



313en23

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;



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- explain different types of reactions: substitution, addition, elimination and molecular rearrangements;
- identify nucleophiles and electrophiles;
- explain electronic effects in a covalent bond such as inductive effect; electromeric effect, resonance, hyperconjugation and steric hindrance;
- explain structural isomerism and stereoisomerism.
- define absolute configuration;
- assign absolute configuration (R-S and D-L) to a chiral centre; and
- qualitative and quantitative analysis of organic compound.

23.1 CLASSIFICATION OF HYDROCARBONS

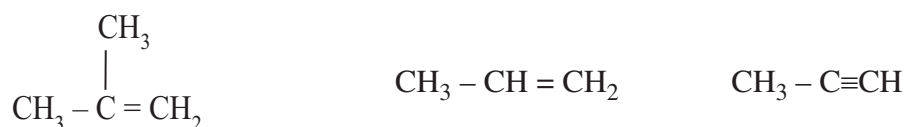
All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

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.

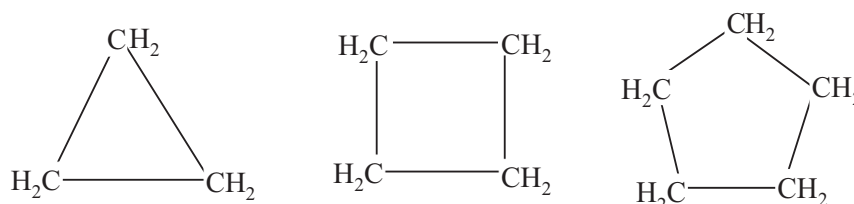
For example :



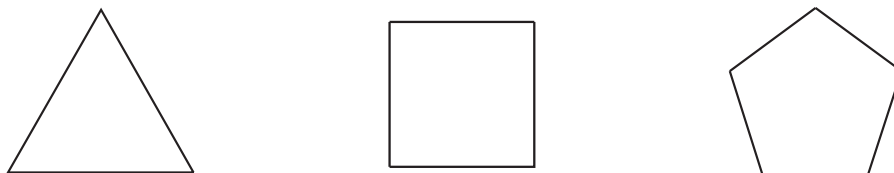
2. **Closed-chain or cyclic compounds:** These compounds have at least one ring (cyclic) system. These are further divided into two sub-classes: **homocyclic** and **heterocyclic** based on the atoms present in the ring. They are called **homocyclic** or **carbocyclic** when the ring is formed by carbon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

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

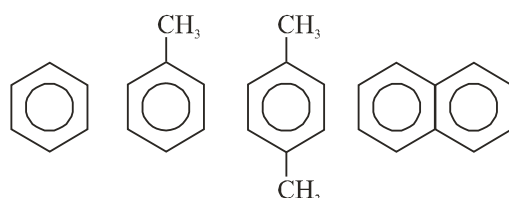
- (i) **Alicyclic compounds:** This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:



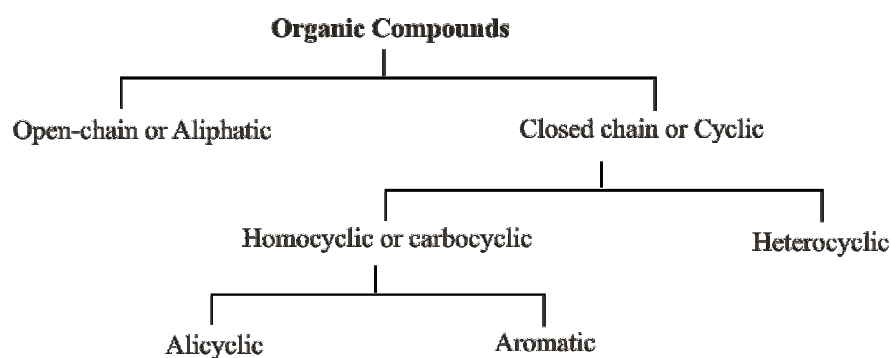
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a $-\text{CH}_2-$ group.



(ii) **Aromatic compounds:** The group of homocyclic compounds having special set of properties are called aromatic compounds which will be discussed in Lesson 24. 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 :

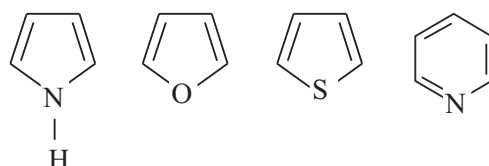


The above classification of the organic compounds can be summarised as below:



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:



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23.2 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 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 23.1.

Table 23.1: Homologous series of hydrocarbons

Saturated		Unsaturated			
General Name : <i>Alkanes</i>		<i>Alkenes</i>		<i>Alkynes</i>	
General Formula : $\text{C}_n\text{H}_{2n+2}$		C_nH_{2n}		$\text{C}_n\text{H}_{2n-2}$	
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
...
...
...

23.2.1 IUPAC Nomenclature of Acyclic Hydrocarbons

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



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(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 23.2.

Table 23.2 : 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 23.3.

Table 23.3 : 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

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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 23.4.

Table 23.4: Some alkyl groups

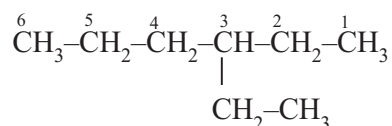
Parent Chain	Formula R-H	Alkyl group R-	Name
Methane	CH ₄	CH ₃ -	Methyl
Ethane	CH ₃ CH ₃	CH ₃ CH ₂ -	Ethyl
Propane	CH ₃ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ -	Propyl
		$\begin{array}{c} \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$	Isopropyl
Butane	CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₂ -	Butyl
		$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}-\text{CH}_3 \\ \end{array}$	<i>sec</i> -butyl
Isobutane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2- \end{array}$	Isobutyl
		$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \end{array}$	<i>tert</i> -butyl

Notes

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 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*.

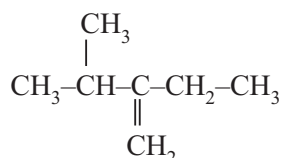
Let us consider the following example:



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**.

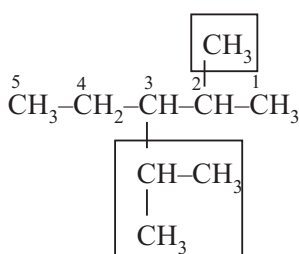
Similarly,



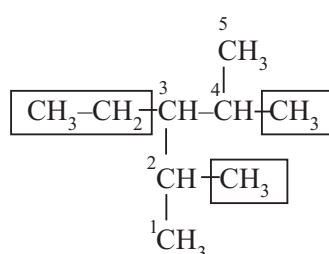
Wordroot - **But** + Suffix - **ene**

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.



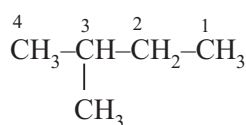
Main chain has 2 branches (Wrong)



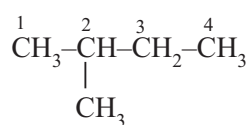
Main chain has 3 branches (Correct)

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.

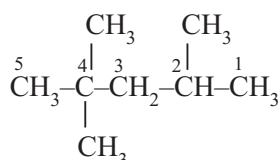


Wrong numbering

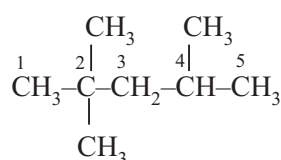


Correct numbering

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 :



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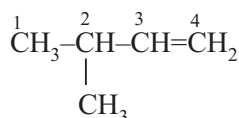
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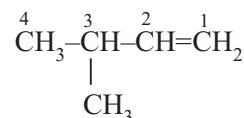


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Wrong numbering



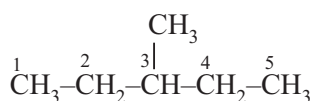
Correct numbering

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*.

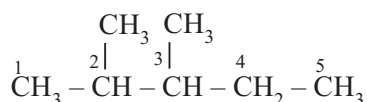
Let us consider a compound represented by the following structure:



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.

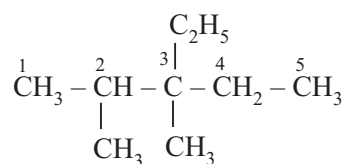


You can see that they are attached to the positions 2 and 3 of the main chain. Hence, the name of the compound is 2,3-dimethylpentane.

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.

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.

