

- **Classification, nomenclature and isomerism**

Classification of Organic Compounds

Common and IUPAC systems of nomenclature of organic compounds

(up to 10 Carbons open chain and carbocyclic compounds) Structural isomerisms in organic compounds

## Classification and Nomenclature of Organic Compounds

In the early stages of the development of organic chemistry, relatively small number of compounds were known. Therefore, their study did not pose any serious problem. With the passage of time, the number of organic compounds discovered continued to increase. At present there are known as many as about three million organic compounds and their structural formulas established. The study of such a large number of compounds would be well nigh impossible without a systematic classification having 'structural basis'.

### PRINCIPAL SERIES

The organic molecules may be made of carbon-carbon open chains or cyclic structures. The cyclic structures may contain only carbon atoms or carbon atoms and another atom (O, N, S). Broadly speaking, the entire population of organic compounds could be embraced by the following *principal series*.

#### Acyclic Series

The compounds whose molecules contain an open-chain of carbon atoms, are said to constitute the **Acyclic** or **Noncyclic Series**. For example,



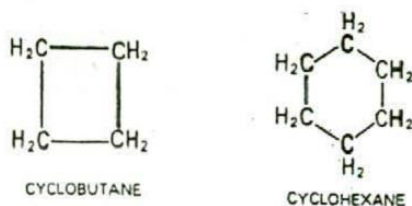
The compounds of this series are also called **Aliphatic Compounds** and the series **Aliphatic Series**. The term aliphatic is derived from the Greek word *aleipher*, meaning 'fatty' since the earliest known compounds of this type were obtained from fats.

## Cyclic Series

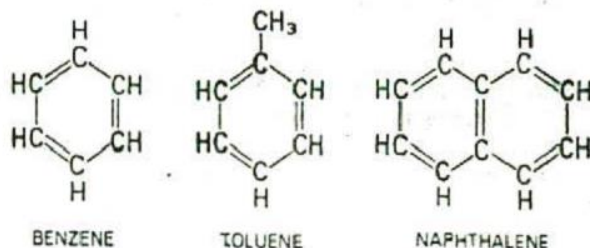
The compounds whose molecules contain ring structures constitute this series. It consists of two types of compounds :

(1) **Carbocyclic Compounds** which have a ring made of carbon atoms only. The carbocyclic compounds are again divided into two categories.

(a) **Alicyclic compounds** which contain a cyclic structure made of atoms only joined by single covalent bonds. They behave like *aliphatic* compounds and are hence named as *alicyclic*. Example are

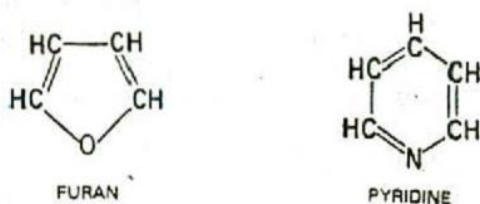


(b) **Aromatic Compounds** (Greek *aroma* = fragrant smell) which contain one or more benzenoid rings. This type of compounds are said to constitute the **Aromatic Series**. Thus benzene, toluene and naphthalene are examples of aromatic compounds.



Aromatic compounds are designated as **monocyclic**, **bicyclic** and **tricyclic** according as they contain one, two or three rings.

(2) **Heterocyclic Compounds**. The cyclic compounds which include one or two atoms other than carbon (O,N,S) in the ring, are called heterocyclic compounds or **Heterocycles** (*hetero*, meaning different). Thus furan and pyridine are heterocyclic compounds.



The heterocyclic compounds with five and six atoms in the ring are referred to as *five-membered* and *six-membered heterocycles* respectively.

A complete genealogical table given below indicates the broad classification of organic compounds into the principal series.

# ORGANIC COMPOUNDS

Hydrocarbons and their derivatives

## Open Chain or Aliphatic Compounds

Compounds containing straight or branched chains of carbon atom skeletons with appropriate number of H atoms and functional groups. Some examples are:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_5$

## Cyclic Compounds

Compounds containing closed ring skeletons

### Homocyclic or Carbocyclic Compounds

Ring skeleton of such compounds contains only carbon atoms

### Heterocyclic Compounds

The ring skeletons of these compounds contain one or more atoms other than carbons

### Alicyclic Compounds

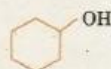
These compounds show resemblance in properties with aliphatic compounds. Some examples are:



Cyclobutane



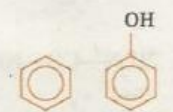
Cyclohexane



Cyclohexanol

### Aromatic Compounds

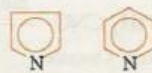
Aromatic hydrocarbons and their derivatives. They contain  $(4n + 2)\pi$ -electrons delocalised over their flat structures. Common examples are



