

Applied Organic Chemistry (Part-B)

Chapter 4.

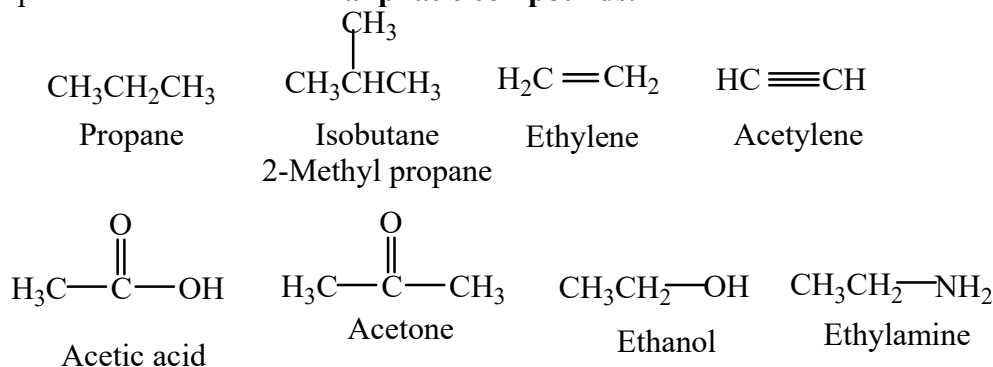
Classification, Functional Groups & Nomenclature

Classification of Organic compounds:

Organic compounds have been classified on the basis of carbon skeleton (structure) or functional groups or the concept of homology.

Classification based on structure: All the known organic compounds have been divided into two main types:

1. Acyclic or Open-chain compounds: These are the compounds in which the carbon atoms are linked to each other forming chain of **straight** or **branched** compounds. These compounds are also called as **aliphatic compounds**.





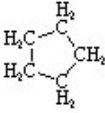
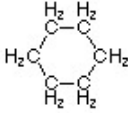
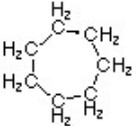





2. Cyclic or Closed-chain compounds: These are the compounds in which the carbon atoms are linked to each other or to the atoms of other elements forming closed cyclic rings structures. The compounds with only one ring of atoms in the molecule are known as **monocyclic** but those with more than one ring of atoms are termed as **polycyclic**. These are further divided into two subgroups:

(a) Homocyclic or carbocyclic, (b) Heterocyclic.

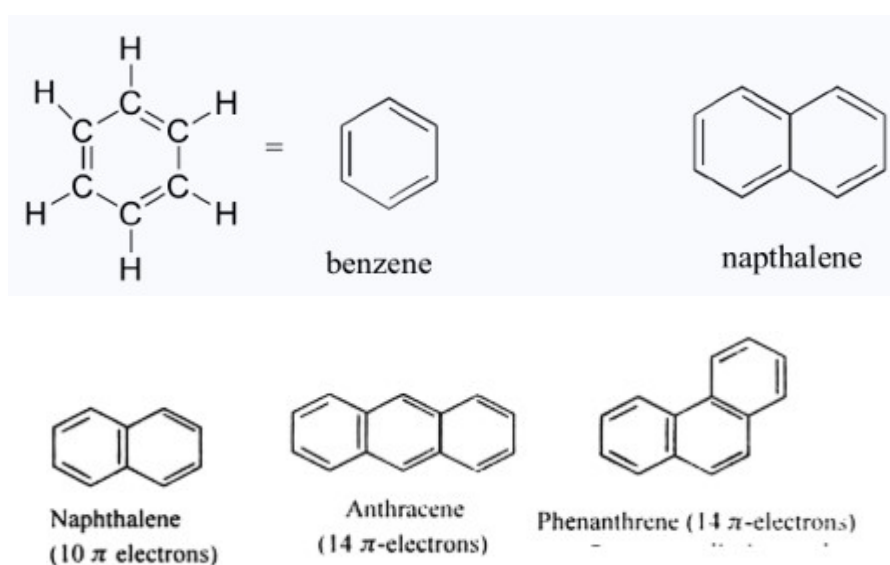
(a) Homocyclic or Carbocyclic: These are the compounds having a ring or rings of carbon atoms only in the molecule. These are again divided into two types:

(i) Alicyclic compounds (ii) Aromatic compounds.