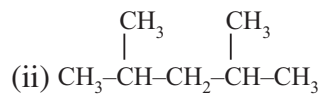
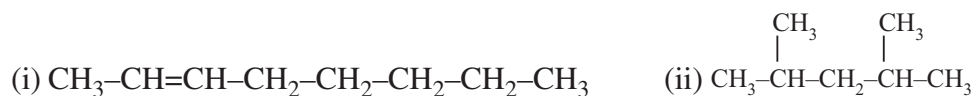


INTEXT QUESTIONS 23.1

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



2. Give IUPAC name to the following compounds

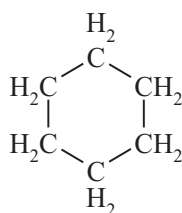


23.2.2 Nomenclature of Cyclic Hydrocarbons

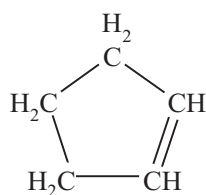
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) Alicyclic Compounds

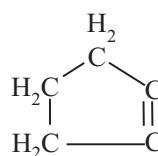
As we have already discussed (in Section 23.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix* 'cyclo' before the *word root*. The suffix **ane**, **ene** or **yne** are written according to the saturation or unsaturation in the ring structure. Given below are some examples of alicyclic compounds.



Cyclohexane



Cyclopentene



Cyclopentyne



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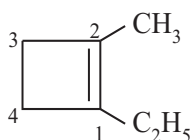
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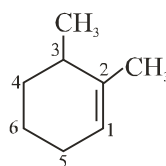
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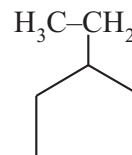
If an alkyl substituent is present, it is indicated by the appropriate *prefix* and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



1-Ethyl-2-methylcyclobutene



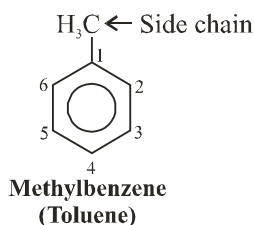
2,3-Dimethylcyclohexene



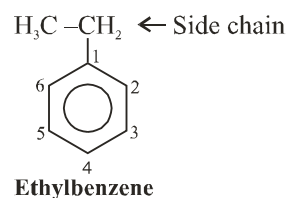
Ethylcyclopentane

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.

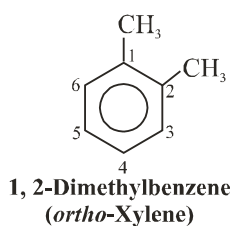


Methylbenzene
(Toluene)

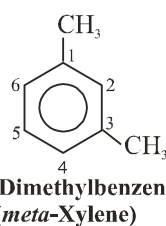


Ethylbenzene

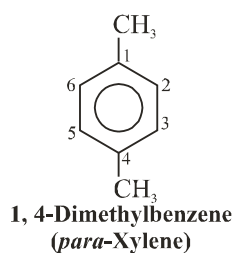
Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1,2; 1,3 and 1,4 derivatives. These are also known as *ortho-* (or *o-*), *meta-* (or *m-*) and *para-* (or *p-*) substituted compounds, respectively.



1, 2-Dimethylbenzene
(*ortho*-Xylene)



1, 3-Dimethylbenzene
(*meta*-Xylene)



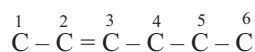
1, 4-Dimethylbenzene
(*para*-Xylene)

23.2.3 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

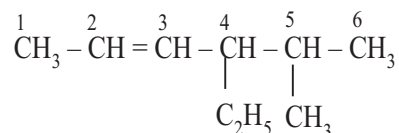
Step 1 The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C₂ is drawn.



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

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:



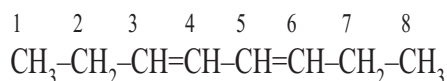
Example 2. Writing the structure of **Octa-3,5-diene**

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

Step 2- Make C=C at C₃ and at C₅.

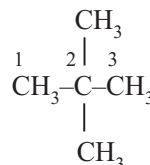
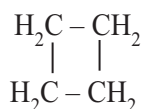
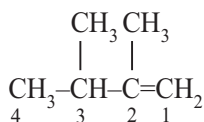
Step 3- Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms.

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

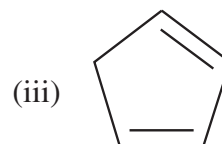
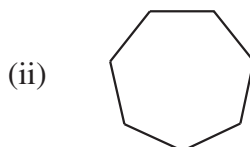
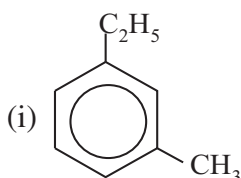


After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.



INTEXT QUESTIONS 23.2

1. Write IUPAC names for the following compounds :



2. Write the structural formula for the following compounds:

(i) 1,3-Dimethylcyclohexane (ii) Ethylcyclobutane (iii) *n*-Propylbenzene



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23.2.4 IUPAC Nomenclature of Aliphatic Organic Compounds Containing Functional Groups

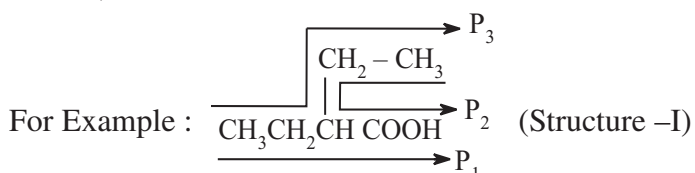
A **functional group** is an atom or group of atoms which is responsible for characteristic properties of a compound. For example :

-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 23.5). 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.

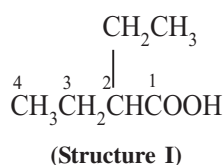


P₁ or P₂ are correct selections of chain of carbon atoms whereas P₃ is wrong selection as it does not include the carbon atom of the functional group.

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.



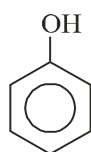
Rule 5: While writing the name of the compound, place the substituents in the alphabetical order.

Table 23.5 lists some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

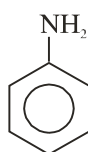
Table 23.5: Some Common Functional Groups and their Aliphatic Derivatives

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



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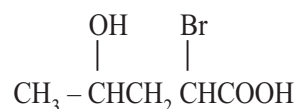
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b) Naming of Organic compounds with more than one functional group: In case of organic compounds containing more than one functional group, one group is given preference over the other(s) in deciding the parent compound. The priority order of the various functional groups is as follows; $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, $-\text{COX}$, $-\text{CONH}_2$, $-\text{CHO}$, $-\text{CO}-$, $-\text{CN}$, $-\text{OH}$, $-\text{SH}$, $-\text{O}-$, $-\text{NH}_2$, $-\text{X}$ (halogen), $-\text{NO}_2$, $-\text{C}=\text{C}-$, and $-\text{C}\equiv\text{C}-$. 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, $-\text{COOH}$ group is given priority over the $-\text{OH}$ and $-\text{Br}$ (halo) groups.

23.3 TYPES OF REACTIONS IN ORGANIC COMPOUNDS

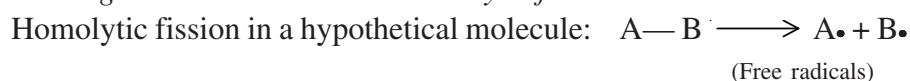
You are aware that a chemical reaction occurs when one substance is converted into another substance(s). A chemical reaction is accompanied by breaking of some bonds and by making of some others. In organic chemistry, this can happen in more than one way involving a variety of reactions. The different 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.

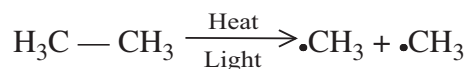
23.3.1 Breaking of a Covalent Bond - Types of Bond Fission

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**.

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



Now consider the following C-C bond fission:

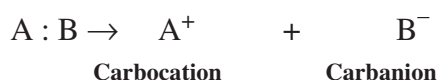


(Free radicals)

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.

2. **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.

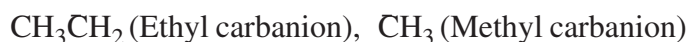


This type of bond fission results in the formation of *ions*. The ion which has a *positive charge on the carbon atom*, is known as the **carbonium ion** or a **carbocation**. For example,



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^+ , $\text{CH}_3\overset{+}{\text{C}}\text{O}$, 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.