Benzene

Phenol

Carbocyclic aromatic



Pyrrole

Pyridine

Heterocyclic aromatic

### Alicyclic Type

Heterocyclic compounds have ring like structure with a heteroatom as a part of the ring. Examples are



Tetrahydrofuran (THF)



Piperidine

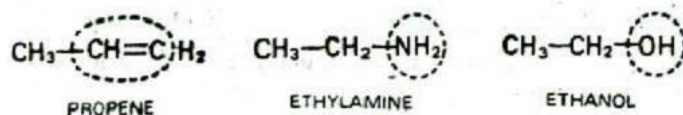
The division of organic compounds into *aliphatic series* and *aromatic series* is particularly useful. These embrace the various types of compounds belonging to all the other series stated above. The basic structural differences between the compounds of the two series are reflected in their chemical reactions. Hence a separate study of aliphatic and aromatic compounds has been preferred in this text.

## FUNCTIONAL GROUPS

The structural formulas of organic compounds are made of a carbon-hydrogen framework which is relatively chemically unreactive. It is the presence of another atom or groups of atoms, or carbon-carbon multiple bonds in the molecule that confer on it chemical reactivity. These sites of reactivity in organic molecules are referred to as functional groups or just 'function'.

A functional group may be precisely defined as an atom or group of atoms which determines the chemical behaviour of an organic compound.

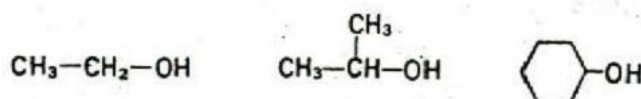
Examples of functional groups (circled) are :



Each functional group gives characteristic reactions which are largely independent of the rest of the molecule. Evidently the reactions of any number of compounds containing a specific functional group are similar. Since there are only a dozen or so functional groups present in simple organic compounds, the study of thousands of organic compounds is made simple. Otherwise, we would have to memorise the chemistry of each individual compound. Table 8.1 lists the most important functional groups encountered in our study.

## CLASSES OF ORGANIC COMPOUNDS

A series of compounds that contain the same functional group are said to constitute a **Class of organic compounds**. For example, each of the following series of compounds contain a hydroxyl group ( $-\text{OH}$ ). These compounds all belong to the class of compounds called *alcohols*.



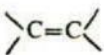
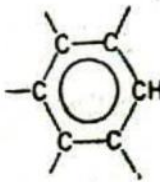
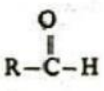
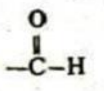
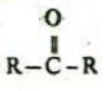
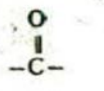
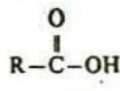
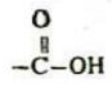
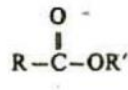
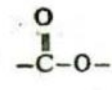
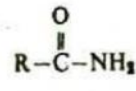
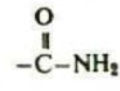
Compounds in the same class undergo similar reactions. This enables us to study a few compounds as representatives of a large number of others. In this manner we can learn the chemical reactions of many thousands of compounds by considering only a few.

Because of the similar reactions among compounds with the same functional group, it is convenient to use a general formula for a class of compounds. If  $\text{R}-$  represents an alkyl group (a group that contains C and H only), we may represent alcohol as  $\text{R}-\text{OH}$ . Similarly, the compounds containing the functional group  $-\text{NH}_2$  constitute a class called *amines*. These have the general formula  $\text{R}-\text{NH}_2$ . In Table 8.1 are listed the important functional groups and classes of compounds with general formula.

## HOMOLOGOUS SERIES

When members of a class of compounds having similar structures are arranged in order of increasing molecular weight, they are said to constitute a **Homologous Series**. Each member of such a series is referred to as a **Homologue** of its immediate neighbour. For example, the following sequence of straight chain alcohols forms a homologous series.

Table 8.1. Common Classes of Organic Compounds

General Formula	Name	Functional Group
R-H	Alkanes	None
RCH=CH <sub>2</sub>	Alkenes	 double bond
R-C≡C-H	Alkynes	-C≡C- triple bond
ArH	Arenes	 aromatic ring
R-X	Alkyl halides	-F fluoro group -Cl chloro group -Br bromo group -I iodo group
R-OH	Alcohols	-OH hydroxy group
R-O-R'	Ethers	-O- ether group
R-NH <sub>2</sub>	Amines	-NH <sub>2</sub> amino group
R-SH	Thiols	-SH sulphdryl group
R-S-R	Sulphides	-S- sulphide group
	Aldehydes	 aldehyde group
	Ketones	 ketonic group
	Carboxylic acids	 carboxyl group
	Esters	 ester group
	Amides	 amide group
R-C≡N	Nitriles	-C≡N nitrile group
R-NO <sub>2</sub>	Nitro compounds	-NO <sub>2</sub> nitro group
R-SO <sub>2</sub> -OH	Sulphonic acids	-SO <sub>2</sub> -OH sulphonic acid

$\text{CH}_3\text{—OH}$	Methyl alcohol
$\text{CH}_3\text{—CH}_2\text{—OH}$	Ethyl alcohol
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$	Propyl alcohol
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$	Butyl alcohol, etc.