(i) Alicyclic compounds: These are the compounds which contain rings. These compounds resembles to aliphatic compounds than aromatic compounds. Some of the examples are given below.

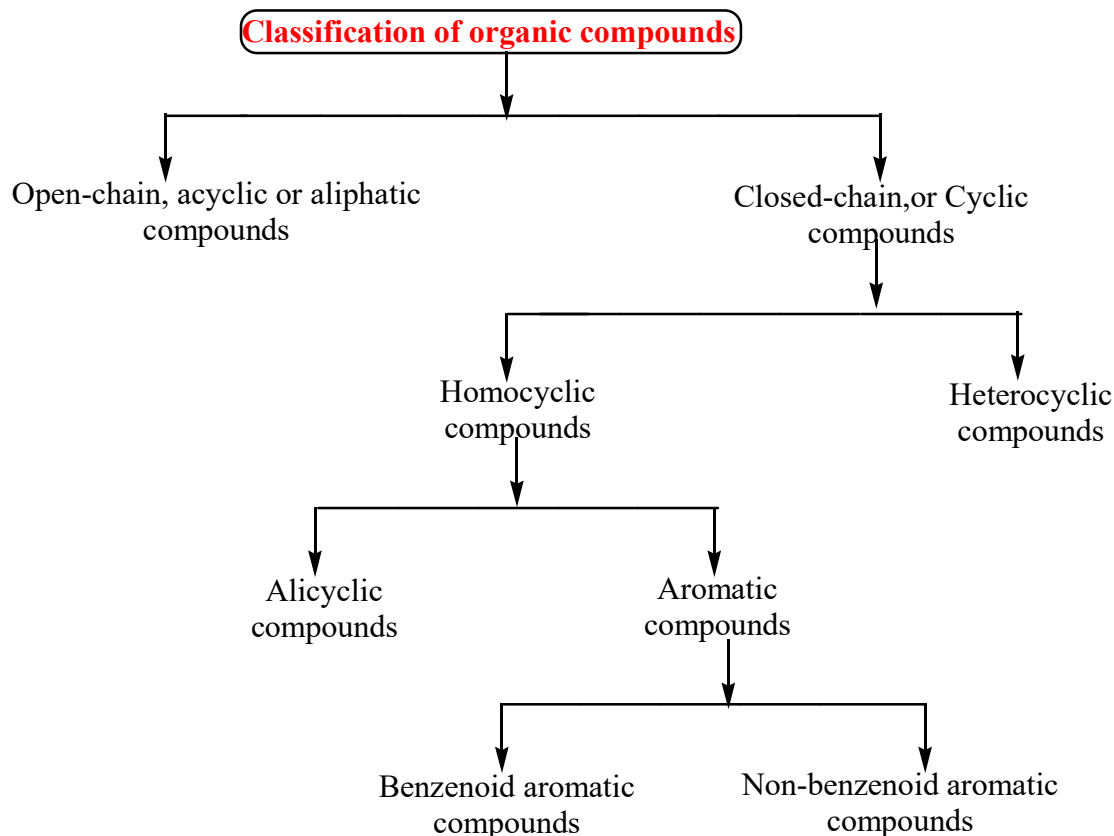
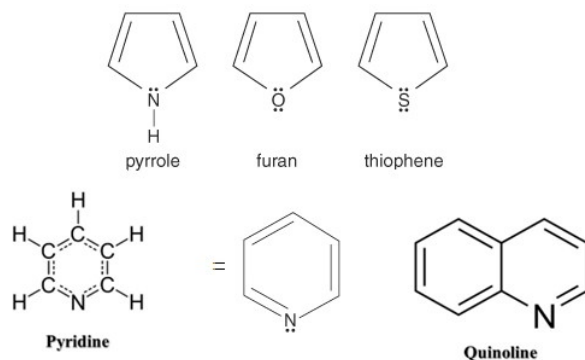
Name	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane	Cycloheptane
Molecular Formula	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}
Structural Formula					
Line Formula					

(ii) Aromatic compounds: These compounds consist of at least one benzene **ring**. Generally, these compounds have some fragrant odour and hence, named as aromatic. Some of the examples are given below.

