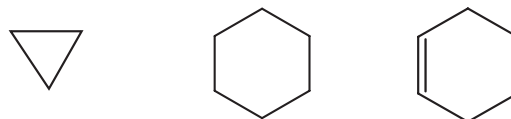


II Cyclic or closed chain or ring compounds

(a) Alicyclic compounds

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

(homocyclic).



Cyclopropane Cyclohexene Cyclohexane

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



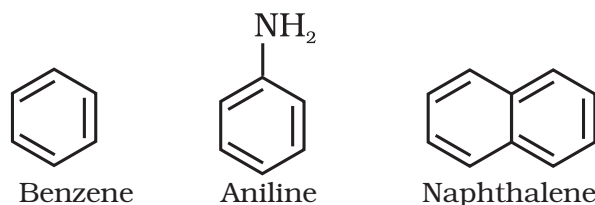
Tetrahydrofuran

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

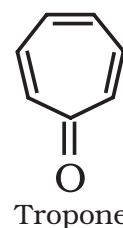
(b) Aromatic compounds

Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 9. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic compounds may also have hetero atom in the ring. Such compounds are called heterocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds



Non-benzenoid compound



Tropone

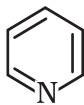
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into *families* or *homologous series*.

8.4.1 Functional Group

The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group ($-\text{OH}$), aldehyde group ($-\text{CHO}$) and carboxylic acid group ($-\text{COOH}$) etc.

8.4.2 Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called *homologues*. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-\text{CH}_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanolic acids, amines etc.

It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

8.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named

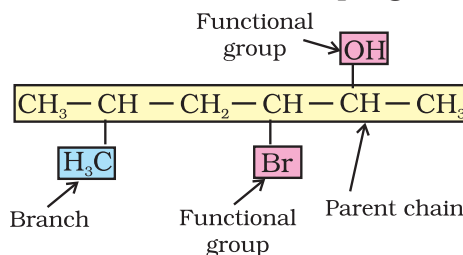
so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are considered as *trivial* or *common names*. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 8.1.

Table 8.1 Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_3$	<i>n</i> -Butane
$(\text{H}_3\text{C})_2\text{CHCH}_3$	Isobutane
$(\text{H}_3\text{C})_4\text{C}$	Neopentane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{OH}$	<i>n</i> -Propyl alcohol
HCHO	Formaldehyde
$(\text{H}_3\text{C})_2\text{CO}$	Acetone
CHCl_3	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$\text{C}_6\text{H}_5\text{OCH}_3$	Anisole
$\text{C}_6\text{H}_5\text{NH}_2$	Aniline
$\text{C}_6\text{H}_5\text{COCH}_3$	Acetophenone
$\text{CH}_3\text{OCH}_2\text{CH}_3$	Ethyl methyl ether

8.5.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.



By further using *prefixes* and *suffixes*, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is *alkane*. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

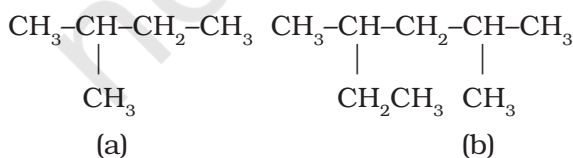
8.5.2 IUPAC Nomenclature of Alkanes

Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix ‘-ane’ and carry a prefix indicating the number of carbon atoms present in the chain (except from CH₄ to C₄H₁₀, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 8.2. The alkanes in Table 8.2 differ from each other by merely the number of -CH₂ groups in the chain. They are homologues of alkane series.

Table 8.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH ₄	Heptane	C ₇ H ₁₆
Ethane	C ₂ H ₆	Octane	C ₈ H ₁₈
Propane	C ₃ H ₈	Nonane	C ₉ H ₂₀
Butane	C ₄ H ₁₀	Decane	C ₁₀ H ₂₂
Pentane	C ₅ H ₁₂	Icosane	C ₂₀ H ₄₂
Hexane	C ₆ H ₁₄	Triacontane	C ₃₀ H ₆₂

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:

