

25

NOMENCLATURE AND GENERAL PRINCIPLES

Organic compounds are all around us in several forms. They are present in a vast range of substances like fuels, foods, polymers and plastics, textiles, dyes, drugs, medicines, explosives, cosmetics, paints and pesticides. The word organic is derived from the word organism because the body of living things is composed mainly of organic compounds. In addition to the organic compounds of animals and plants origin, a large number of them have been synthesized in the laboratory. All organic compounds are known to contain carbon. The carbon atoms have a unique property called ‘catenation’ which is the ability to form long chains, rings and networks of carbon atoms resulting into the formation of large number of carbon compounds.

The basic organic compounds are *hydrocarbons* (compounds of carbon and hydrogen) which can be converted to different types of organic compounds by performing different reactions. The *organic chemistry* is the branch of chemistry which deals with the study of compounds of carbon. Some compounds containing carbon are not studied in this branch of chemistry such as oxides of carbon, metal carbides, metal cyanides, and metal carbonates and these come under ‘Inorganic Chemistry’.

This lesson describes various rules for naming of organic compounds based upon IUPAC system. A distinction between different types of bond fission in organic compounds is also explained. Various types of reactions and electronic effects are discussed with examples. This lesson also covers different types of isomerism.



Objectives

After reading this lesson, you will be able to:

- name various types of organic compounds according to IUPAC system;
- distinguish between different types of bond fission;
- explain different types of reactions: substitution, addition, elimination and molecular rearrangements;
- identify nucleophiles and electrophiles;

Chemistry of Organic Compounds



Notes

- explain electronic effects in a covalent bond such as inductive effect, electromeric effect, resonance, hyperconjugation and steric hindrance, and
- explain structural isomerism and stereoisomerism.

25.1 Classification of Hydrocarbons

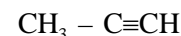
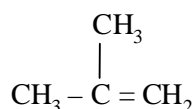
All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

1. **Open-chain or Aliphatic compounds:** This class includes all hydrocarbons (saturated and unsaturated) and their derivatives which have open-chain structures. Saturated hydrocarbons are those which contain single bonds between all carbon atoms such as



On the other hand, unsaturated compounds contain a double ($-\text{C} = \text{C}-$) or a triple ($-\text{C} \equiv \text{C}-$) bond between two carbon atoms.

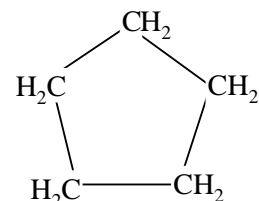
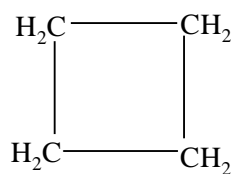
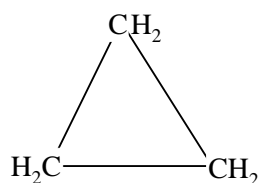
For example :



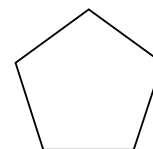
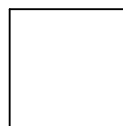
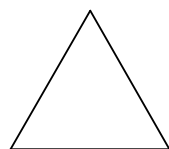
2. **Closed-chain or cyclic compounds:** These compounds have atleast one ring (cyclic) system. These are further divided into two sub-classes: **homocyclic** and **heterocyclic** based on the atoms present in the ring. They are called **homocyclic** or **carbocyclic** when the ring is formed by carbon atoms only.

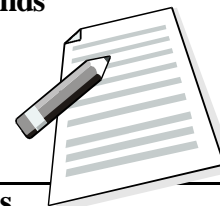
Homocyclic (carbocyclic) compounds may again be divided into two groups namely **alicyclic** and **aromatic** compounds.

- (i) **Alicyclic compounds:** This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:



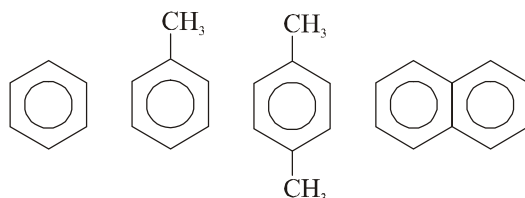
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a $-\text{CH}_2-$ group.



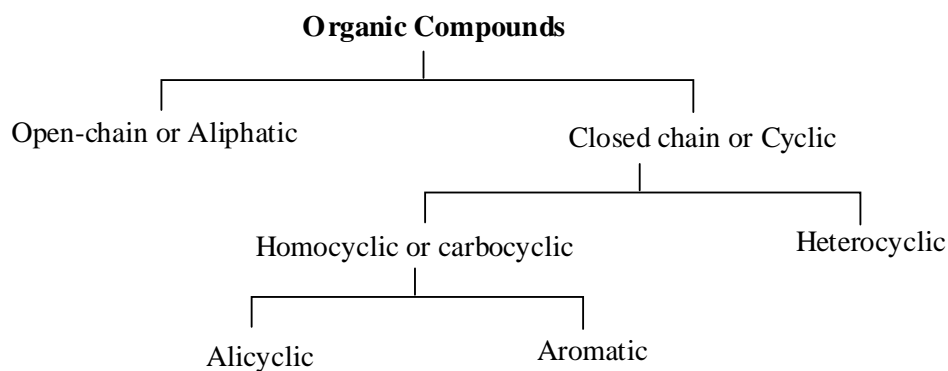


Notes

(ii) **Aromatic compounds:** The group of homocyclic compounds having special set of properties are called aromatic compounds which will be discussed in Lesson 26. They also have characteristic smell or *aroma* and hence called *aromatic*. These include aromatic hydrocarbons and their derivatives are examples of such compounds are as follows :

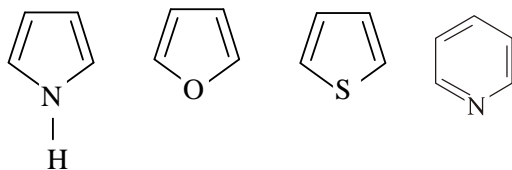


The above classification of the organic compounds can be summarised as below:



On the other hand, **heterocyclic compounds** contain one or more atom (usually O, N or S atom) other than the carbon atoms.

Some examples of heterocyclic compounds are as follows:



25.2 Nomenclature of Organic Compounds

In the beginning, the organic compounds were named after the source from which they were obtained e.g. methane was named as marsh gas as well as damp fire because it was obtained from marshy places. Similarly, formic was named so because it was obtained from red ants (Latin name *formica*). These names of organic compounds are called common names or trivial names. There was no systematic basis for naming them and it was very difficult task to remember the names of so many organic compounds. Even the same compound was known by different names. In order to bring uniformity and rationality in naming the organic compounds throughout the world, International Union of Chemistry (in 1958) came out with a system of nomenclature later known as IUPAC (International

Chemistry of Organic Compounds



Notes

Union of Pure and Applied Chemistry) system. Before explaining IUPAC system of nomenclature, we shall discuss about homologous series.

Homologous Series: A series of compounds in which the molecular formula of a compound differs from those of its neighbouring compounds by the CH_2 group, is known as a **homologous series**. Each of such homologous series is given a general name. For example, homologous series of open chain saturated hydrocarbons is known as **alkanes** and open chain unsaturated hydrocarbons form *two* series of compounds namely **alkenes** and **alkynes**, which contain carbon - carbon double bond and triple bond, respectively. Some members of homologous series of aliphatic hydrocarbons are listed in the Table 25.1.

Table 25.1 : Homologous series of hydrocarbons

Saturated		Unsaturated			
General Name : <i>Alkanes</i> General Formula : $\text{C}_n\text{H}_{2n+2}$		<i>Alkenes</i> C_nH_{2n}		<i>Alkynes</i> $\text{C}_n\text{H}_{2n-2}$	
CH_4	Methane				
C_2H_6	Ethane	C_2H_4	Ethene	C_2H_2	Ethyne
C_3H_8	Propane	C_3H_6	Propene	C_3H_4	Propyne
C_4H_{10}	Butane	C_4H_8	Butene	C_4H_6	Butyne
C_5H_{12}	Pentane	C_5H_{10}	Pentene	C_5H_8	Pentyne
C_6H_{14}	Hexane	C_6H_{12}	Hexene	C_6H_{10}	Hexyne
...
...
...