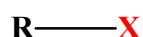


The above compounds are also known as benzenoid aromatic compounds as their molecules consist of benzene rings or rings.

(b) Heterocyclic compounds: These are cyclic compounds having ring or rings built up of more than one kind of atoms. The most common atoms other than carbon are O, N and S.


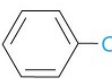
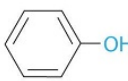




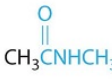
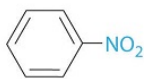


Functional groups: Most of the organic compounds consist of two parts, each of which is called a group. Both of these groups are responsible for the properties of the compounds. The group R represents the carbon hydrogen framework (chain) which mainly affects the physical properties while group X is known as **functional group** which is responsible for the chemical properties of the compound.



A functional group is an atom or group of atoms present in a molecule that give the molecule its characteristic chemical properties. Double and triple bonds are also considered as functional groups.

Examples for functional groups are hydroxyl groups (---OH), aldehyde group (---CHO), and carboxylic acid group (---COOH).

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH ₃ CH ₃	ethane	-ane
Alkenes	RR'C=CR''R'''	H ₂ C=CH ₂	ethylene (ethene)	-ene
Alkynes	RC≡CR'	HC≡CH	acetylene (ethyne)	(-yne)
Arenes	ArH ^a		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH ₃ CH ₂ Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX ^a		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH ^a	CH ₃ CH ₂ OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH ^b		phenol	-ol
Ethers	ROR'	H ₃ CH ₂ COCH ₂ CH ₃	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR'C=O		acetone (2-propanone)	-one
Carboxylic acids	RCO ₂ H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO ₂ R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR'		N-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH ₂ , RNHR', RNR'R''	CH ₃ CH ₂ NH ₂	ethylamine	-amine
Nitriles	RC≡N	H ₃ C≡N	acetonitrile	-nitrile
Nitro compounds	ArNO ₂ ^a		nitrobenzene	nitro-

^aR indicates an alkyl group ^bAr indicates an aryl group.

Homologous series: A homologous series can be defined as a group of compounds in which the various members have similar structural features and similar chemical properties and the successive members differ in their molecular formula by CH_2 .

General characteristics of Homologous series:

- All compounds in the series are composed of same elements and contain the same functional group.
- All compounds in the series can be represented by one general formula. For example alkanes have general formula of $\text{C}_n\text{H}_{2n+2}$.
- The molecular mass of every two adjacent members differs by 14 ($-\text{CH}_2-$).
- All compounds in the series have similar chemical properties because of the presence of same functional group.
- Compounds in the series have different physical properties such as density, physical nature, melting and boiling points etc., because they differ in molecular weight.

Some of the important homologous series are alkanes, alkenes, alkynes, alcohols, alkylhalides, alcanoic acids, amines, etc.

THE HOMOLOGOUS SERIES

# C's	Alkane Structure	Parent name	Substituent name
1	CH_4	methane	methyl
2	CH_3CH_3	ethane	ethyl
3	$\text{CH}_3\text{CH}_2\text{CH}_3$	propane	propyl
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	butane	butyl
5	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	pentane	pentyl
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	hexane	hexyl
7	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	heptane	heptyl
8	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	octane	octyl
9	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	nonane	nonyl
10	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	decane	decyl

Nomenclature of organic compounds: Nomenclature means the assignment of names to organic compound. There are two mains systems of nomenclature of organic compounds.