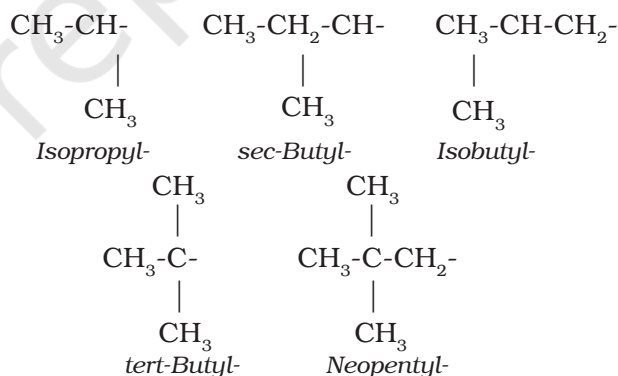


In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH₄ becomes -CH₃ and is called *methyl group*. An alkyl group is named by substituting ‘yl’ for ‘ane’ in the corresponding alkane. Some alkyl groups are listed in Table 8.3.

Table 8.3 Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH ₄	Methane	-CH ₃	Methyl
C ₂ H ₆	Ethane	-CH ₂ CH ₃	Ethyl
C ₃ H ₈	Propane	-CH ₂ CH ₂ CH ₃	Propyl
C ₄ H ₁₀	Butane	-CH ₂ CH ₂ CH ₂ CH ₃	Butyl
C ₁₀ H ₂₂	Decane	-CH ₂ (CH ₂) ₈ CH ₃	Decyl

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.

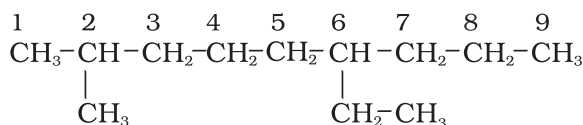


Common branched groups have specific trivial names. For example, the propyl groups can either be *n*-propyl group or isopropyl group. The branched butyl groups are called *sec*-butyl, *isobutyl* and *tert*-butyl group. We also encounter the structural unit, -CH₂C(CH₃)₃, which is called *neopentyl* group.

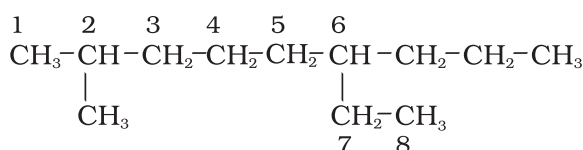
Nomenclature of branched chain alkanes:

We encounter a number of branched chain alkanes. The rules for naming them are given below.

- First of all, the **longest carbon chain in the molecule is identified**. In the example (I) given below, the longest chain has nine carbons and it is considered as the *parent* or *root* chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.

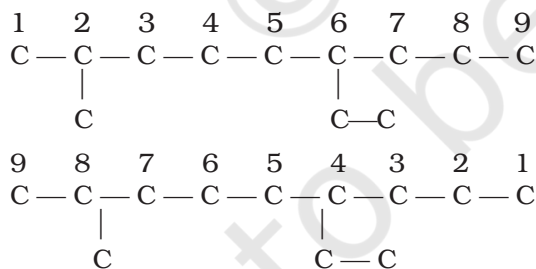


I



II

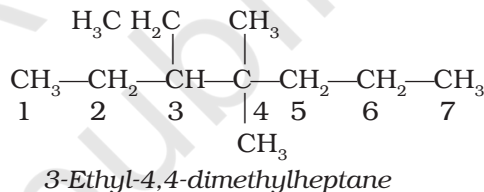
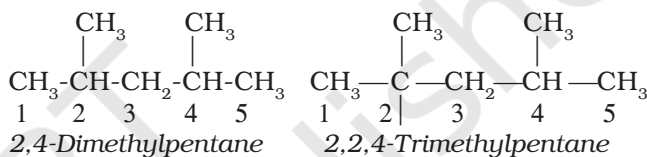
- The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.** Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).



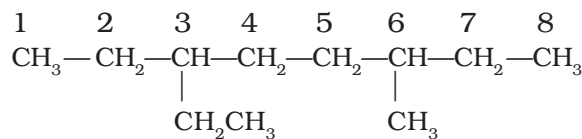
- The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are

separated from the groups by hyphens and there is no break between methyl and nonane.]

- If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:



- If the two substituents are found in equivalent positions, the **lower number is given to the one coming first in the alphabetical listing**. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



- The branched alkyl groups can be named by following the above mentioned procedures. However, the **carbon atom of the branch that attaches to the root alkane** is numbered 1 as exemplified below.