#### Characteristics of a Homologous Series

- (1) Any member of the series differs from the next by the unit  $\text{—CH}_2\text{—}$  (methylene group).
- (2) The series may be represented by a general formula. The general formula for alcohols is  $\text{C}_n\text{H}_{2n+1}\text{OH}$  which gives the molecular formulas of the members by putting  $n=1, 2, 3$ , etc.
- (3) The chemical properties of the members of a homologous series are similar, though in some series the first member shows different behaviour.
- (4) The physical properties such as density, melting point and boiling point show a gradation in a rather semi-regular fashion.

The organisation of organic compounds into homologous series makes the study of organic chemistry particularly interesting and useful. This allows to learn about many compounds while only having to remember the trends applicable to a specific series. The existence of these series is of great importance on account of their predictive value. As we learn about one homologous series, much of the information would be applicable to the other similar homologous series.

## A SURVEY OF ORGANIC NOMENCLATURE

In the middle of the 19th century, many compounds were known and used without any knowledge of their structures. Since these compounds had to be called something, names were given to them. These names often reflected the properties or the origins of the compounds. In some cases, compounds were named after friends or relatives of chemists who first discovered them. For example, ethane ( $\text{C}_2\text{H}_6$ ) is quite inflammable and its name was derived from the Greek word *aithen*, meaning to kindle or blaze. Formic acid ( $\text{HCOOH}$ ) was so named because it was obtained by the distillation of red ants (Latin *formica*=ants). Barbituric acid was named after a lady friend of the German chemist who discovered the compound.

*A name assigned to an organic compound by the discoverer as he thought appropriate and not having any structural bearing, is referred to as the Common name or the Trivial name.*

It was not long before that chemists around the world realised the futility of the haphazard **Common Nomenclature** (system of assigning common or trivial names). It was ridiculous to have different names of the same compound in different countries. And, then to remember such quaint names of thousands of organic compounds (now about three million) would be a mad man's job. Therefore, the chemists felt the need of a **Systematic Nomenclature** which could assign a logical name to each known organic compound on the basis of molecular structure.

The rational name of an organic compound derived from its structure, is called the **Systematic Name**.

The systematic nomenclature which has been developed and is used in modern practice, is the **IUPAC Nomenclature**. The names assigned according to this system are referred to as the **IUPAC Names**. Although the older common names are now obsolete, some of these are still used as 'nick names' because they are so handy.

In our study of organic chemistry, we will be using *systematic names* in general and *common names* that have been adopted on account of long usage. Let us recapitulate that :

- (1) A **COMMON NAME** is whimsy and has no structural relevance. These names have been accepted for continued use through years.

(2) A SYSTEMATIC NAME is based on the structural formula of a compound and is unambiguous. That is each name stands for one compound and one structure.

### THE IUPAC SYSTEM OF NOMENCLATURE

In 1892, an assembly of chemists from different countries met in Geneva, Switzerland, to devise a rational system of naming organic compounds. This international body was eventually formalised as the International Union of Pure and Applied Chemistry (IUPAC). The primary nomenclature formulated by IUPAC was adopted unanimously at a meeting in Paris in 1957. This official system of naming organic compounds is referred to as the IUPAC System of Nomenclature or simply IUPAC ("you-pack") Nomenclature. The IUPAC organisation is responsible for further development and constant revision of the systematic organic nomenclature so as to keep it up to date.

The IUPAC system provides set rules for assigning names to all the known about three million organic compounds and to many more yet to be synthesised. The rules are so simple that a student of chemistry familiar with them can write the name of any organic compound whose structure is given. In the same way, one is also able to derive the structure of a compound from its IUPAC name.

Now we proceed to discuss the systematic naming of continuous-chain or straight-chain alkanes and the other classes of compounds derived from them. This will be followed by a study of the IUPAC rules for assigning names to branched-chain hydrocarbons and compounds containing the various common functional groups stated earlier.