23.3.2 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



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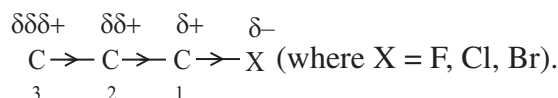
Nomenclature and General Principles

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.



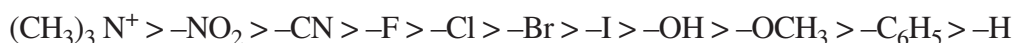
The carbon atom gets a partial +ve charge ($\delta+$) and halogen atom a partial negative charge ($\delta-$). This positively charged C_1 attracts bonded electrons of $\text{C}_1 - \text{C}_2$ bond, thus making C_2 atom a little less positive than C_1 . Similarly, this +ve charge is shifted to C_3 but 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.

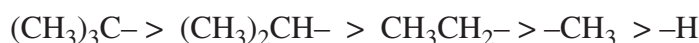
Groups with – I Effect (Electron Withdrawing Groups) :

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) :

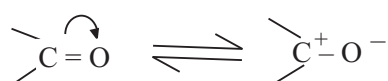
Any atom or group of atoms that repels electrons more strongly than hydrogen, is said to have +I effect. Following are the various groups in the decreasing order of +I effect.



(b) **Electromeric effect** : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g.

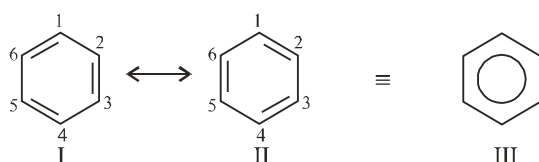
$\diagup \text{C}=\text{C} \diagdown$, $\diagup \text{C}=\text{O}$, $\diagup \text{C}=\text{N}$ etc.). It involves the complete transfer of electrons

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.

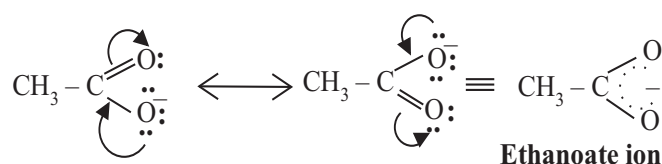
(c) **Resonance** : This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound 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 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:



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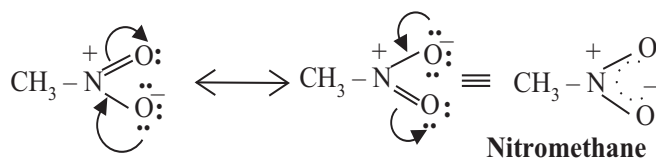
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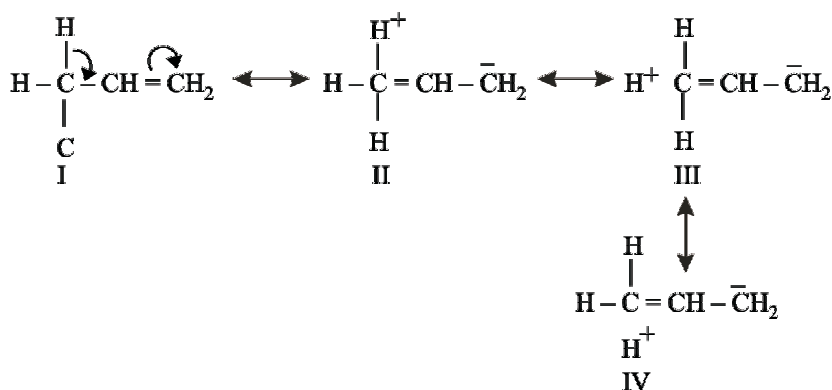
Nomenclature and General Principles



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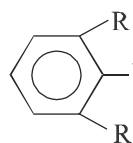
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance*. It involves the conjugation of σ (sigma) bond with π (pi) bond. For example, hyperconjugation in propene can be represented as follows.



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

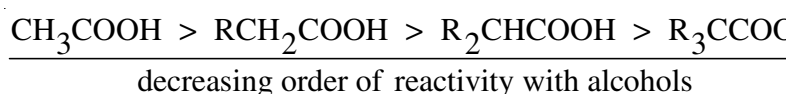
23.3.3 Steric Hinderance

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, $\text{Y} = -\text{COOH}, -\text{CONH}_2, -\text{CHO}, -\text{NH}_2$ etc. and $\text{R} = -\text{CH}_3,$

$-\text{C}_2\text{H}_5$ etc) is treated with the reagents such as $\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-$, 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.





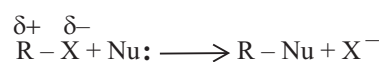
INTEXT QUESTIONS 23.3

1. What is the condition of polarity for a covalent bond?
2. Identify the groups with $-I$ and $+I$ effect from the following species :
 $-\text{NO}_2$, $-\text{CH}_3$, $-\text{CN}$, $-\text{C}_2\text{H}_5$, $-\text{C}_6\text{H}_5$ and $\text{CH}_3-\underset{|}{\text{CH}}-\text{CH}_3$
3. What is the difference between electromeric and inductive effects?
4. Classify the following species as electrophiles or nucleophiles :
 (i) H_3O^+ (ii) NO_2^+ (iii) Br^- (iv) $\text{C}_2\text{H}_5\text{O}^-$
 (v) CH_3COO^- (vi) SO_3 (vii) CN^- (viii) $^+\text{CH}_3$ (ix) $:\text{NH}_3$

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

23.3.5 Substitution Reactions

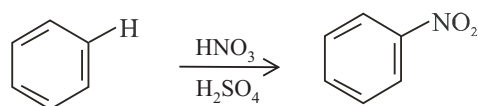
A substitution reaction involves the displacement of one atom or group in a molecule by another atom or group. Aliphatic compounds undergo **nucleophilic substitution** reactions. For example, a haloalkane can be converted to a wide variety of compounds by replacing halogen atom (X) with different nucleophiles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



Haloalkane

(where R- is an alkyl group and Nu:= $-\text{OH}$, $-\text{NH}_2$, $-\text{CN}$, $-\text{SH}$, $-\text{OR}'$, $-\text{NHR}'$ 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 $-\text{NO}_2$ group replaces one hydrogen atom of benzene.



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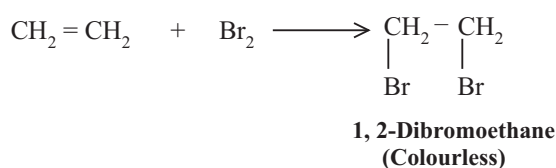
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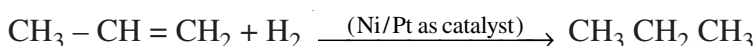
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23.3.6 Addition Reactions

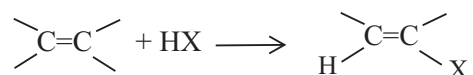
Unsaturated hydrocarbons such as alkenes and alkynes are extremely reactive towards a wide variety of reagents. The carbon-carbon double bond ($-C=C-$) of an alkene contains two types of bonds; one σ (sigma) bond and another π (pi) bond. In alkynes, out of the three carbon-carbon bonds, one is σ (sigma) 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.



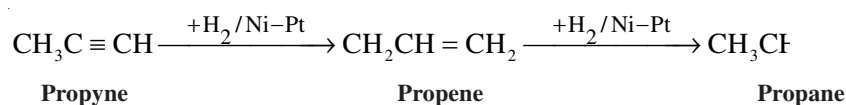
Similarly, hydrogen, halogen acids and chlorine add on to a $-C=C-$ double bond, as shown below.



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

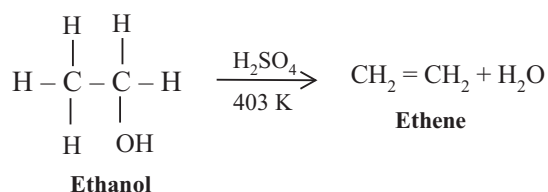


23.3.7 Elimination Reactions

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.

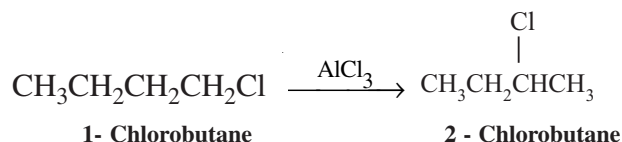


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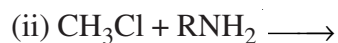
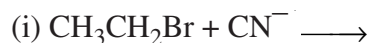
23.3.8 Molecular Rearrangements

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.