25.2.1 IUPAC Nomenclature of Acyclic Hydrocarbons

Acyclic hydrocarbons include straight chain as well as branched chain compounds.

(a) Straight chain Hydrocarbons: The names of these hydrocarbons consist of two parts. The first one is word **root** and second one is **suffix**. The word root designates the number of carbon atoms in the chain. Special word roots (*Meth-, Eth-, Prop-, But-, etc.*) are used for chains containing *one to four carbon atoms* but for chains of *five and more carbon atoms*, Greek number roots such as Pent-, Hex - etc. are used the in IUPAC word roots for a few carbon chains are given below in Table 25.2.

Table 25.2 : Some Word Roots and corresponding number of carbon atoms

Number of C-Atoms	Word root	Number of C-Atoms	Word root
1	Meth -	6	Hex -
2	Eth -	7	Hept-
3	Prop -	8	Oct-
4	But -	9	Non-
5	Pent-	10	Dec-

The general word root for any carbon chain is **alk**.

In order to write the IUPAC name, a suffix is added to the word root to indicate saturation or unsaturation in the hydrocarbons. These suffixes are listed below in the Table 25.3.

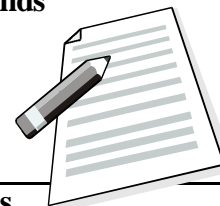


Table 25.3 : Types of hydrocarbons and suffixes in their name

Class of compound	Suffix	General name
Saturated	-ane	Alkane
Unsaturated ($>C=C<$)	-ene	Alkene
Unsaturated ($-C\equiv C-$)	-yne	Alkyne

Let us consider some examples:

Compound	IUPAC Name	Word root	Suffix
$CH_3CH_2CH_3$	Propane	Prop-	ane
$CH_3CH_2CH_2CH_2CH_3$	Pentane	Pent-	ane
$CH_2=CH_2$	Ethene	Eth-	ene
$CH_3-C\equiv CH$	Propyne	Prop-	yne

b) Branched chain Hydrocarbons

In branched chain hydrocarbons, one or more alkyl groups are present as side chain attached to the main straight chain of carbon atoms. The carbon atoms of the side chain constitute **alkyl groups**. These alkyl groups are written as prefixes in the IUPAC name. An alkyl group is obtained from an alkane by removing one hydrogen atom. Since the general formula of alkane is C_nH_{2n+2} , the general formula of alkyl group is C_nH_{2n+1} . The alkyl groups are generally represented by R- and named by replacing the suffix **ane** of the corresponding alkane by **yl**. Let us see some examples of the alkyl groups given in the Table 25.4.

Table 25.4 : Some alkyl groups

Parent Chain	Formula R-H	Alkyl group R-	Name
Methane	CH_4	CH_3-	Methyl
Ethane	CH_3CH_3	CH_3CH_2-	Ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2-$	Propyl
		$\begin{array}{c} \\ CH_3-CH-CH_3 \end{array}$	Isopropyl
Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$	Butyl
		$\begin{array}{c} CH_3CH_2-CH-CH_3 \\ \end{array}$	<i>sec</i> -butyl
Isobutane	$\begin{array}{c} CH_3 \\ \\ H_3C-CH-CH_3 \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH_2- \end{array}$	Isobutyl
		$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_3 \\ \end{array}$	<i>tert</i> -butyl

Branched chain hydrocarbons are named using the following rules in IUPAC system.

Rule 1. Longest chain Rule: According to this rule, the longest possible chain of carbon

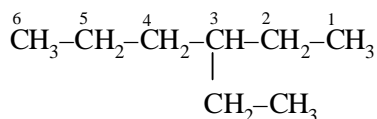
Chemistry of Organic Compounds



Notes

atoms is considered and the compound is named as the derivative of the corresponding alkane. *If some multiple bond is present, the selected chain must contain the carbon atoms of the multiple bond.* The number of carbon atoms in the selected chain determines the *word root* and the saturation or unsaturation will determine the *suffix*.

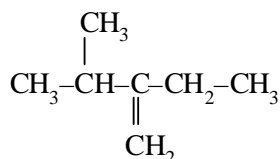
Let us consider the following example:



Word root **-Hex** + Suffix **-ane**

Since it has a main chain of *six* carbon atoms; hence, it will be named as a derivative of **hexane**.

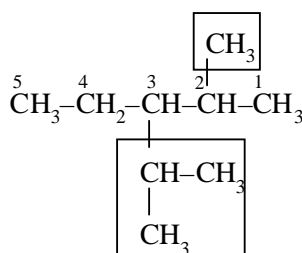
Similarly,



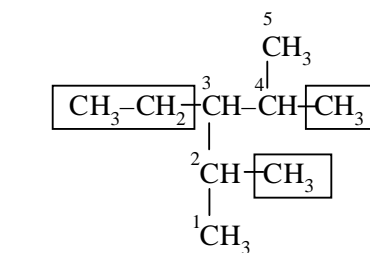
Wordroot **-But** + Suffix **-ene**

The main chain of carbon atoms containing double bond consists of *four* carbon atoms. Therefore, the compound will be a derivative of butene.

If two equally long chains are possible, the chain with maximum number of side chains is selected as the main chain.



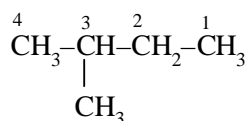
Main chain has 2 branches (Wrong)



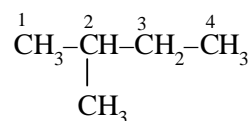
Main chain has 3 branches (Correct)

Rule 2: Lowest number or lowest sum rule: The longest carbon chain is numbered from one end to another and the positions of the side chain are indicated by the number of carbon atoms to which these are attached. The numbering is done in such a way that :

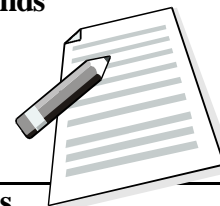
a) The substituted carbon atoms have the lowest possible numbers.



Wrong numbering

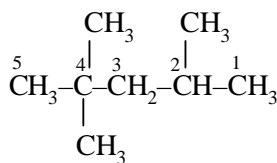


Correct numbering

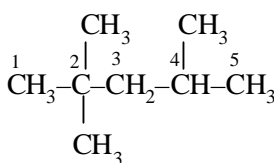


Notes

- b) The sum of numbers used to indicate the positions of various alkyl groups must be the lowest.

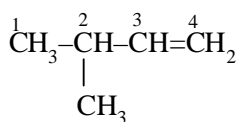


Sum of positions = $2+4+4 = 10$
(Wrong)

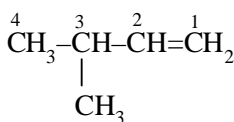


Sum of positions = $2+2+4 = 8$
(Correct)

Rule 3 : If some multiple bond is present in the chain the carbon atoms involved in the multiple bond should get the lowest possible numbers. For example :



Wrong numbering



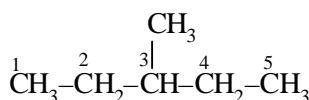
Correct numbering

Rule 4 : Naming of compounds with one alkyl group as the substituent (side chain)

The name of a substituted hydrocarbon consists of the following parts.

Position of substituent - Name of *substituent*, Word *root*, *Suffix*.

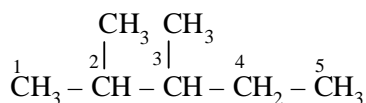
Let us consider a compound represented by the following structure:



In the given structure, we find that the longest chain consists of *five* carbon atoms and the substituent is *methyl* group at position number 3. The word root is **Pent** and suffix is **ane**. Hence, the name is 3-methylpentane.

Rule 5 : Naming the same alkyl groups at different positions or more than one alkyl groups

If the compound contains more than one identical alkyl groups, their positions are indicated separately and the prefixes *di* (for two), *tri* (for three) etc. are attached to the name of the substituents. The positions of the substituents are separated by commas (.). In the following structure, two methyl groups are attached to the main chain of five carbon atoms.