#### A. Alkanes

The compounds composed of carbon and hydrogen only are called hydrocarbons. The hydrocarbons whose molecules contain carbon atoms joined to each other by single bonds can add no more hydrogen atoms. These are referred to as Saturated hydrocarbons, meaning saturated with hydrogen.

The open-chain saturated hydrocarbons as a class are named Alkanes according to the IUPAC system. The IUPAC name of saturated hydrocarbons with a cyclic carbon-structure is Cycloalkanes.

The alkanes whose molecules are made of continuous or straight carbon-chains, are referred to as Continuous-chain or Straight-chain Alkanes. The foundations of the IUPAC system are the names of the continuous-chain alkanes. The structures and names of the first ten continuous-chain alkanes are listed in Table 8.2.

Table 8.2. The structural formulas and names of the First Ten Continuous-Chain Alkanes.

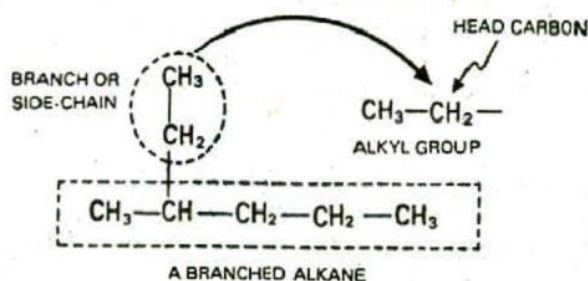
Structural formula	No of Carbon atoms in chain	IUPAC Name
$\text{CH}_4$	1	methane
$\text{CH}_3\text{--CH}_3$	2	ethane
$\text{CH}_3\text{--CH}_2\text{--CH}_3$	3	propane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3$	4	butane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	5	pentane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	6	hexane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	7	heptane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	8	octane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	9	nonane
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	10	decane

The names of alkanes in Table 8-2, end in **-ane**, which is the IUPAC ending for a saturated hydrocarbon. The first part of the name of the first four alkanes (methane to butane) is derived from the trivial name of the respective alkane. For higher alkanes (pentane on), the first part of the alkane name is derived from the Greek word for the number of carbon atoms in the molecule. For example, the prefix "pent" comes from the Greek word *penta*, meaning five. Thus the prefix *pent* in 'pentane' indicates that the alkane contains 5 carbons and the ending *-ane* denotes that it is a saturated hydrocarbon.

**Use of prefix *n*-.** The alkanes with a continuous carbon-chain or normal carbon-chain are referred to as **normal alkanes**. For clarity, the prefix *n*- is sometimes added to the alkane name to indicate that it contains a continuous carbon-chain. For example,  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$  is named as *n*-butane. *But the prefix n- is not strictly necessary in the IUPAC system.* Thus the name butane (without prefix *n*-) denotes  $\text{C}_4\text{H}_{10}$  containing a continuous C-chain.

### Branched Alkanes

When an alkane has a shorter side-chain attached to the continuous-chain, it is designated as a **Branched alkane**. The continuous chain is called the **root** or **parent**, while the side-chain the **alkyl group**. The carbon of the alkyl group bonded directly to the parent chain is referred to as the **head carbon**.



### Nomenclature of Alkyl groups

The hydrocarbon units derived by removal of one H of an alkane, are called **Alkyl groups**. The IUPAC name of an alkyl group is obtained by replacing the ending *-ane* of the parent alkane with *-yl* (alkane—ane + yl = alkyl). Thus  $\text{CH}_3\text{CH}_3$  is ethane and  $\text{CH}_3\text{CH}_2\text{—}$  is named as ethyl group.

**Normal or Continuous-chain Alkyl groups.** The alkyl groups obtained by dropping the terminal H atom of a *normal* or *continuous-chain* alkane, are referred to as **normal** or ***n*-alkyl groups**. However, in the IUPAC system the use of the prefix *n*- is redundant since the absence of a prefix implies a continuous chain. The names of the first five continuous-chain alkyl groups are listed in Table 8-3.

Table 8-3. IUPAC names of the First five Continuous-chain Alkyl groups.

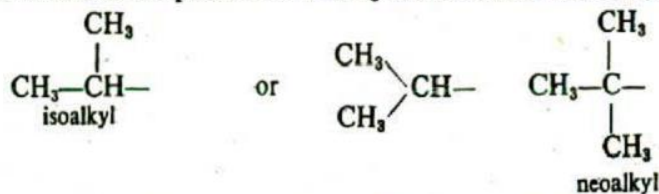
Structure	IUPAC Name
$\text{CH}_3\text{—}$	methyl
$\text{CH}_3\text{—CH}_2\text{—}$ or $\text{C}_2\text{H}_5\text{—}$	ethyl
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}$	propyl
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$	butyl (or <i>n</i> -butyl)
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$	pentyl (or <i>n</i> -pentyl)

**Branched-chain Alkyl groups.** These are derived by dropping a hydrogen on a middle carbon of alkane chain. The stem name of a branched alkyl group is determined by the number of carbons they contain. Thus propyl has 3 carbons, butyl 4 and pentyl 5. This type of



branched-chain is indicated by a specific prefix added to the stem name. The common prefixes used are :

- (1) **iso** indicates the presence of a  $\text{CH}_3$  branch at the end of the chain



- (2) **neo** indicates the presence of two  $\text{CH}_3$  branches at the end of the chain.