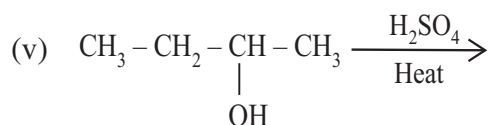
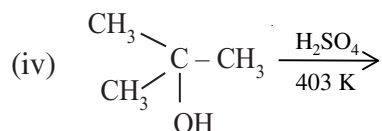
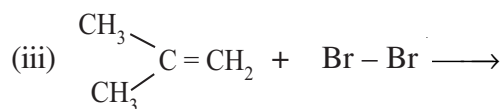
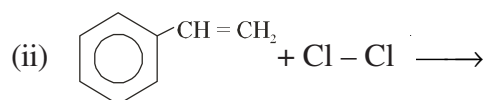
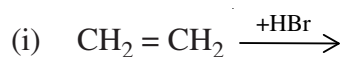
INTEXT QUESTIONS 23.4

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



2. Write the conditions for nitration of benzene.

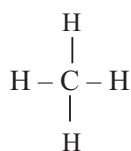
3. Predict the products of the following reactions :



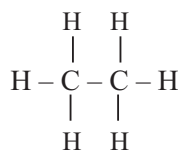
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23.4 ISOMERISM

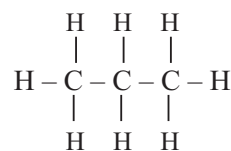
The simple alkanes containing upto three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below :



Methane

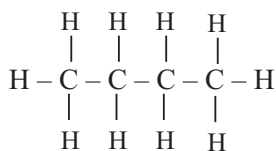


Ethane

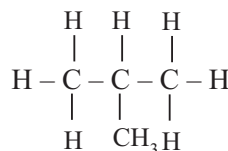


Propane

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**.

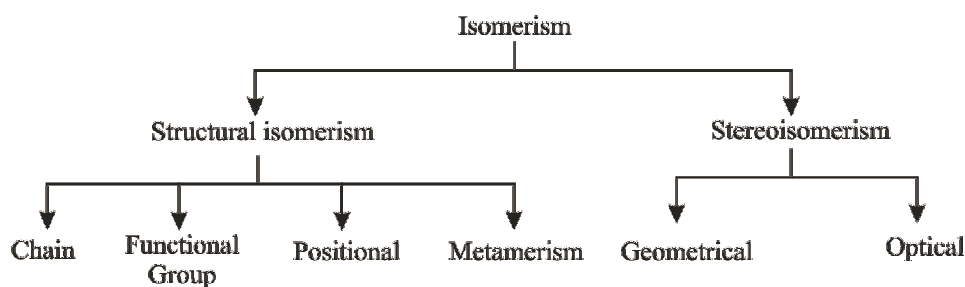


Butane (b.p.- -5°C) 268 K



(2-Methylpropane) (b.p.- 12°C) 261 K

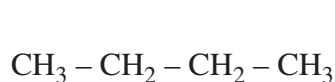
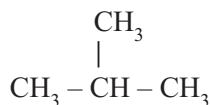
Thus, there are two types of butane which are different compounds and they show different properties. *Different substances which have the same molecular formula but differ in their structures, physical or chemical properties are called isomers* and this phenomenon is known as **isomerism**. The isomerism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

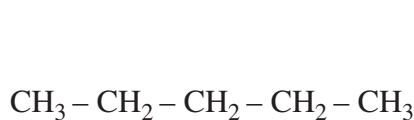
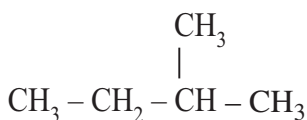
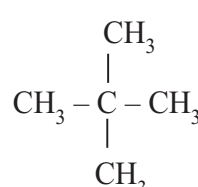
(i) **Chain isomerism :** These isomers differ in the chain of the carbon atoms, for instance, *n*-butane and isobutane are two isomers of C_4H_{10} .

Notes

*n*-Butane

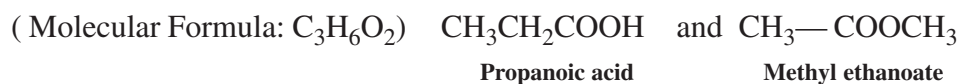
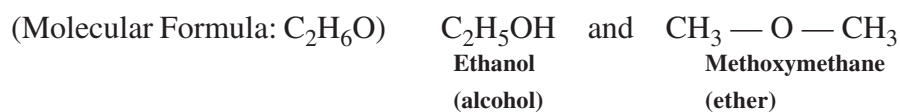
Isobutane

Similarly, pentane (C₅H₁₂) has the following three isomers :

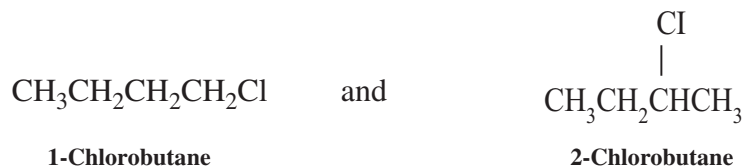
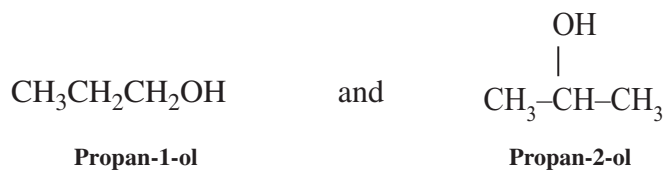
*n*-Pentane2-Methylbutane
(Isopentane)2,2- Dimethylpropane
(Neopentane)

Similarly, hexane (molecular formula C₆H₁₄) 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 C₂H₆O, belong to two different classes of organic compounds. Similarly, the two isomers corresponding to molecular formula C₃H₆O₂ are, an acid and an ester having quite distinct structures and properties.



- (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.



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1-Methoxypropane



Ethoxyethane

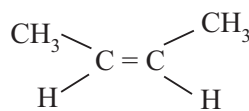
2. Stereoisomerism : Stereoisomerism is exhibited by the compounds which have the same structural formula i.e. their atoms are connected in the same order, but they differ from each other in the way these atoms (or groups) are arranged in space.

Stereoisomerism can be further divided into **conformational isomerism** and **Configurational isomerism**.

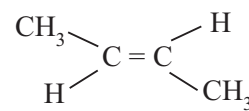
The **absolute configuration** of a compound is the actual three dimensional arrangement of the groups or atoms in space. Thus, configurational isomers have unique configuration. These isomers cannot be converted to each other without breaking of bonds. The configurational isomerism could be further subdivided into **geometrical** and **optical isomerisms**. These are explained below.

Conformational isomerism is exhibited by those isomers which can be interconverted without breaking of bonds. Thus, conformational isomers are obtained by rotation about single bonds. The conformational isomerism is explained using ethane as the example, see section 24.13.

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

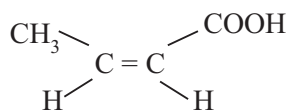


cis- But-2-ene

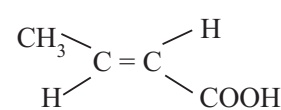


trans- But-2-ene

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 –CH₃ groups on the same side) and *trans*-2-butene (two –CH₃ 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**.



cis- But-2-enoic acid



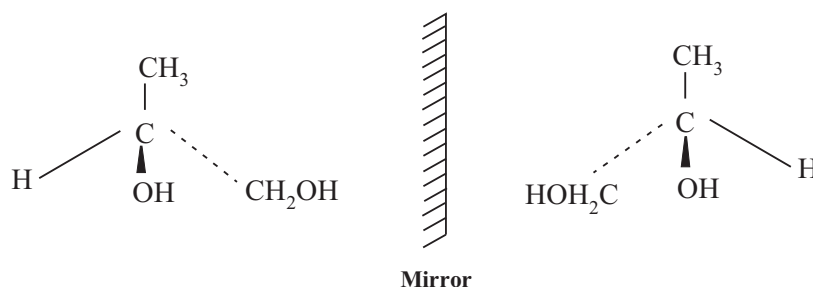
trans-But-2-enoic acid

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).