You can see that they are attached to the positions 2 and 3 of the main chain. Hence, the name of the compound is 2,3-dimethylpentane.

Rule 6: Naming different alkyl substituents

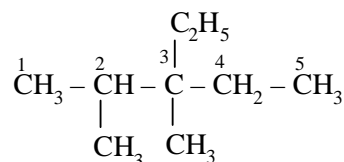
If there are different alkyl substituents present in the compound, their names are written in the alphabetical order. However, the prefixes *di*, *tri*, etc. are not considered in deciding the alphabetical order.

Chemistry of Organic Compounds



Notes

For example, in the compound shown below the longest chain consists of **five carbon atoms**; hence, the parent hydrocarbon is pentane. The main chain has two methyl groups at C₂ and C₃ and one ethyl group at C₃ as substituents. The names of these alkyl

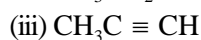
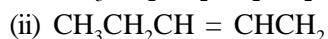


groups are written before the name of parent alkane and their positions are indicated by number of carbon atom to which they are attached. Thus, the name of the compound will be 3-ethyl-2, 3-dimethylpentane.



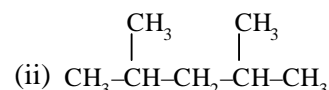
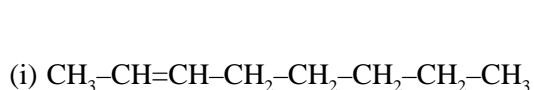
Intext Questions 25.1

1. Identify word *root* and *suffix* for the following :



.....

2. Give IUPAC name to the following compounds



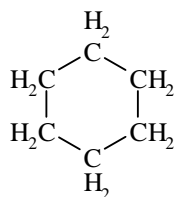
.....

25.2.2 Nomenclature of Cyclic Hydrocarbons

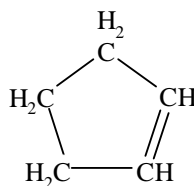
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) Alicyclic Compounds

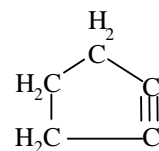
As we have already discussed (in Section 25.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix 'cyclo'* before the *word root*. The suffix **ane**, **ene** or **yne** are written according to the saturation or unsaturation in the ring structure. Given below are some examples of alicyclic compounds.



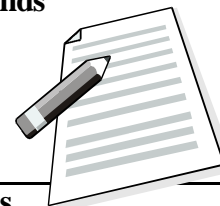
Cyclohexane



Cyclopentene

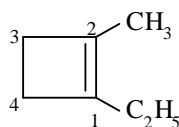


Cyclopentyne

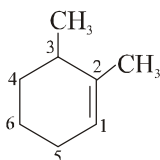


Notes

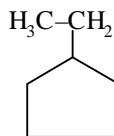
If an alkyl substituent is present, it is indicated by the appropriate *prefix* and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



1-Ethyl-2-methylcyclobutene



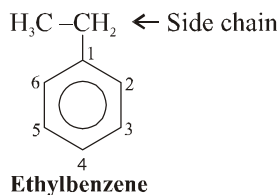
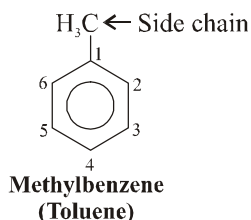
2,3-Dimethylcyclohexene



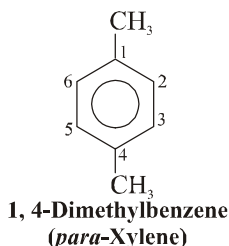
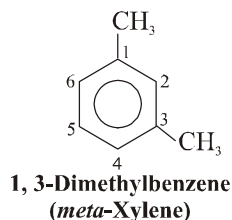
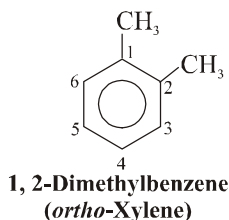
Ethylcyclopentane

b) Aromatic Compounds

The most important members of this class are benzene and its derivatives. For naming an alkyl substituted benzene, the carbon atoms of benzene are numbered from 1 to 6 by giving the lowest possible number to the position of the side chain or substituent. This is shown below.



Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1,2; 1,3 and 1,4 derivatives. These are also known as *ortho*- (or *o*-), *meta*- (or *m*-) and *para*- (or *p*-) substituted compounds, respectively.

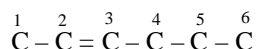


25.2.3 Writing Structure of Hydrocarbons from their IUPAC Names

Till now, we have named hydrocarbons from their structures using IUPAC nomenclature. Let us now do the reverse exercise i.e. writing structure of hydrocarbons when their IUPAC names are given. Let us take some examples to write structures for given IUPAC names.

Example 1. Writing the structure of 4-Ethyl-5-methylhex-2-ene

Step 1 The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C₂ is drawn.



Step 2 Attach ethyl group at C₄ and methyl group at C₅.

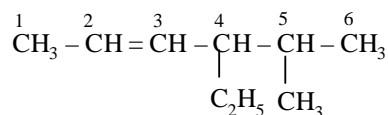
Chemistry of Organic Compounds



Notes

Step 3 Attach H-atoms to the C-atoms of main chain to satisfy tetravalency of all the carbon atoms.

Thus, the correct structure of the compound is as given below:



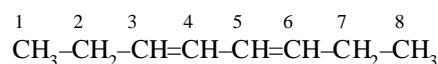
Example 2. Writing the structure of **Octa-3,5-diene**

Step 1- The skeleton of parent hydrocarbon chain of **eight** carbon atoms is drawn.

Step 2- Make C=C at C₃ and at C₅.

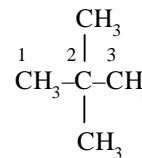
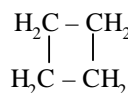
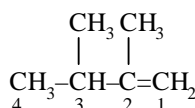
Step 3- Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms.

The correct structure of the compound is as follows :



The following compounds illustrate some more examples:

- (i) 2,3-Dimethylbut-1-ene (ii) Cyclobutane (iii) 2,2-Dimethylpropane

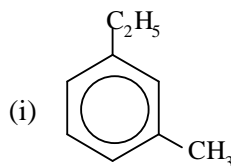


After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.

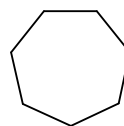


Intext Questions 25.2

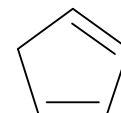
1. Write IUPAC names for the following compounds :



(ii)



(iii)



.....

.....

.....

2. Write the structural formula for the following compounds:

(i) 1,3-Dimethylcyclohexane

(ii) Ethylcyclobutane

(iii) *n*-Propylbenzene

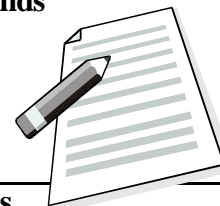
.....

.....

.....

25.2.4 IUPAC Nomenclature of Aliphatic Organic Compounds Containing Functional Groups

A **functional group** is an atom or group of atoms which is responsible for characteristic



Notes

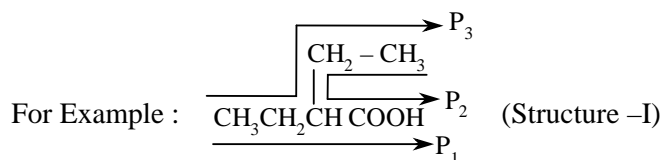
properties of a compound. For example :

–Cl, –Br, –I, –COOH, –OH, –NH₂ etc.

a) Compounds with one functional group (monofunctional Derivatives): The derivatives of hydrocarbons containing only one functional group are called monofunctional derivatives.

Most of the IUPAC names of functional derivatives of hydrocarbons are derived by replacing the suffix **ane** of the parent alkane (corresponding to the number of carbon-atoms in the longest chain) by a specific *suffix* for the functional groups, (see Table 25.5). There are some derivatives in which a particular *prefix* is added to the parent alkane name as in *nitroalkanes*, *haloalkanes*, and *haloarenes* etc. Given below are some rules for the IUPAC nomenclature of organic compounds containing functional groups. In addition to the *rules listed below*, all the general rules discussed earlier for naming of hydrocarbons are also applicable to such compounds.