- (3) **secondary** or **sec-** indicates the presence of two carbons attached to the head carbon.

- (4) **tertiary-** or **tert-** or **t-** indicates the presence of three carbons attached to the head carbon.

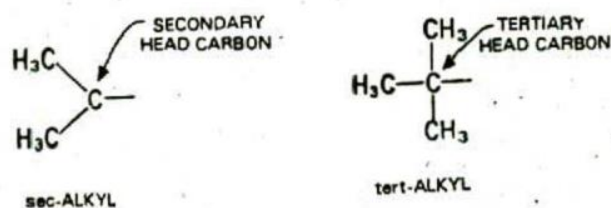
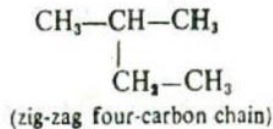
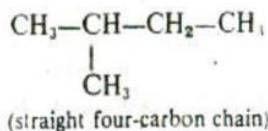


Table 8.4. Branched-chain Alkyl groups having 3, 4, 5 carbon atoms.

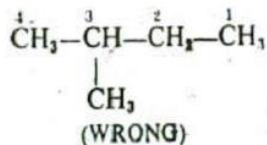
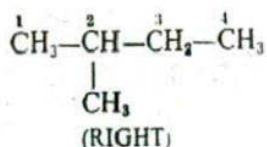
Structure	Name
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}- \\ \text{or} \quad \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}- \\ \diagdown \\ \text{CH}_3 \end{array} \end{array}$	isopropyl
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2- \\ \text{or} \quad \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}-\text{CH}_2- \\ \diagdown \\ \text{CH}_3 \end{array} \end{array}$	isobutyl
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}- \end{array}$	sec-butyl (or s-butyl)
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}- \\   \\ \text{CH}_3 \end{array}$	tert-butyl (or t-butyl)
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2- \end{array}$	isopentyl
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_2- \\   \\ \text{CH}_3 \end{array}$	neopentyl
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}- \end{array}$	sec-pentyl (or s-pentyl)
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}- \\   \\ \text{CH}_3 \end{array}$	tert-pentyl (or t-pentyl)

## IUPAC Rules for Naming Branched Alkanes.

1. Select the longest continuous carbon-chain and name the branched alkane as alkyl derivative of the parent alkane containing this chain. It is not necessary that the longest chain be written in a straight line; it may be straight or zig-zag. Thus the longest continuous chain in the following molecules contains four carbons and the name of the parent alkane in both cases is butane.

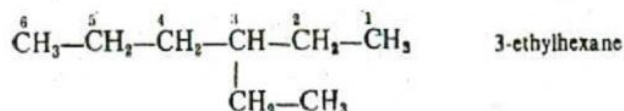


2. The parent-chain carbon atoms are numbered 1, 2, 3, 4, etc., beginning with the end nearest to the branch (alkyl group). This gives the lowest number to the carbon to which the alkyl group is attached.

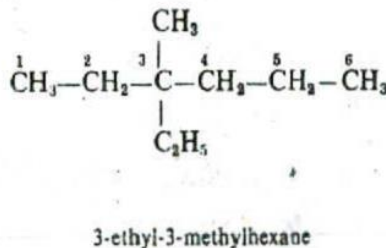
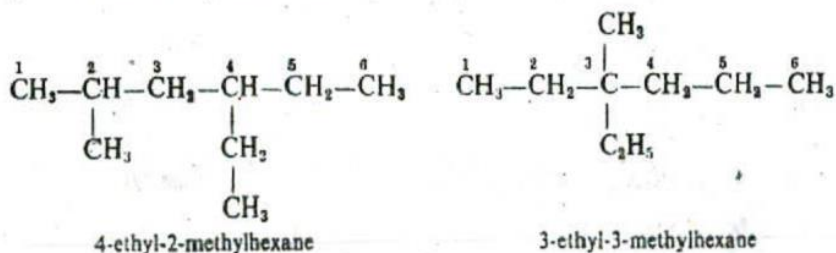


The position of the alkyl group on the parent chain is indicated by the number of the carbon which carries it. This is referred to as its **Position number** (or **Locator number**). The position number is mentioned before the name of alkyl group from which it is separated by a hyphen (-). Thus, if a methyl group is on carbon 2, it is written as 2-methyl.