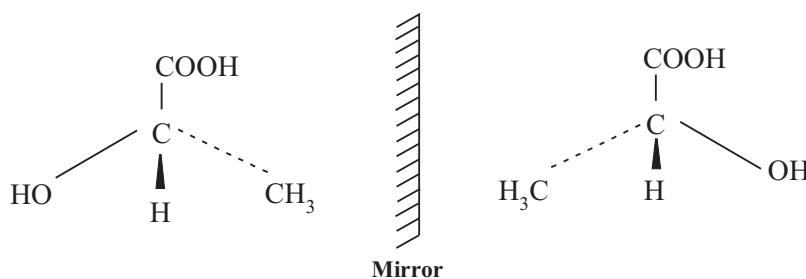
Geometrical isomerism is also shown by cyclic compounds and compounds containing –C=N– bond, about which you will study at higher level.

(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 (\blacktriangle) 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 .



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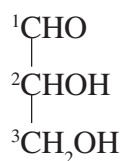
Nomenclature and General Principles

Assignment of Configuration

The nature of rotation whether *laevo* or *dextro*, i.e. *l*- or *d*- does not indicate the actual arrangement of atoms or groups of a molecule in space. In other words, by knowing the optical activity, one cannot tell about the *absolute configuration* of a compound. The absolute configuration in case of geometrical isomers is indicated by the designations *cis*- or *trans*- followed by the name of the compounds.

However, in case of optical isomers, the absolute configuration is given by D, L system and *R*, *S* system. For assigning the absolute configuration of a compound as *D* or *L* or *R* or *S*, the structure of a compound has to be written in a particular way.

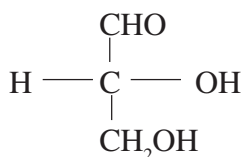
One such way was given by Emil Fischer and the structure represented in such a way is called **Fischer projection**. For drawing such projections, a molecule is oriented vertically so that the carbon atom number 1 which is most highly oxidised is placed at the top in the chain. For example, in case of glyceraldehyde, the carbon atom carrying carbonyl group is placed at the top in the vertical chain as shown below:



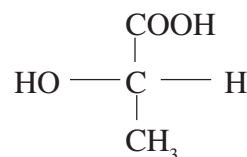
Glyceraldehyde

Then, the main substituent attached to the carbon, for the configuration to be arranged is looked for. Here, in case of glyceraldehyde, the configuration is to be assigned to C-2 atom and the main substituent attached to C-2 atoms is an –OH group. Please note that, here, C-2 atom is attached to 4 different substituents and such a centre (atom) in the molecule is called a **chiral centre**. It is also represented by an asterisk (*) mark in the structure.

If, in a Fischer projection, the main substituent appears on the *right*, then the particular molecule is said to have **D configuration**. In the other situation, if the main substituent in the molecule appears on the *left side* in the Fischer projection, then that compound said to have **L configuration**. The structures of D-glyceraldehyde and L-lactic acid are shown below:



D-(+)-Glyceraldehyde



L-(+)-Lactic acid

Note that in addition to configuration as D or L, the signs of rotation (i.e. + or –) are also given in the names of the compounds above. You can see that both the compounds are dextrorotatory though one is having D configuration while other

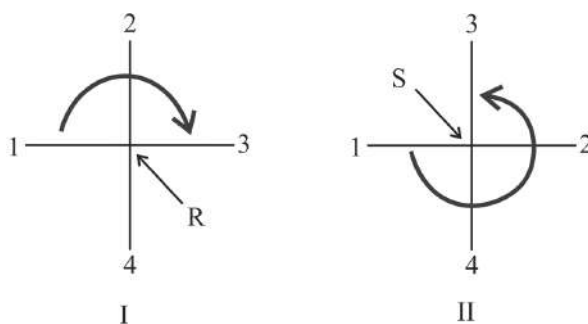
has L configuration. Thus, the configurations are not related to the directions (or signs) of the rotation of plane polarized light. The D, L system of assigning configurations is widely used for carbohydrates and amino acids.

However, this system can not be applied equally well to all compounds because sometimes it is not easy to identify the main chain and the main substituent in the structure of the compound. In such situations, another system called, **R, S convention** is used to assign the absolute configuration of a chiral centre in a compound.

Assignment of Absolute Configuration as R or S

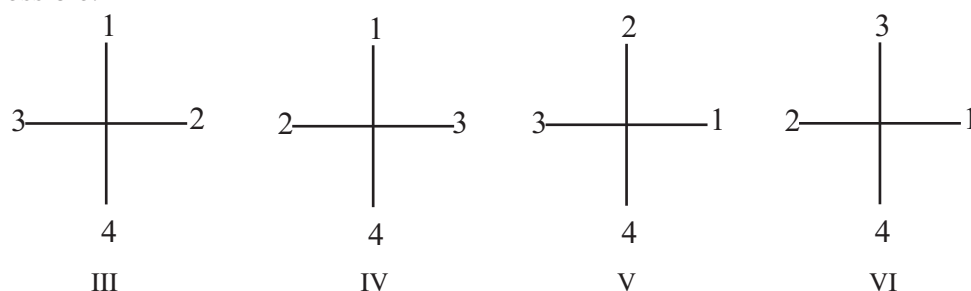
First of all, the Fischer projection of a particular given optical isomer is written. Then, the four substituents attached to the chiral carbon, for which the absolute configuration is to be assigned, are identified. These substituents are then assigned a priority order as 1, 2, 3 and 4 according to certain rules which were given by Cohn-Ingold and Prelog.

The Fischer projection of the molecule is then rearranged, if required, so as to place the substituent of lowest priority, *i.e.* substituent number 4, at the bottom of the Fischer projection. There are also certain rules to convert one Fischer projection to another about which you will study in higher classes. When we place the substituent of lowest priority at the bottom in the Fischer projection, there are two ways in which the other substituents (1, 2 and 3) appear depending upon the actual position of these groups in the molecules. These are shown below.



Now, if we ignore 4 and trace a path from 1 → 2 → 3, it will be *clockwise* in I while *anticlockwise* in II. The isomer I is said to have *R* configuration at chiral centre while in isomer II, the chiral centre is said to have *S* configuration.

You may also be thinking that the following arrangements of 1, 2, 3 are also possible.



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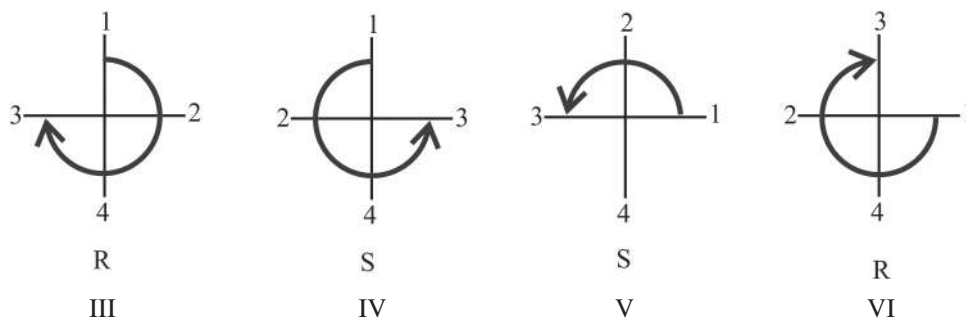
Chemistry of Organic Compounds

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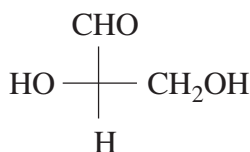
Notes

But again, to assign the configuration we have to follow the same rules. *i.e.* trace the path from 1 → 2 → 3 and see it is *clockwise* or *anticlockwise*. Accordingly, the configuration is given as *R* or *S*. This is illustrated below for the representations II to VI alongwith their absolute configurations *R* or *S*:



INTEXT QUESTIONS 23.5

- Is 1-butene a structural isomer of **cis-** or **trans-**2-butene?
- Identify the type of isomerism exhibited by the following pairs of compounds:
 - $$\text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$$
 - $$\begin{array}{ccc} \text{CH}_3 & & \text{C}_2\text{H}_5 \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} \quad \text{and} \quad \begin{array}{ccc} \text{CH}_3 & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{C}_2\text{H}_5 \end{array}$$
 - $$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{and} \quad \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$$
 - $$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{and} \quad \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3$$
- Write the structures of all the isomers of hexane (C_6H_{14}).
- Which one of the following compounds would show geometrical isomerism?
 - $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$
 - $\text{CHF}=\text{CHF}$
 - $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
- Assign the configuration as *R* or *S* to the following compound



23.5 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Organic compounds contain C and H; in addition to these, they may also contain O, N, S, halogens, and phosphorous.