Rule 1: First of all the longest chain of carbon atoms containing the functional group is identified. In case of carbon containing functional group, (–CHO, –COOH) the main chain must include the carbon atom of the group.

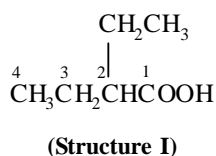


P₁ or P₂ are correct selections of chain of carbon atoms whereas P₃ is wrong selection as it does not include the carbon atom of the functional group.

Rule 2: The longest continuous carbon atom chain is numbered from that end which will give the lowest number to the carbon atom bearing the functional group.

Rule 3: There is a specific **suffix** for each functional group that replaces the ending **-e** in the name of the corresponding parent alkane.

Rule 4: If the carbon chain is branched, then the attached alkyl groups are named and numbered as in Structure I (rule 1) main chain contain a branch of two carbon atoms i.e., ethyl group at position 2.



Rule 5: While writing the name of the compound, place the substituents in the alphabetical order.

Table 25.5 lists some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

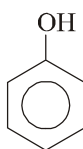


Notes

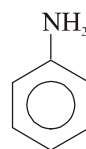
Table 25.5. Some Common Functional Groups and their Aliphatic Derivatives

Functional Group	Suffix/Prefix	General name	Example (IUPAC name)
–OH (Hydroxy)	–ol	Alkanol (Alcohols)	CH ₃ CH ₂ OH (Ethanol)
–COOH (Carboxyl)	–oic acid	Alkanoic acid	CH ₃ COOH (Ethanoic acid)
–SO ₃ H (Sulphonic)	–	Alkylsulphonic acid	CH ₃ CH ₂ SO ₃ H (Ethyl sulphonic acid)
–CHO (Aldehydic)	–al	Alkanal	CH ₃ CHO (Ethanal)
>CO (Ketonic)	–one	Alkanone	CH ₃ COCH ₃ (Propanone)
–CONH ₂ (Amide)	–amide	Alkanamide	CH ₃ CONH ₂ (Ethanamide)
–COX (Carboxyl halide)	–oyl halide	Alkanoyl halide	CH ₃ COCl (Ethanoyl chloride)
–COO– (Ester)	–oate	Alkyl alkanoate	CH ₃ COOCH ₃ (Methyl ethanoate)
–CN (Cyano)	–nitrile	Alkanenitrile	CH ₃ CH ₂ CN (Propanenitrile)
–SH (Thiol)	–thiol	Alkanethiols	CH ₃ CH ₂ SH (Ethanethiol)
–NH ₂ (Amino)	–amine	Alkanamine	CH ₃ CH ₂ NH ₂ (Ethanamine)
–O– (Ether)	–oxy	Alkoxyalkane	CH ₃ –O–CH ₃ (Methoxymethane)
–C≡C– (Yne)	–yne	Alkyne	CH ₃ C≡CCH ₃ (But-2-yne)
–C=C– (Ene)	–ene	Alkene	CH ₃ CH=CHCH ₃ (But-2-ene)
–X = –F, –Cl, –Br, –I	–Halo (Prefix)	Haloalkane	CH ₃ CH ₂ –X (Haloethane)
–NO ₂ (Nitro)	–Nitro (Prefix)	Nitroalkane	CH ₃ CH ₂ NO ₂ (Nitroethane)

Certain derivatives have some specific general names e.g. monohydroxybenzene is called **phenol** and monoaminobenzene as **aniline**.



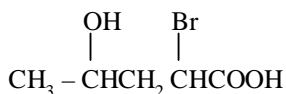
Phenol



Aniline

b) Naming of Organic compounds with more than one functional group: In case of organic compounds containing more than one functional group, one group is given preference over the other(s) in deciding the parent compound. The priority order of the various functional groups is as follows; –COOH, –COOR, –SO₃H, –COX, –CONH₂,

–CHO, –CO–, –CN, –OH, –SH, –O–, –NH₂, –X (halogen), –NO₂, –C=C–, and –C≡C–. Let us try to name a polyfunctional compound by following the priority of the functional groups.



2-Bromo-4-hydroxypentanoic acid

In the above example, –COOH group is given priority over the –OH and –Br (halo) groups.

25.3 Types of Reactions in Organic Compounds

You are aware that a chemical reaction occurs when one substance is converted into another substance(s). A chemical reaction is accompanied by breaking of some bonds and by making of some others. In organic chemistry, this can happen in more than one way involving a variety of reactions. The different types of reactions in organic compounds are: (i) Substitution (ii) Elimination (iii) Addition and (iv) Molecular Rearrangements.

These different ways of occurrence of organic reactions can be understood by the study of reaction mechanisms. A **reaction mechanism** is defined as the detailed knowledge of the steps involved in a process in which the reactant molecules change into products. Let us explain first some of the terms used in reaction mechanism.

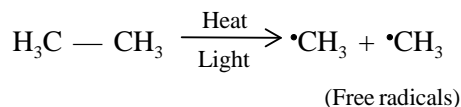
25.3.1 Breaking of a Covalent Bond - Types of Bond Fission

Chemical reactions involve breaking of one or more of the existing chemical bonds in reactant molecule(s) and formation of new bonds leading to products. *The breaking of a covalent bond is known as bond fission.* We know that a covalent bond is formed by the sharing of two electrons from two atoms. During bond breaking or bond fission, the two shared electrons can be distributed equally or unequally between the two bonded atoms. There are **two types of bond fission**.

- Homolytic fission:** *The fission of a covalent bond with equal sharing of bonding electrons is known as homolytic fission.*

Homolytic fission in a hypothetical molecule: $\text{A} - \text{B} \longrightarrow \text{A}^\bullet + \text{B}^\bullet$
(Free radicals)

Now consider the following C-C bond fission:



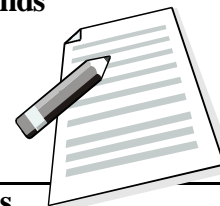
The neutral species so formed are known as **free radicals**.

Free radicals are neutral but reactive species having an unpaired electron and these can also initiate a chemical reaction.

- Heterolytic fission :** *The fission of a covalent bond involving unequal sharing of bonding electrons is known as heterolytic fission.* The heterolytic fission of a hypothetical molecule is shown below.

MODULE - 7

Chemistry of Organic Compounds



Notes

Chemistry of Organic Compounds



Notes

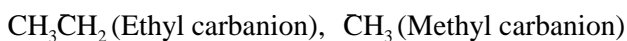


This type of bond fission results in the formation of *ions*. The ion which has a *positive charge on the carbon atom*, is known as the **carbonium ion** or a **carbocation**. For example,



On the other hand, an ion with a *negative charge* on the carbon atom is known as the **carbanion**.

For example,



The charged species obtained by the heterolytic fission initiate chemical reactions and they are classified as electrophiles and nucleophiles.

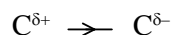
Electrophiles: An electrophile is an electron deficient species and it may be positively charged or neutral. Examples are H^+ , NO_2^+ , Br^+ , Cl^+ , Ag^+ , CH_3CO^+ , BF_3 etc. Thus, an electrophile is an electron seeking species and hence, it attacks at a position of high electron density.

Nucleophiles : A nucleophile is negatively charged or electron rich neutral species. Examples of nucleophiles are OH^- , NO_2^- , H_2O , $:\text{NH}_3$ etc. Nucleophiles attacks a position of low electron density.