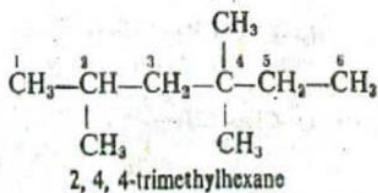
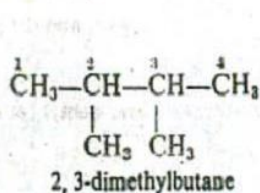
3. The complete name of the branched alkane is written as one word by prefixing the name of the alkyl group to the name of the parent alkane. For example,



4. When two or more different alkyl groups are present on the parent chain, assign position-number to each and list them alphabetically with a hyphen in between.



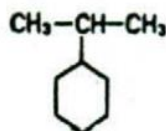
5. When two or more identical groups are present, indicate this by the use of the prefixes *di*, *tri*, *tetra*, etc., immediately before the alkyl group. Commas are used to separate position-numbers from each other.





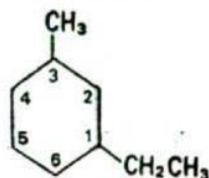


METHYLCYCLOHEXANE



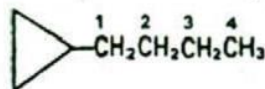
ISOPROPYLCYCLOHEXANE

2. When more than one side-chain is present, we number the ring beginning with one side-chain so that the next side-chain gets the lower number possible.



1-ETHYL-3-METHYLCYCLOHEXANE

NOT 1-ethyl-5-methylcyclohexane



1-CYCLOPROPYLBUTANE

NOT butylcyclopropane

3. If the alkane chain has a greater number of carbons than the ring, we designate the ring as the substituent. (See above)

## B. Alkenes

A hydrocarbon with one double bond (C=C) is called an *alkene*. The IUPAC name of a particular alkene is derived by changing the **ane** of the corresponding alkane (same number of carbons) to **ene**. That is,



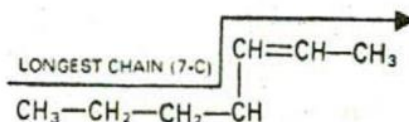
The functional group of alkenes is C=C, which is designated by the suffix *ene*. The IUPAC names and trivial names of some simple unbranched alkenes are listed in Table 8-5.

Table 8-5. Names of some Unbranched Alkenes

Structure	IUPAC Name	Trivial Name
$\text{CH}_2=\text{CH}_2$	ethene	ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	propene	propylene
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	1-butene	butylene
$\text{CH}_3\text{CH}=\text{CHCH}_3$	2-butene	
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$	1-pentene	
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$	3-hexene	

**IUPAC Rules for Naming Alkenes.** The alkenes containing four or more carbons are named by the following rules.

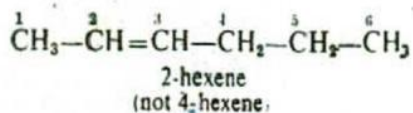
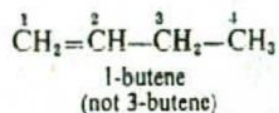
1. Select the longest continuous chain that contains both carbons of the double bond and change the name of the corresponding alkane name from **ane** to **ene**. This gives the parent name



of the alkene. The compound has 7-carbon chain containing the double bond. Therefore, the corresponding alkane is heptane and the parent alkene heptene.

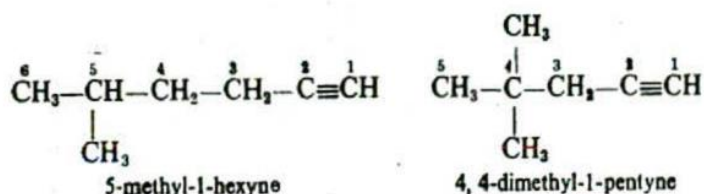
NOTE. It may be noted that the above selected chain may or may not be the longest continuous chain in the structure.

2. Number the parent chain beginning at the end nearer the double bond and indicate the position of the double bond by using the number of the first carbon of the double bond as prefix. For example,





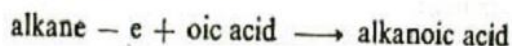
3. The names of substituents with locator numbers are given as for branched alkanes. Thus,



4. When there are two or more triple bonds in a molecule, it is named as **Alkadiyne**, **Alkatryne**, etc. The Chain containing the maximum number of triple bonds is selected and numbered so as to give lowest possible numbers to the triple bonds.