23.5.1. Detection of C and H

Many organic compounds burn with a sooty flame or char when strongly heated. C and H are detected by heating the compound with CuO (copper oxide) in a dry test tube. They are oxidised to CO₂ and H₂O, respectively. CO₂ turns lime water milky and H₂O turns anhydrous CuSO₄ to hydrated CuSO₄ which is blue in colour.

- (i) $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$
- (ii) $H + CuO \xrightarrow{\Delta} Cu + H_2O$
- (iii) $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$
- (iv) $CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$
- White Blue

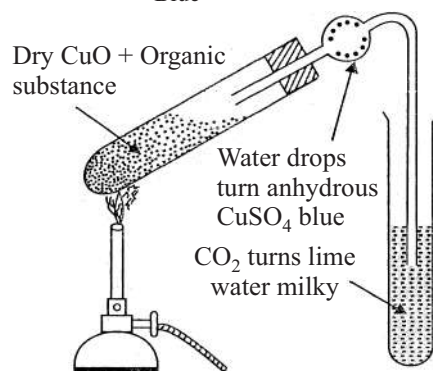
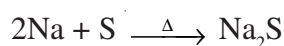


Fig. 23.1 Detection of carbon and hydrogen

23.5.2 Detection of Other Elements

N, S, halogens, and phosphorus present in an organic compound are detected by **Lassaigne's test**, by fusing the compound with sodium metal, which converts the elements present in the compound from covalent to ionic form. The following reactions occur:



C, N, S, and X come from organic compound.

NaCN, Na₂S, and NaX so formed are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne's extract (L.E.).



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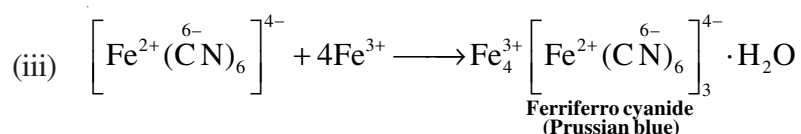
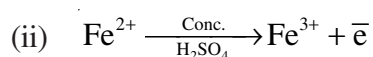
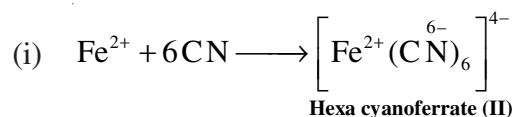
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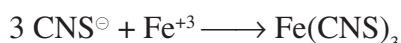
(a) **Test for nitrogen:** The sodium fusion extract or L.E. is boiled with FeSO_4 and then acidified with conc. H_2SO_4 . The appearance of Prussian blue colour confirms the presence of N. The following reactions occur:



(iv) This test is not given by compounds which do not contain C atoms but contain N atoms, for example, NH_2NH_2 (hydrazine), NH_2OH (hydroxylamine). Since these compounds do not contain C atoms, so in sodium fusion extract, CN ion is not formed and Prussian blue colour is not observed.

(v) This test is also not given by diazonium salts (e.g, $\text{Ph N}\equiv\text{N-X}$), although they contain both C and N elements, because they decompose and lose N_2 on heating much before they have a chance to react with the fused sodium metal.

(vi) If S is present along with N, the appearance of blood red colour confirms the presence of both.

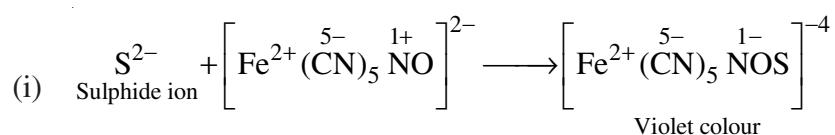


Thiocyanate ion Ferric thiocyanate
(Blood-red colour)

(vii) If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to give cyanide and sulphide. These ions give usual tests.



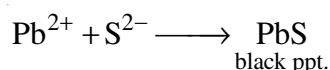
(b) **Test for sulphur:** The sodium fusion extract or L.E. is treated with sodium nitroprusside. The appearance of violet colour indicates the presence of S.



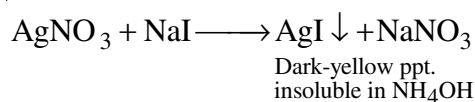
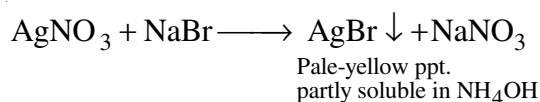
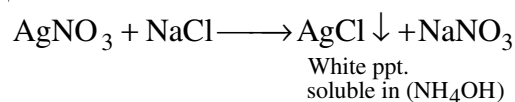


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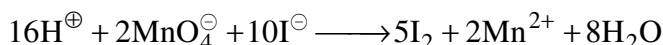
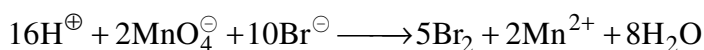
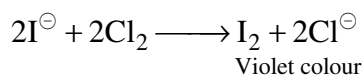
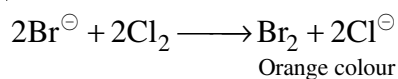
- (ii) The L.E. is acidified with acetic acid and lead acetate is added to it. The appearance of black precipitate of lead sulphide indicates the presence of S.

**(c) Test for halogens**

- (i) L.E. is acidified with HNO_3 and then treated with AgNO_3 . A white precipitate soluble in NH_4OH indicates the presence of Cl, a pale yellow precipitate partially soluble in NH_4OH indicates the presence of Br, and a yellow precipitate insoluble in NH_4OH shows the presence of I.



- (ii) If N and S are also present in the compound, the L.E. is first boiled with conc. HNO_3 to decompose the NaCN or Na_2S formed during Lassaigne's test. These ions would otherwise interfere with the AgNO_3 test for halogens. If these ions are not removed, they would give a white precipitate of AgCN or Ag_2S with AgNO_3 and will confuse it for AgCl .
- (iii) **Organic layer test:** Add CS_2 or CCl_4 to the L.E. and then add Cl_2 water or KMnO_4 , shake, and keep it for some time. The appearance of orange colour in organic layer confirms the presence of Br, while violet colour confirms iodine.



- (iv) **Beilstein test:** The organic compound is heated on a clean copper wire in Bunsen flame. A green or blue colour due to the formation of volatile copper halides confirms the presence of halogens. This test is not satisfactory as some compounds which do not contain halogens also

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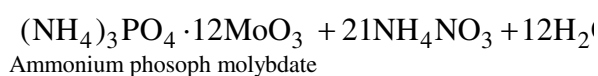
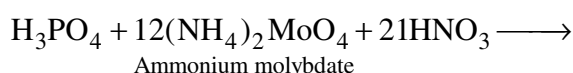
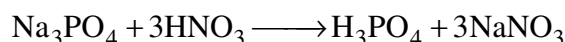


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give this test, for example urea and thiourea. Moreover, this test does not tell which halogen is present in the compound.

- (d) **Test for phosphorus:** The organic compound is heated with an oxidising agent (sodium peroxide). Phosphorus is oxidised to phosphate. The solution is then boiled with cone. HNO_3 and treated with ammonium molybdate. A yellow precipitate confirms the presence of phosphorus.



23.6 QUANTITATIVE ANALYSIS

- (a) **Estimation of C and H:** The percentage composition of elements present in an organic compound is determined by the methods based on the following principle:

Liebig's combustion method: A known mass of compound is heated with CuO . The carbon present is oxidised to CO_2 and hydrogen to H_2O . The CO_2 is absorbed in KOH solution, while H_2O vapours are absorbed in anhydrous CaCl_2 and weighed (Fig. 23.2).