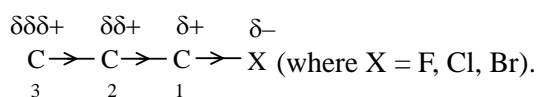
25.3.2 Electron Displacements in a Covalent Bond

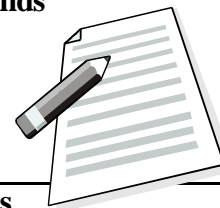
For a reaction to take place by breaking of a covalent bond, with the attack of a nucleophile or electrophile, the molecule or bond under attack must develop polarity on some of its carbon atoms. This polarity can only be developed by the displacement (partial or complete) of bonding electrons due to certain effects. Some of these electronic effects are permanent (e.g. inductive) and others are temporary (e.g. electromeric) in nature. Such changes or effects involving displacement of electrons in the substrate molecules (molecule under attack of a reagent) are known as electron displacement or **electronic effects**. Some of these effects are discussed below.

a) Inductive effect: In a covalent bond between the two dissimilar atoms, the shared electron pair is attracted more towards the atom having greater electronegativity. Let us consider the case of a haloalkane (higher than halomethane). The halogen atom (X) being more electronegative than carbon atom, pulls the bonded electrons of the C–X bond. Thus, the C–X bond is polarised as shown below.



The carbon atom gets a partial +ve charge ($\delta+$) and halogen atom a partial negative charge ($\delta-$). This positively charged C_1 attracts bonded electrons of C_1-C_2 bond, thus making C_2 atom a little less positive than C_1 . Similarly, this +ve charge is shifted to C_3 but to a very less magnitude (nearly zero +ve charge is present after third atom)

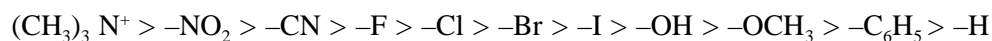




This transmission of induced charges along a chain of σ bonded carbon atoms is known as **inductive effect**. The inductive effect is a permanent polarisation in the molecule and it decreases as we move along a chain of carbon atoms, away from the electronegative atom. Many of the properties of organic compounds such as acidic strength of carboxylic acids are explained on the basis of inductive effect.

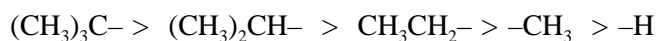
Groups with – I Effect (Electron Withdrawing Groups) :

Any atom or group of atoms that withdraws electrons more strongly than the H-atom, is said to have – I effect. Following are various groups arranged in the decreasing order of their –I effect.



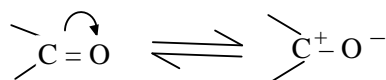
Groups with + I Effect (Electron Releasing Groups) :

Any atom or group of atoms that repels electrons more strongly than hydrogen, is said to have +I effect. Following are the various groups in the decreasing order of +I effect.



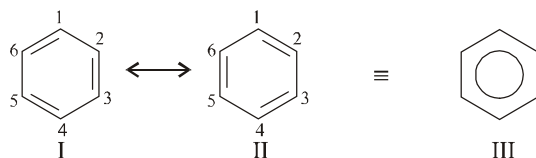
(b) Electromeric effect : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g. $\text{>C}=\text{C}<$, $\text{>C}=\text{O}$, $\text{>C}=\text{N}$ etc.). It

involves the complete transfer of electrons resulting into the development of +ve and –ve charges within the molecule. The electromeric effect takes place in the direction of more electronegative atom and is generally shown by an arrow starting from the original position of the electron pair and ending at the new position of the electron pair. In a carbonyl group it operates as follows :



The electromeric effect is represented by the symbol **E**. It is known as **+E effect** when displacement of electron pair is away from the atom or group, or **–E effect** when the displacement is towards the atom or group. As in above example it is +E effect for C and –E effect for O.

(c) Resonance : This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound are arrived at by the redistribution of valence electrons. The true structure of the compound is an intermediate of all the possible resonating structures or canonical structures and thus called a *resonance hybrid*. For example, the benzene molecule (C_6H_6) may be represented by the following two structures, I and II.



Resonating or canonical structures Resonance hybrid

The evidence in support of the hybrid structure (III) of 'benzene' is available from the

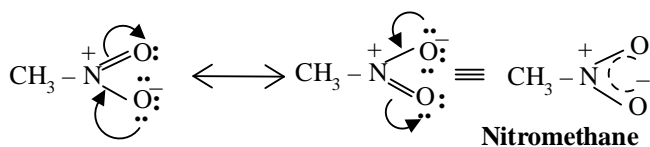
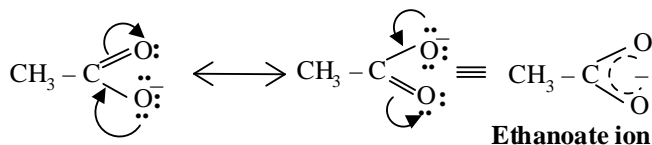
Chemistry of Organic Compounds



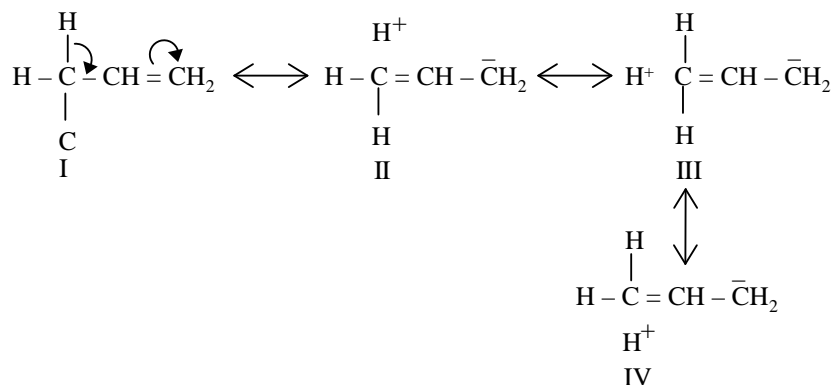
Notes

bond length data. Equal bond lengths of all C–C bonds (139 pm), which is an intermediate value of C–C single bond (154 pm) and C=C double bond (130 pm) lengths, indicates that each C–C bond in benzene (structure III) has a partial double bond character. Hence, structure III, a resonance hybrid, represents the benzene molecule.

Some more examples of resonance structures are as follows:



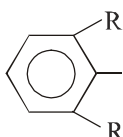
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance*. It involves the conjugation of σ (sigma) bond with π (pi) bond. For example, hyperconjugation in propene can be represented as follows.



The structures II to IV have no bond between one of the H-atom and the C-atom.

25.3.3 Steric Hinderance

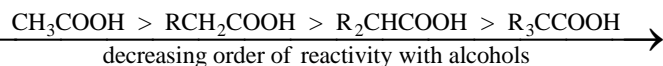
The effect is caused by the large bulky groups present in the vicinity of the reaction centre. This effect was first observed by Hofmann (1872) and Meyer (1874). They regarded it as mechanical hinderance for the attacking species to approach the reaction site. Hofmann

(1872) observed that when a compound of the type  (where, Y = –COOH,

–CONH₂, –CHO, –NH₂ etc. and R = –CH₃, –C₂H₅ etc.) is treated with the reagents such as Cl[–], Br[–], I[–], OH[–], etc., the reaction is hindered or retarded by the substituents at 'R'. The magnitude of hinderance is proportional to the size and number of substituents present in the vicinity of reaction site. Meyer (1874) observed that rate of esterification of aliphatic carboxylic acids and found that their activity was decreased by increasing the number of substituents at the carbon atom adjacent to the COOH group.



Notes

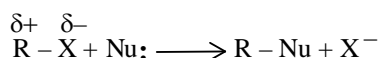
**Intext Questions 25.3**

- What is the condition of polarity for a covalent bond?
.....
- Identify the groups with -I and +I effect from the following species :
-NO₂, -CH₃, -CN, -C₂H₅, -C₆H₅ and $\text{CH}_3-\underset{\text{|}}{\text{CH}}-\text{CH}_3$
.....
- What is the difference between electromeric and inductive effects?
.....
- Classify the following species as electrophiles or nucleophiles :
(i) H₃O⁺ (ii) NO₂⁺ (iii) Br⁻ (iv) C₂H₅O⁻
(v) CH₃COO⁻ (vi) SO₃ (vii) CN⁻ (viii) ⁺CH₃ (ix) :NH₃
.....