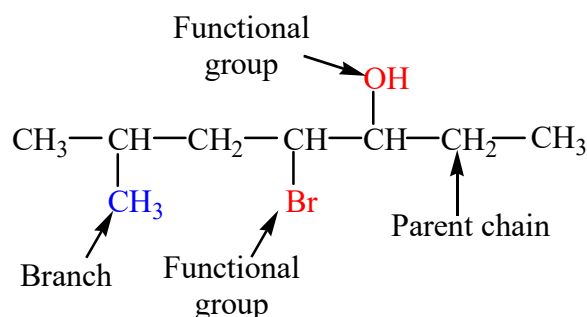
I. Trivial system, II. IUPAC system.

I. Trivial system: Trivial names are called **common names** and generally based on the source, from which they were obtained. Examples:

- a) Acetic acid derives its name from vinegar of which it is the chief constituent (Latin: *acetum* = vinegar).
- b) Formic acid was named as it was obtained from red ants. The Greek word for the red ants is *formicus*.
- c) Methane was named as marsh gas because it was produced in marshes, etc.,

II. IUPAC system. Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature.

A systematic name of organic compound generally derived by identifying the parent hydrocarbon chain, and the functional group(s) attached to it followed by using *prefixes* and *suffixes*.



In the IUPAC system of naming of hydrocarbons the name consists of three parts:

I. Word root II. Suffix III. Prefix

I. Word root: The number of carbon atoms present in the parent chain is given by the ‘**word root**’. In chains containing up to four carbon atoms, word roots such as Meth, Eth, Prop, But, etc., are used and for those containing more than four carbon atoms Greek numerals such as Pent, Hex, Hept, Oct, etc., are used.

Number of carbon atoms	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂
Word root	Meth	Eth	Prop	But	Pent	Hex	Hept	Oct	Non	Dec	Undec	Dodec

II. Suffix: The word root is linked to the suffix. The nature of linkages (i.e., single, double or triple bond) is indicated by the suffix.

Class of compound	Type of bond	Suffix	Name
Aliphatic saturated hydrocarbon	Single	–ane	Alkane
Aliphatic unsaturated hydrocarbon	Double	–ene	Alkene
	Triple	–yne	Alkyne

a. Aliphatic saturated hydrocarbons: Alkanes (Word root + *suffix*)

Structural formula	IUPAC name
CH ₄	Methane
CH ₃ CH ₃	Ethane
CH ₃ CH ₂ CH ₃	Propane
CH ₃ CH ₂ CH ₂ CH ₃	Butane
CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane

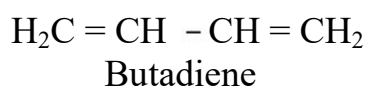
i) Aliphatic unsaturated hydrocarbons: Alkenes (Word root + *suffix*)

Structural formula	IUPAC name
CH ₂ = CH ₂	Ethene
CH ₂ = CH CH ₃	Propene
CH ₂ = CH CH ₂ CH ₃	Butene
CH ₂ = CH CH ₂ CH ₂ CH ₃	Pentene

ii) Alkynes (Word root + *suffix*)

Structural formula	IUPAC name
CH ≡ CH	Ethyne
CH ₃ – C ≡ CH	Propyne
CH ₃ CH ₂ – C ≡ CH	Butyne
CH ₃ CH ₂ CH ₂ C ≡ CH	Pentyne

iii) If more than one double or triple bonds are present, then the prefixes such as **di** (for two), **tri** (for 3), **tetra** (for 4), **penta** (for 5), etc., are added to the suffix, e.g.,