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } \text{CO}_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } \text{H}_2\text{O}}{\text{Mass of compound}} \times 100$$

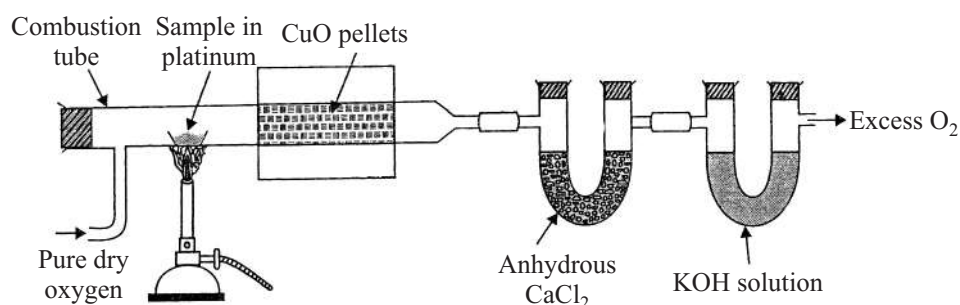


Fig. 23.2 Estimation of carbon and hydrogen

- b. **Estimation of halogens:**

Carius method: A known mass of compound is heated with cone. HNO_3 in the presence of AgNO_3 contained in a hard glass tube known as Carius tube (Fig. 23.3 in a furnace). C and H are oxidised to CO_2 and H_2O . The halogen forms the corresponding AgX . It is filtered, dried, and weighed.

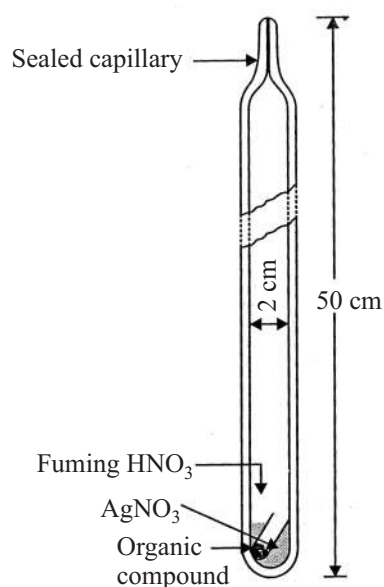


Fig. 23.3 Carius method

- i. Percentage of X = $\frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$
- ii. Percentage of Cl = $\frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$
- iii. Percentage of Br = $\frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$
- iv. Percentage of I = $\frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$

(c) **Estimation of sulphur:** A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in the presence of BaCl_2 solution in Carius tube. Sulphur is oxidised to H_2SO_4 and precipitated as BaSO_4 . It is filtered, dried, and weighed.

$$\begin{aligned} \text{Percentage of S} &= \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} \\ &= \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} \end{aligned}$$

(d) **Estimation of phosphorus**

First method: A known mass of compound is heated with fuming HNO_3 in Carius tube which converts phosphorus to H_3PO_4 (phosphoric acid). It is precipitated as ammonium phosphomolybdate $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ by adding NH_3 and ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$. It is filtered, dried, and weighed.



Notes

MODULE - 7

Chemistry of Organic Compounds



Notes

Nomenclature and General Principles

Percentage of P

$$\begin{aligned} &= \frac{\text{Atomic mass of P}}{\text{Molecular mass of ammonium phospho molybdate}} \times \frac{\text{Mass of ammonium phospho molybdate} \times 100}{\text{Mass of compound}} \\ &= \frac{31}{1877} \times \frac{\text{Mass of } (\text{NH}_4)_3 \cdot \text{PO}_4 \cdot 12\text{MoO}_3 \times 100}{\text{Mass of compound}} \end{aligned}$$

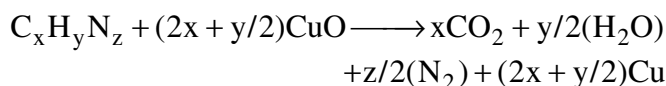
Second method: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in Carius tube which converts phosphorous to H_3PO_4 . Magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{Cl}$) is then added, which gives the precipitate of magnesium ammonium phosphate ($\text{MgNH}_4 \cdot \text{PO}_4$) which on heating gives magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), which is weighed.

Percentage of P

$$\begin{aligned} &= \frac{\text{Atomic mass of P}}{\text{Molecular mass of } \text{Mg}_2\text{P}_2\text{O}_7} \times \frac{\text{Mass of } \text{Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}} \\ &= \frac{62}{222} \times \frac{\text{Mass of } \text{Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}} \end{aligned}$$

(e) **Estimation of nitrogen:** There are two methods for the estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) **Dumas method:** A known mass of compound is heated with copper oxide (CuO), in an atmosphere of CO_2 , which gives free nitrogen along with CO_2 and H_2O .



The gaseous mixture is passed over a heated copper gauze which converts traces of nitrogen oxides formed to N_2 . The gaseous mixture is collected over an aqueous solution of KOH which absorbs CO_2 , and nitrogen is collected in the upper part of the graduated tube (Fig. 23.4).

Let the volume of N_2 collected be V_1 ml

$$\text{Volume of } \text{N}_2 \text{ at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1} = V \text{ ml}$$

where p_1 and V_1 are the pressure and volume of N_2 , and p_1 = atmospheric pressure – aqueous tension. 22400 ml of N_2 at STP weighs 28 g

$$V \text{ ml of } \text{N}_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

Percentage of N is

$$\frac{\text{Molecular mass of N}_2}{22400 \text{ ml}} \times \frac{\text{Volume of N}_2 \text{ at STP} \times 100}{\text{Mass of compound}}$$

$$= \frac{28}{22400} \times \frac{V \text{ ml} \times 100}{\text{Mass of compound}}$$

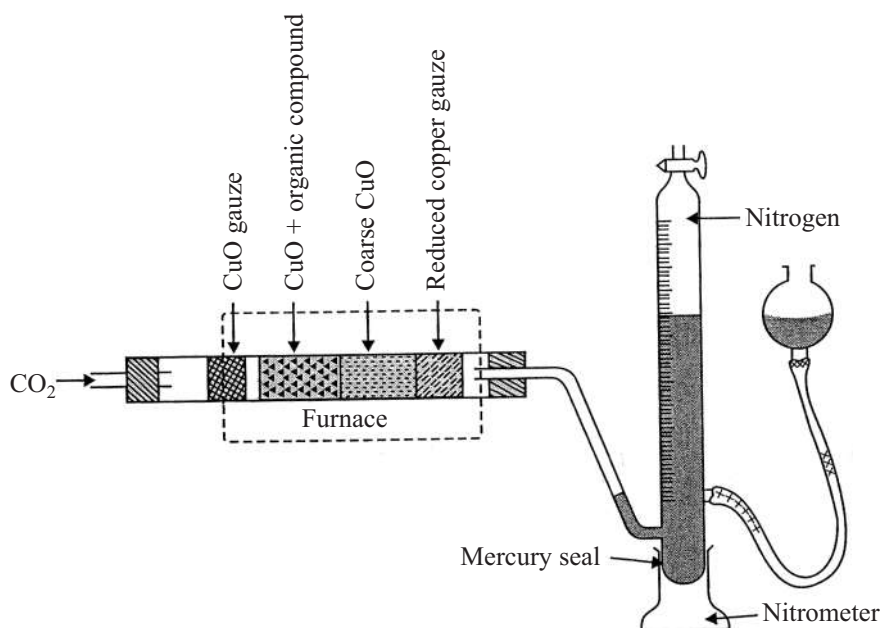


Fig. 23.4 Dumas method

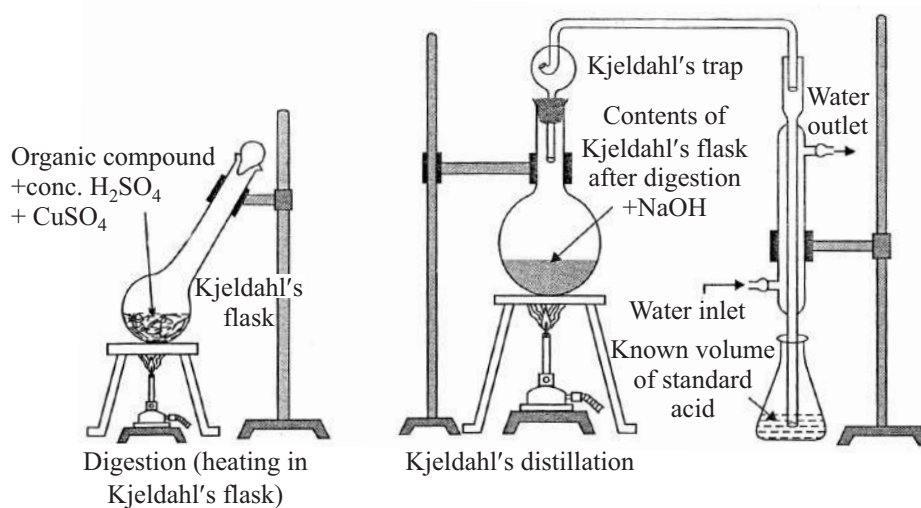


Fig. 23.5 Kjeldahl's method

- (ii) **Kjeldahl's method:** A known mass of organic compound (0.5 g) is mixed with K_2SO_4 (10 g) and CuSO_4 (1.0 g) or a drop of mercury (Hg) and conc. H_2SO_4 (25 ml), and heated in Kjeldahl's flask. CuSO_4 or Hg acts as a catalyst, while K_2SO_4 raises the boiling point of H_2SO_4



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Chemistry of Organic Compounds



Notes

Nomenclature and General Principles

(Fig. 23.5). The nitrogen in the organic compound is quantitatively converted to ammonium sulphate. The resulting mixture is then distilled with excess of NaOH solution and the NH_3 evolved is passed into a known but excess volume of standard HCl or H_2SO_4 . The acid left unused is estimated by titration with some standard alkali. The amount of acid used against NH_3 can thus be known and from this the percentage of nitrogen is calculated.