### I. Carboxylic Acids

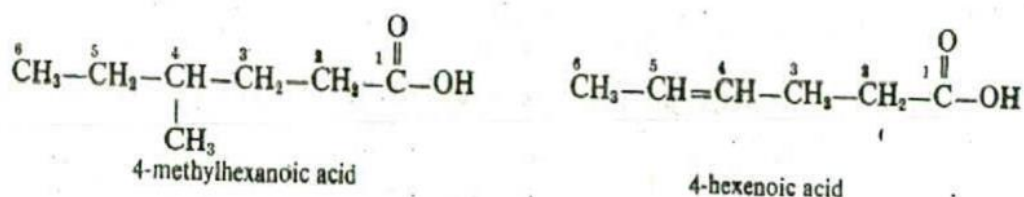
The IUPAC name of aliphatic carboxylic acids ( $\text{RCOOH}$ ) is **Alkanoic acids**, while the functional group  $\text{COOH}$  is referred to as *carboxyl group*. The name of a particular, carboxylic acid is obtained by replacing the final e with *oic acid*,



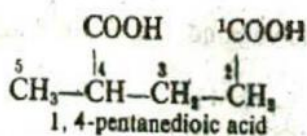
For naming higher carboxylic acids :

(1) The longest chain containing  $\text{COOH}$  is selected and the basic name is derived by changing *ane* of the corresponding alkane to *oic acid*.

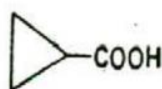
(2) The chain is numbered starting with carboxyl carbon as 1. Thus it is unnecessary to give the number of  $\text{COOH}$ . For example,



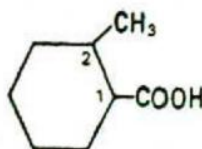
(3) A dicarboxylic acid is named as **Alkanedioic acid** with position numbers of  $\text{COOH}$  groups prefixed with it.



(4) When the  $\text{COOH}$  group is attached to a cyclic structure, —carboxylic acid becomes appropriate suffix.



CYCLOPROPANE -  
CARBOXYLIC ACID



2-METHYLCYCLOHEXANE -  
CARBOXYLIC ACID

The IUPAC and trivial names of some carboxylic acids are listed in Table 8.10.

Table 8.10. Names of some Carboxylic acids

Structure	IUPAC Name	Trivial Name
HCOOH	methanoic acid	formic acid
CH <sub>3</sub> COOH	ethanoic acid	acetic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	propanoic acid	propionic acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	butanoic acid	butyric acid
CH <sub>2</sub> =CHCOOH	propenoic acid	acrylic acid

The trivial names for the first few carboxylic acids are accepted by the IUPAC.

#### Nomenclature Priority for Citation as Principal Function (IUPAC)

(Highest Priority is at the top)

Class Name	Functional Group	Denoted by	
		Prefix	Suffix
Carboxylic acid	-COOH	-	-oic acid
Sulphonic acid	-SO <sub>3</sub> H	-	-sulphonic acid
Acid halide	-COX	-	-oyl chloride
Amide	-CONH <sub>2</sub>	Amido-	-amide
Nitrile	CN	Cyano-	-nitrile
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$ or -CHO	Alkanoyl-	-al
Ketone	$\begin{array}{c} \text{O} \\   \\ -\text{C}- \end{array}$	Oxo-	-one
Thiol	-SH	Mercapto-	-thiol
Amine	-NH <sub>2</sub>	Amino	-amine
Alkene	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	-	-ene
Alkyne	$-\text{C}\equiv\text{C}-$	-	-yne
Alkane	$\begin{array}{c}   \quad   \\ -\text{C}-\text{C} \\   \quad   \end{array}$	-	-ane
Ether	-OR	Alkoxy	-
Halides	-F, -Cl, -Br, -I	Halo-	-
Nitro	-NO <sub>2</sub>	Nitro-	-
Alkyl	-R	Alkyl	-



## ISOMERISM AND STRUCTURAL ISOMERISM

In the study of Organic chemistry we come across many cases when two or more compounds are made of equal number of like atoms. *These compounds possess the same molecular formula but differ from each other in physical or chemical properties, and are called Isomers* and the phenomenon is termed **Isomerism** (Greek, *isos*=equal ; *meros*=parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. Broadly speaking, isomerism is of two types :

(i) *Structural Isomerism* ; and (ii) *Stereoisomerism*.