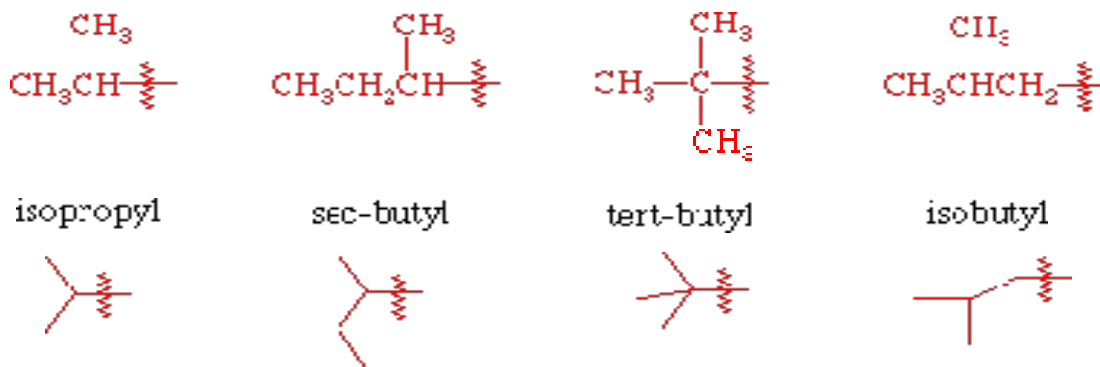


Prefix: Branches in a chain of carbon atoms are regarded as substituents or side chains. These are represented as prefixes, i.e., placed before the word root in the IUPAC name of the compound. e.g. alkyl groups. When the substituent is an alkane containing one hydrogen less it is termed as alkyl. They are named by replacing suffix 'ane' of alkane by 'yl'

Alkane		Alkyl group	
<u>Molecular formula</u>	<u>Name</u>	<u>Molecular formula</u>	<u>Name</u>
CH ₄	Methane	– CH ₃	Methyl
CH ₃ CH ₃	Ethane	– CH ₂ CH ₃	Ethyl

$\text{CH}_3 \text{CH}_2 \text{CH}_3$	Propane	$-\text{CH}_2 \text{CH}_2 \text{CH}_3$	Propyl
$\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3$	Butane	$-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3$	Butyl
$\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3$	Pentane	$-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3$	Pentyl

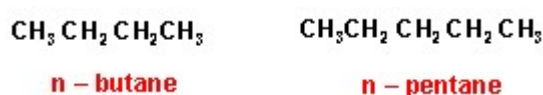
There are a few common branched substituent which you should memorize. These are shown below.



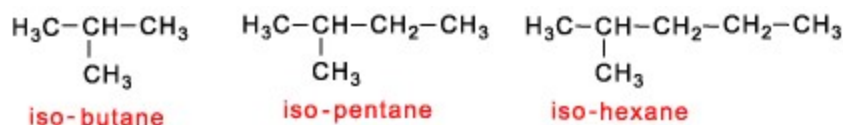
Nomenclature of alkanes: They are saturated hydrocarbons. They have only σ -bond without any π -bonds between carbon atoms. They are chemically inert and hence alkane are also called **paraffins**. They have general formula $\text{C}_n\text{H}_{2n+2}$.

Common system: Hydrocarbons with less than four carbon atoms are always **straight chain** compounds. Hydrocarbons with four or more carbon atoms can either be straight chain compounds or **branched chain**. In the common system, all isomeric alkanes will have the same parent name. The various isomers can be distinguished by prefixes **n-**, **iso-**, **neo-**, etc.

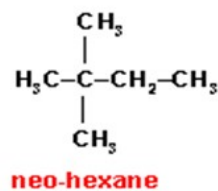
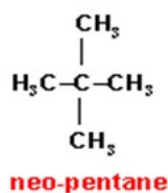
Prefix 'n': Straight chain compounds (with no branching) will carry prefix 'n'. e.g,



The prefix 'iso' : It is used for those **alkanes** in which one methyl group is attached to the **next-to-end** (last but one) carbon atom of the main (continuous) chain. e.g.



Prefix 'neo': Prefix 'neo' is used for those alkanes in which two methyl groups are attached to the **next-to-end** carbon atom of the continuous chain



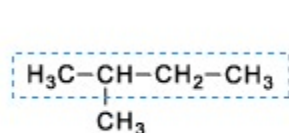
IUPAC system

The following steps are followed for IUPAC nomenclature of alkanes.

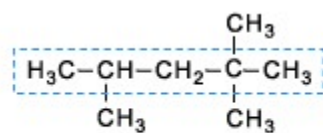
1. Selection of longest continuous chain:

The longest continuous chain of carbon atoms in the molecule is selected. This is regarded as the parent chain and it gives the name of the parent hydrocarbon.

The other carbon atoms not included in the parent chain (if any) are regarded as the substituents.