- $$\text{C} + \text{H} + \text{S} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_2$$
- $$\text{N} \xrightarrow{\text{Conc. H}_2\text{SO}_4} (\text{NH}_4)_2\text{SO}_4$$
- $$(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$$
- $$2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4$$

Calculation of percentage of N

Let the mass of organic compound m g.

Volume of H_2SO_4 of molarity M [or $(2M)$ normality] taken = V ml

Volume of NaOH of molarity M (or M normality)

used for titration excess of $\text{H}_2\text{SO}_4 = V_1$ ml

mEq. of excess $\text{H}_2\text{SO}_4 = \text{mEq. of NaOH} = M V_1$ mEq.

Total mEq. of H_2SO_4 taken = $2MV$

mEq. of H_2SO_4 used for neutralisation of $\text{NH}_3 = (2MV - MV_1)$

\therefore mEq. of $\text{NH}_3 = (2MV - MV_1)$

1000 mEq. or 1000 ml of M NH_3 solution contains = 17 g of $\text{NH}_3 = 14$ g of N

$\therefore (2MV - MV_1)$ mEq. of NH_3 solution contains

$$= \frac{14 \times (2MV - MV_1)}{1000} \text{ g of N}$$

$$\text{Percentage of N} = \frac{14 \times (2MV - MV_1) \times 100}{1000 \times m}$$

$$= \frac{1.4 \times 2M(V - V_1/2)}{m}$$

$$\text{Percentage of N} = \frac{1.4 \times \text{mEq. of H}_2\text{SO}_4 \text{ used to neutralise NH}_3}{\text{Mass of the compound}}$$

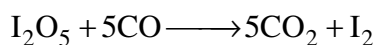
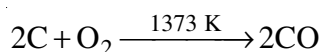
- (iii) This method is not applicable to compounds containing N in nitro and azo groups, and N present in the ring (e.g., pyridine) as N of these compounds does not change to $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulphate) under these reaction conditions.

(f) Estimation of oxygen

First method: It is usually found by the difference between the total percentage composition (100) and sum of the percentages of all the other elements, e.g.,

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N)

Second method (Aluise's method): A known mass of compound is decomposed by heating it in the presence of N_2 gas. The mixture of gaseous products containing O_2 is passed over red hot coke when all the O_2 is converted to CO. This mixture is heated with I_2O_5 (iodine pentoxide) in which CO is oxidised to CO_2 liberating I_2 . Organic compound $\xrightarrow{\Delta}$ Other gaseous product + O_2



Percentage of O

$$\begin{aligned} &= \frac{\text{Molecular mass of O}_2}{\text{Molecular mass of CO}_2} \times \frac{\text{Mass of CO}_2 \times 100}{\text{Mass of compound}} \\ &= \frac{32}{44} \times \frac{\text{Mass of CO}_2 \times 100}{\text{Mass of compound}} \end{aligned}$$

- (g) CHN elemental analyser:** Nowadays, the estimation of elements in an organic compound is carried out with automatic experimental techniques using micro quantities of the compound. The elements C, H, and N present in an organic compound are determined by an automatic instrument called CHN elemental analyser using a very small amount of the compound (1-3 mg), which displays the result within a very short time.



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).



MODULE - 7

Chemistry of Organic Compounds



Notes

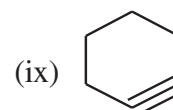
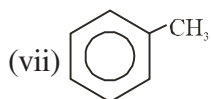
Nomenclature and General Principles

- **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 plain polarized light in opposite directions.
- The absolute configuration of a chiral carbon can be specified as *R* or *S*.



TERMINAL EXERCISE

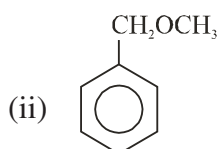
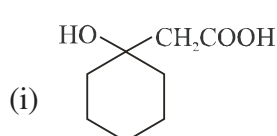
1. What are hydrocarbons? Explain giving two examples.
2. Give two examples of aromatic hydrocarbons.
3. Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names.
 - (i) $(\text{CH}_3)_3\text{CH}$
 - (ii) $\text{CH}_3\text{CH} = \text{CH}_2$
 - (iii) $(\text{CH}_3)_4\text{C}$
 - (iv) $\text{CH}_3\text{C} \equiv \text{CH}$
 - (v) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 - (vi) $\text{CH}_2 = \text{CH}_2$





Notes

4. Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula:
 - (i) C_5H_{10} and (ii) C_5H_8 .
5. Write the structures of the following compounds :
 - (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 :



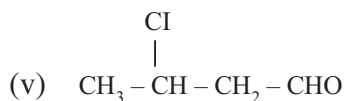
- (iii) $CH_3COCH_2C \equiv CH$
- (iv) $CH_3CH_2CH_2 - O - CH_3$

MODULE - 7

Chemistry of Organic
Compounds



Notes



15. Describe hyperconjugation in terms of resonance.



ANSWERS TO INTEXT QUESTIONS

23.1

1. **Word root** **Suffix**

- (i) Hex ane
- (ii) Pent 2-ene
- (iii) Prop yne

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

23.2

- 1. (i) 1-ethyl-3-methylbenzene
- (ii) Cycloheptane
- (iii) Cyclopenta-1,3-diene

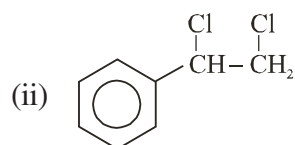
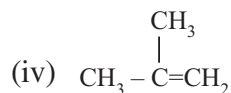


23.3

- 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

23.41. (i) $\text{CH}_3\text{CH}_2\text{CN}$ (ii) CH_3NHR 2. HNO_3 in presence of H_2SO_4 .3. (i) $\text{CH}_3\text{CH}_2\text{Br}$ (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)**23.5**

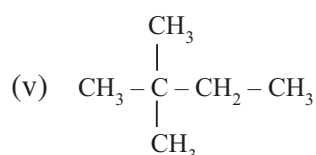
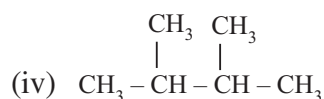
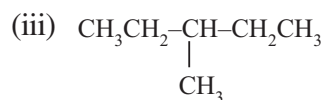
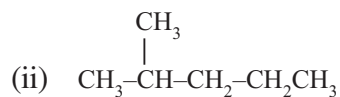
1. Yes

2. (i) Positional isomerism

(ii) Geometrical isomerism

(iii) Chain isomerism

(iv) Functional group isomerism

3. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ **MODULE - 7**Chemistry of Organic
Compounds**Notes**

MODULE - 7

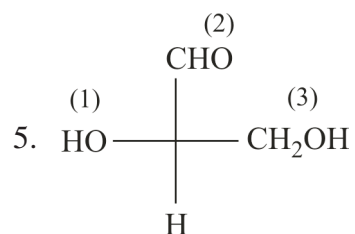
Chemistry of Organic Compounds



Notes

Nomenclature and General Principles

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



- (i) Priority of groups is shown as (1), (2) and (3)
(ii) path from (1) \rightarrow 2 \rightarrow 3 is clockwise, therefore, the absolute configuration of chiral chain is R.