With the above general background, let us study various types of reactions in a little more details.

25.3.4 Substitution Reactions

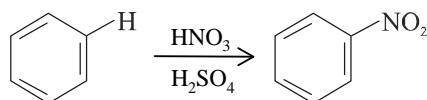
A substitution reaction involves the displacement of one atom or group in a molecule by another atom or group. Aliphatic compounds undergo **nucleophilic substitution** reactions. For example, a haloalkane can be converted to a wide variety of compounds by replacing halogen atom (X) with different nucleophiles as shown below.



Haloalkane

(where R- is an alkyl group and Nu: = -OH, -NH₂, -CN, -SH, -OR', -NHR' etc.)

There is yet another type of substitution reaction which takes place in an aromatic hydrocarbons. In this case, an **electrophilic reagent** attacks the aromatic ring because the latter is electron rich. The leaving group, in this case, is always one of the hydrogen atom of the ring.



Nitrobenzene

For example, in case of nitration the -NO₂ group replaces one hydrogen atom of benzene.

25.3.5 Addition Reactions

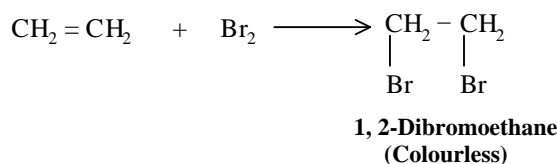
Unsaturated hydrocarbons such as alkenes and alkynes are extremely reactive towards a

Chemistry of Organic Compounds



Notes

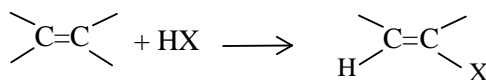
wide variety of reagents. The carbon-carbon double bond (--C=C--) of an alkene contains two types of bonds; one σ (sigma) bond and another π (pi) bond. In alkynes, out of the three carbon-carbon bonds, one is σ (sigma) bond and the other two are π (pi) bonds. The π (pi) bond is weaker than the σ (sigma) bond and breaks easily. For example, the colour of bromine solution disappears when added to the unsaturated hydrocarbons. This is due to the following addition reaction.



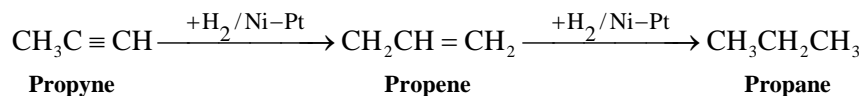
Similarly, hydrogen, halogen acids and chlorine add on to a --C=C-- double bond, as shown below.



The multiple bond of an alkene or alkyne is a region of high electron density. Therefore, it is easily attacked by the electrophilic reagents. One of the most thoroughly studied addition reactions is that of halogen acids.

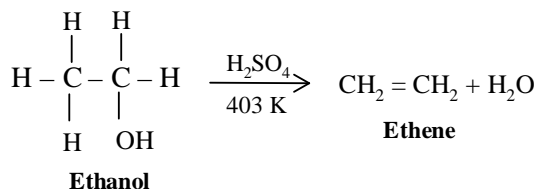


In alkynes ($\text{--C}\equiv\text{C--}$), two molecules of hydrogen add; first to give an alkene and finally the corresponding alkane, as shown below:



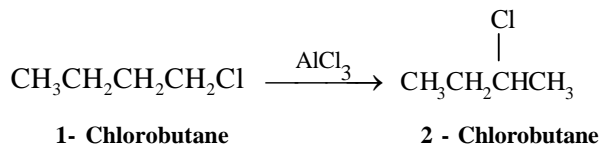
25.3.6 Elimination Reactions

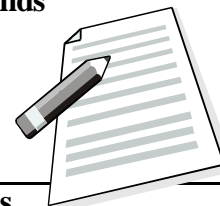
From the above discussion, you know that we get a saturated compound by the addition reaction of an alkene. The reverse reaction i.e. the formation of an alkene from a saturated compound, can also be carried out and is called an **elimination reaction**. An elimination reaction is characterized by the removal of a small molecule from adjacent carbon atoms and the formation of a double bond. For example, when alcohols are heated with a strong acid as the catalyst, a molecule of water is removed and a double bond is formed.



25.3.7 Molecular Rearrangements

A molecular rearrangement proceeds with a fundamental change in the hydrocarbon skeleton of the molecule. During this reaction, an atom or group migrates from one position to another. For instance, 1-chlorobutane in the presence of a Lewis acid (AlCl_3) rearranges to 2-chlorobutane.



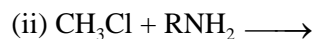
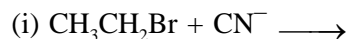


Notes



Intext Questions 25.4

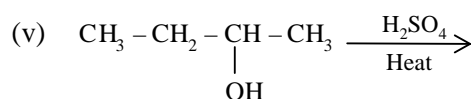
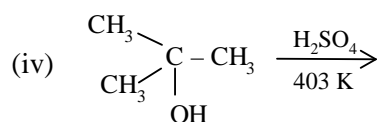
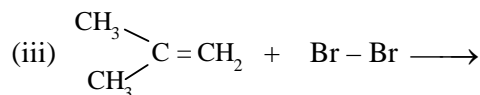
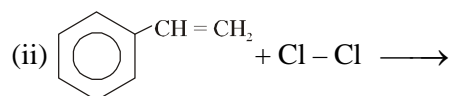
1. Write the products of each of the following reactions:



2. Write the conditions for nitration of benzene.

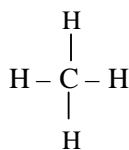
.....

3. Predict the products of the following reactions :

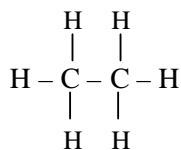


25.4 Isomerism

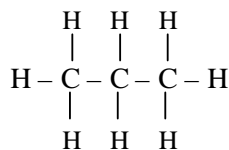
The simple alkanes containing upto three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below :



Methane



Ethane



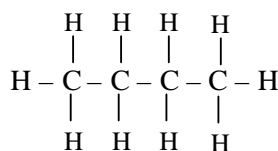
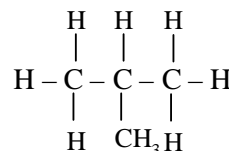
Propane

But for next higher hydrocarbon i.e. butane (C_4H_{10}), there are two possible ways in which the carbon atoms can be linked together. They may be linked to form a **straight chain** or a **branched chain**.

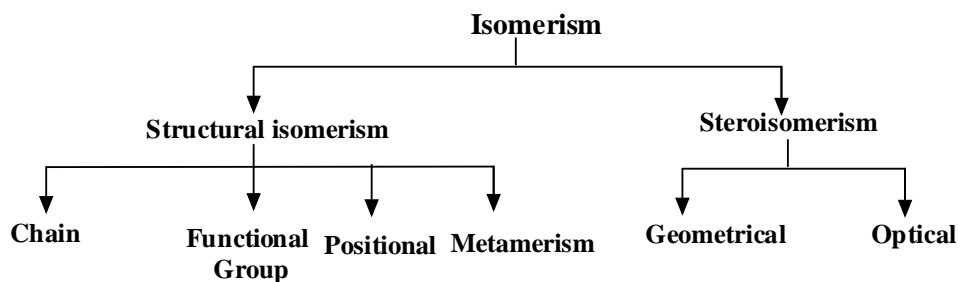
Chemistry of Organic Compounds



Notes

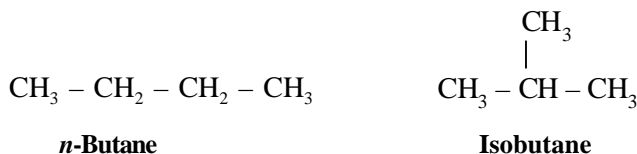
Butane (b.p. -5°C) 268 K(2-Methylpropane) (b.p. -12°C) 261 K

Thus, there are two types of butane which are different compounds and they show different properties. *Different substances which have the same molecular formula but differ in their structures, physical or chemical properties are called isomers* and this phenomenon is known as **isomerism**. The isomerism can be of various types as shown below :

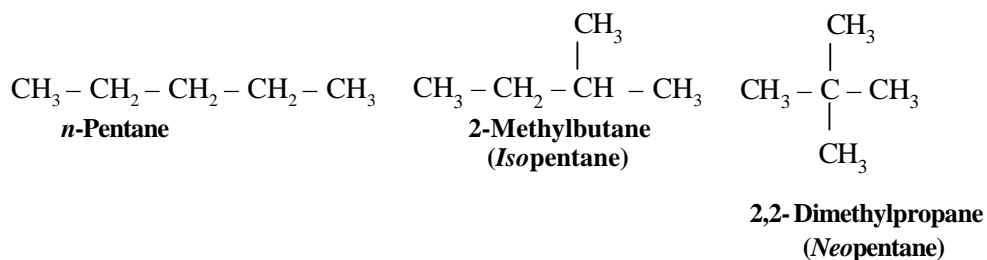


1. Structural Isomerism : Compounds which have the same molecular formula but differ in their structure are called **structural isomers** and the phenomenon is called **structural isomerism**. This is further subdivided into four types; **chain**, **functional**, **positional isomerism**, and **metamerism**.