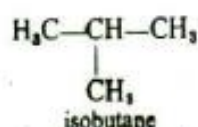
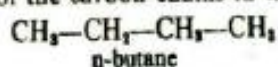
**Structural Isomerism.** *When the isomerism is simply due to difference in the arrangement of atoms within the molecule without any reference to space, the phenomenon is termed Structural Isomerism.* In other words, the structural isomers while they have the same molecular formulas, possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules, includes :

- (a) *Chain or Nuclear Isomerism* ;
- (b) *Positional Isomerism* ;
- (c) *Functional Isomerism*; and
- (d) *Metamerism*.

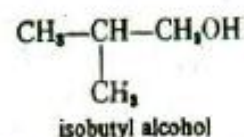
(e) *Tautomerism*

## CHAIN OR NUCLEAR ISOMERISM

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule. It is, therefore, named as **Chain or Nuclear Isomerism**. For example, there are known two butanes which have the same molecular formula ( $C_4H_{10}$ ) but differ in the structure of the carbon chains in their molecules.



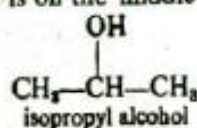
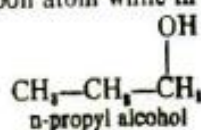
While n butane has a continuous chain of four carbon atoms, isobutane has a branched chain. These chain isomers have somewhat different physical and chemical properties, n-butane boiling at  $-0.5^\circ$  and isobutane at  $-10.2^\circ$ . This kind of isomerism is also shown by other classes of compounds. Thus n-butyl alcohol and isobutyl alcohol having the same molecular formula  $C_4H_{10}O$  are chain isomers.



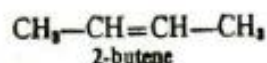
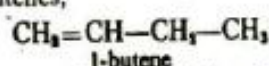
It may be understood clearly that the molecules of chain isomers differ only in respect of the linking of the carbon atoms in the alkanes or in the alkyl radicals present in other compounds.

## POSITIONAL ISOMERISM

When two or more compounds have structural formulas which differ only in the position of the substituent atom or group on the carbon chain, these are called **Position isomers** and the phenomenon is termed **Positional isomerism**. Thus n-propyl alcohol and isopropyl alcohol offer an example of positional isomerism. They possess the same molecular formula ( $C_3H_8O$ ) and their molecules are made of a chain of three carbon atoms. In n-propyl alcohol, the OH group is on the end carbon atom while in isopropyl alcohol it is on the middle carbon atom.

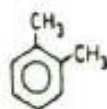


The positional isomerism may also be extended to alkanes and alkynes which differ only in the position of the double or triple bond in their molecules. Thus the molecular formula  $C_4H_8$  stands for two butenes,

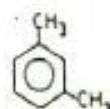


in which the position of the double bond is different.

In the aromatic series, the disubstitution products of benzene also exhibit positional isomerism due to different relative positions occupied by the two substituents on the benzene ring. Thus xylene,  $C_6H_4(CH_3)_2$ , exists in the following three forms which are positional isomers



o-XYLENE  
(ortho)



m-XYLENE  
(meta)

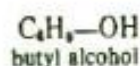
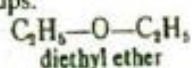


p-XYLENE  
(para)

## FUNCTIONAL ISOMERISM

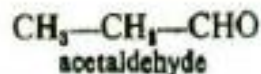
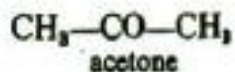
When any two compounds have the same molecular formula but possess different functional groups, they are called **Functional isomers** and the phenomenon is termed **Functional isomerism**. In other words substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus,

(1) Diethyl ether and butyl alcohol both have the molecular formula  $C_4H_{10}O$ , but contain different functional groups.



The functional group in diethyl ether is ( $-\text{O}-$ ), while in butyl alcohol it is ( $-\text{OH}$ ).

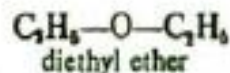
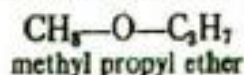
(2) Acetone and Propionaldehyde both with the molecular formula  $\text{C}_3\text{H}_6\text{O}$  are functional isomers.



In acetone the functional group is ( $-\text{CO}-$ ), while in acetaldehyde it is ( $-\text{CHO}$ ).

### METAMERISM

*This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, methyl propyl ether and diethyl ether both have the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ . The number of carbon atoms attached to the ethereal group  $-\text{O}-$ ,*



*in methyl propyl ether is 1 and 3, while in diethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, ketones and amines where the central functional group is flanked by two chains. The individual isomers are known as **Metamers**.*

### (E) TAUTOMERISM

**Tautomers** are isomers of a compound which differ only in the position of the protons and electrons. The carbon skeleton of the compound is unchanged. A reaction which involves simple proton transfer in an intramolecular fashion is called a **tautomerism**