- (i) **Chain isomerism :** These isomers differ in the chain of the carbon atoms, for instance, *n*-butane and isobutane are two isomers of C_4H_{10} .



Similarly, pentane (C_5H_{12}) has the following three isomers :



Similarly, hexane (molecular formula C_6H_{14}) can have five chain isomers.

- (ii) **Functional isomerism :** These isomers differ in the type of functional group. For example; *ethanol* and *ether* the two isomers having molecular formula $\text{C}_2\text{H}_6\text{O}$, belong to two different classes of organic compounds. Similarly, the two isomers corresponding



to molecular formula $C_3H_6O_2$ are, an acid and an ester having quite distinct structures and properties.

(Molecular Formula: C_2H_6O)

C_2H_5OH
Ethanol
(alcohol)

and

$CH_3 - O - CH_3$
Methoxymethane
(ether)

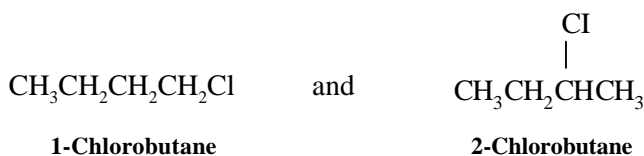
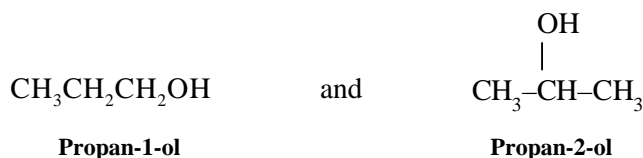
(Molecular Formula: $C_3H_6O_2$)

CH_3CH_2COOH
Propanoic acid

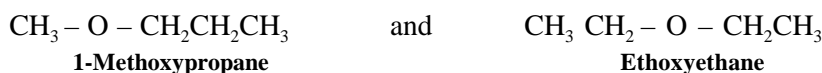
and

$CH_3 - COOCH_3$
Methyl ethanoate

- (iii) **Positional isomerism:** These isomers differ in the attachment of the functional group to the chain at different positions. Examples are as follows :



- (iv) **Metamerism** is exhibited by those compounds in which functional group comes in between the carbon chain and breaks the continuity of the chain. This breaking occurs at different positions and different isomers are formed which are called Metamers. For example, 1-methoxypropane and ethoxyethane are two metamers differing in chain length (size of alkyl groups) on the two sides of oxygen atom as shown below.



2. Stereoisomerism : Stereoisomerism is exhibited by the compounds which have similar attachment of atoms but differ in their arrangement in space. There is two types of stereoisomerism—**geometrical** and **optical**.

- (i) **Geometrical Isomerism:** Consider two isomers of 2-butene as shown below.

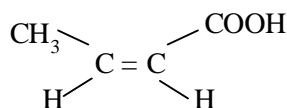


A *cis*- **isomer** is the one having identical groups on same side of double bond. On the other hand, a *trans*-**isomer** has identical groups on opposite side. In the above structures, *cis*-2- butene (two $-CH_3$ groups on the same side) and *trans*-2-butene (two $-CH_3$ groups on different sides) are two geometrical isomers (stereoisomers) as they differ in the geometries of the groups around the double bond. Another example of *cis*-and *trans*-isomerism is **2-butenic acid** or **But-2-enoic acid**.

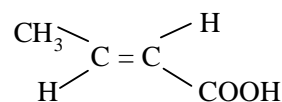
Chemistry of Organic Compounds



Notes



cis- But-2-enoic acid



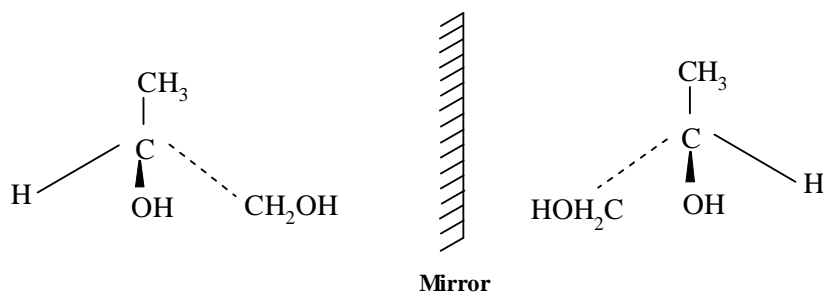
trans-But-2-enoic acid

Note that in the above examples, the two isomers exist because the rotation of groups across C=C bond is not possible (it is also called as restricted rotation).

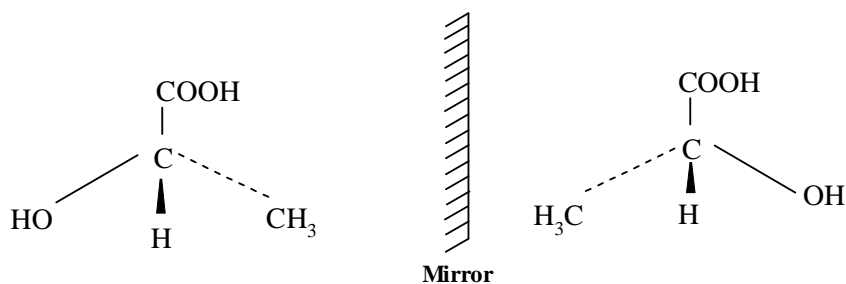
Geometrical isomerisms is also shown by cyclic compounds and compounds containing –C=N– bond, about which you will study at higher level.

(ii) **Optical Isomerism:** The optical isomerism is shown by the compounds having at least one carbon atom joined to four different atoms or groups. Such a carbon atom is called **asymmetric** or **chiral** carbon atom; and those which are not chiral (do not have four different groups) are called **achiral**. A chiral compound can have two different arrangements of groups attached to the chiral carbon as shown below for 1,2-dihydroxypropane.

The wedge sign (▲) shows that the direction of the bonds is towards the viewer and dotted line (.....) indicates backward direction of the bonds.



The resulting isomers are non-superimposable mirror images of each other and are called enantiomers. Thus, the enantiomers differ in the three-dimensional arrangement of atoms or groups. Another example of enantiomers is that of lactic acid as shown below:



Enantiomers of Lactic acid

The optical isomers have identical physical properties except optical activity. They rotate the plane of plain polarized light in opposite directions. The **plain polarized light** is defined

as the light that vibrates in one plane only. *The rotation of the plane of polarized light is called optical activity.* Those substances that can rotate the plane of polarized light are said to be **optically active**. Compounds that rotate the plane of plane polarized light to the right (clockwise) are said to be **dextrorotatory**. The dextrorotatory is denoted by '**d**' or (+) before the name of the compound. Similarly, compounds that rotate the plane to the left (anticlockwise) are called **laevorotatory** and this is denoted by placing '**l**' or (-) before the name of the compound. A mixture containing equal amounts of **d**- and **l**- isomers is called a **racemic mixture** and is optically inactive denoted by **dl** or \pm .

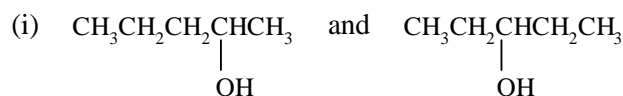


Intext Questions 25.5

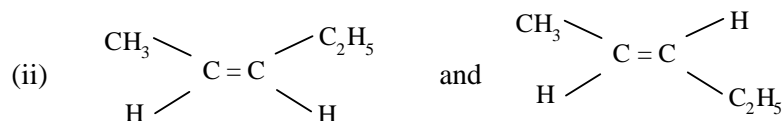
1. Is 1-butene a structural isomer of **cis**- or **trans**-2-butene?

.....

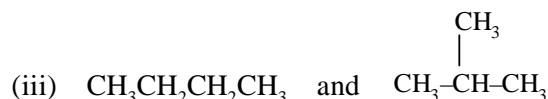
2. Identify the type of isomerism exhibited by the following pairs of compounds:



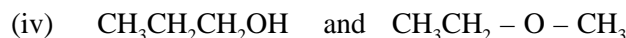
.....



.....



.....



.....

3. Write the structures of all the isomers of hexane (C_6H_{14}).

.....

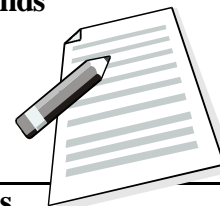
4. Which one of the following compounds would show geometrical isomerism?



.....

MODULE - 7

Chemistry of Organic Compounds



Notes

Chemistry of Organic Compounds



Notes



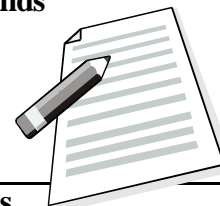
What You Have Learnt

- Organic compounds are classified into **aliphatic** (open-chain), **homocyclic** (closed ring) or **carbocyclic (alicyclic and aromatic)** hydrocarbons and their derivatives, and **heterocyclic** compounds (contain at least one heteroatom i.e., N,S,O in the ring).
- Homologous series** of organic compounds and IUPAC naming of different classes.
- The substitution, elimination, additions reactions and molecular rearrangements.
- Homolytic** fission of a covalent bond produces free radicals because each of the parting away atoms takes away its shared electron.
- Heterolytic fission** of a covalent bond produces ions because one of the atoms takes away both the shared electrons.
- Electrophiles** are positively charged or electron deficient species.
- Nucleophiles** are negatively charged or electron rich species.
- Benzene ring undergoes aromatic substitution reactions.
- A **functional group** is an atom or group responsible for specific properties of a compound.
- The compounds which have the same molecular formula but different structure are called structural **isomers**.
- Isomerism is classified into **structural isomerism** and **stereoisomerism**.
- A carbon atom attached to four different groups is called **chiral** atom or **asymmetric** carbon atom.
- The non-superimposable mirror image isomers of a compound are called enantiomers. They are optically active and rotate the plane of plane polarized light in opposite directions.



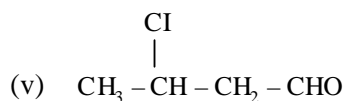
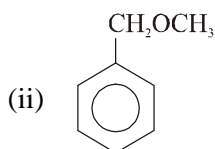
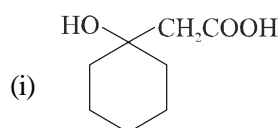
Terminal Exercise

- What are hydrocarbons? Explain giving two examples.
- Give two examples of aromatic hydrocarbons.
- Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names.
 - $(\text{CH}_3)_3\text{CH}$
 - $\text{CH}_3\text{CH} = \text{CH}_2$
 - $(\text{CH}_3)_4\text{C}$
 - $\text{CH}_3\text{C} \equiv \text{CH}$
 - $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 - $\text{CH}_2 = \text{CH}_2$
- Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula:
 - C_5H_{10}
 - C_5H_8
- Write the structures of the following compounds :
 -
 -
 -



Notes

- (i) Isobutylbenzene
 - (ii) 4-Methyl-2-pentene
 - (iii) Hepta-1,6-diene
 - (iv) Cyclobutene
6. Write the structures for the following compounds:
- (i) 1-Bromo-3-methylhexane
 - (ii) 3-Chloro-2,4-dimethylpentane
 - (iii) 3-Methylbutanal
 - (iv) Ethyl propanoate
 - (v) 2-Methylbutanenitrile
 - (vi) Cyclohexene
 - (vii) 3-Methylhexan-2-one
7. What are electrophilic aromatic substitution reactions? How will you prepare nitrobenzene from benzene?
8. Draw all the possible structural isomers having the molecular formula C_4H_9Cl and give their IUPAC names.
9. What is a nucleophilic aliphatic substitution reaction? Give one example.
10. Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.
11. Write a short note on the following : (i) Structural isomerism (ii) Stereoisomerism
12. Define a functional group. Identify the functional group(s) present in following compounds :



15. Describe hyperconjugation in terms of resonance.



Answers to Intext Questions

25.1

1. Word root Suffix

- (i) Hex ane



(ii) Pent 2-ene

(iii) Prop yne

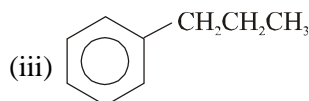
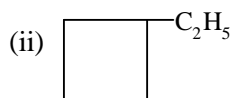
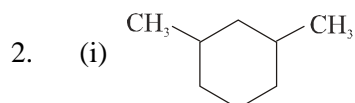
2. (i) Oct-2-ene (ii) 2, 4-Dimethylpentane

25.2

1. (i) 1-ethyl-3-methylbenzene

(ii) Cycloheptane

(iii) Cyclopenta-1,3-diene



25.3

1. Covalent bond between two different atoms having large difference in their electronegativities.

2. **-I effect groups** $-\text{NO}_2$, $-\text{CN}$, $-\text{C}_6\text{H}_5$ +

I effect groups $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, CH_3CHCH_3 .

3. Electromeric effect is temporary polarization, whereas inductive effect is permanent polarisation of a covalent bond.

4. (i) Electrophile (ii) Electrophile

(iii) Nucleophile (iv) Nucleophile

(v) Nucleophile (vi) Nucleophile

(vii) Nucleophile (viii) electrophile

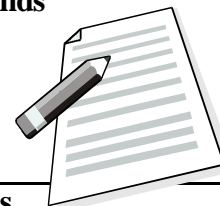
(ix) Nucleophile

25.4

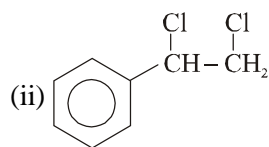
1. (i) $\text{CH}_3\text{CH}_2\text{CN}$ (ii) CH_3NHR

2. HNO_3 in presence of H_2SO_4 .

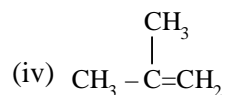
3. (i) $\text{CH}_3\text{CH}_2\text{Br}$



Notes



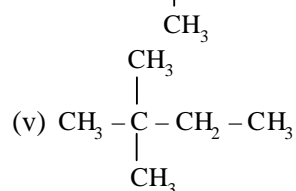
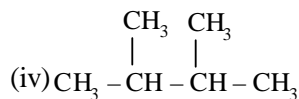
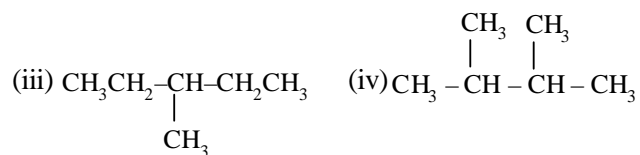
(iii) $(\text{CH}_3)_2\text{CBr} - \text{CH}_2\text{Br}$ (major product)



(v) $\text{CH}_3 - \text{CH} = \text{CHCH}_3$ (major product)

25.5

- Yes
- Positional isomerism
 - Geometrical isomerism
 - Chain isomerism
 - Functional group isomerism



4. (i) Yes (ii) Yes (iii) No