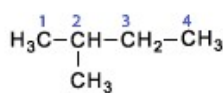
Parent hydrocarbon : butane



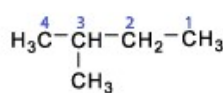
Parent hydrocarbon : pentane

2. Numbering the parent chain

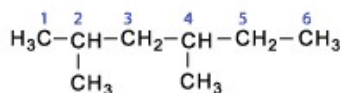
The carbon atoms of the parent chain are numbered from end to end in such a way that the substituents get the smallest possible number.



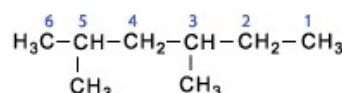
Right Numbering



Wrong Numbering



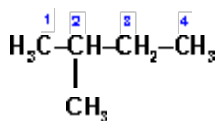
Right Numbering



Wrong Numbering

3. Naming the substituents

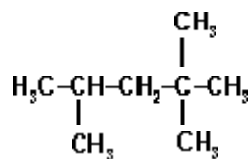
The substituents are alkane molecules with one less hydrogen atom. Hence, they are named by replacing 'ane' in its name by 'yl'. The position of each substituent is written before the name of the alkyl group, which is separated using **hyphens**. **The substituent is written before the parent name.**



2-methylbutane

4. Naming similar substituents

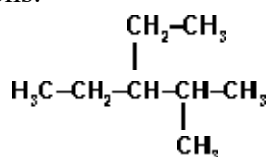
If two or more similar substituents are present then the prefix di (for 2), tri (for 3) tetra (for 4), etc., are used before the name of the substituents and the position of each substituent is specified and separated by commas.



2,2,4-trimethylpentane

5. Naming different substituents

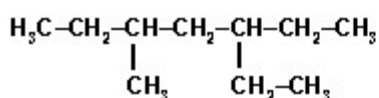
If two or more different substituents are present, they are named in the alphabetical order along with their appropriate positions.



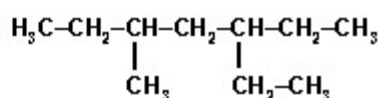
3-ethyl-2-methylpentane

6. Naming different substituents at equivalent positions

If the compound contains two or more different substituents at equivalent positions from the two ends of the parent chain, they are numbered in such a way that the least possible number is given to the substituent that comes first in alphabetical order.

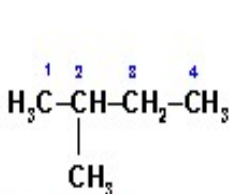


3-ethyl-5-methylheptane (Right)

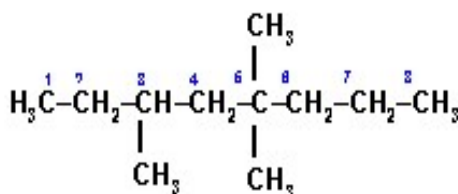


5-ethyl-3-methylheptane (Wrong)

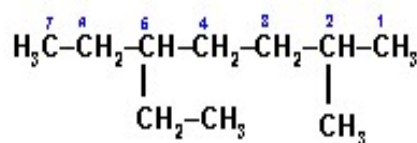
Examples for IUPAC nomenclature of alkanes



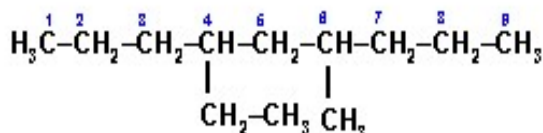
2-methylbutane



3,5,5-trimethyloctane



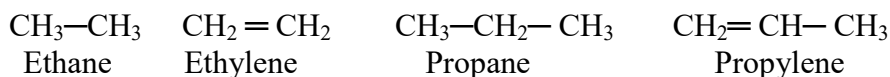
5-ethyl-2-methylheptane



4-ethyl-6-methylnonane

Nomenclature of alkenes: They are unsaturated hydrocarbons. There is double bond between two carbon atoms. They have general formula C_nH_{2n} .

Common system: The common names are derived from the corresponding alkanes by replacing 'ane' by 'ylene'. e.g.



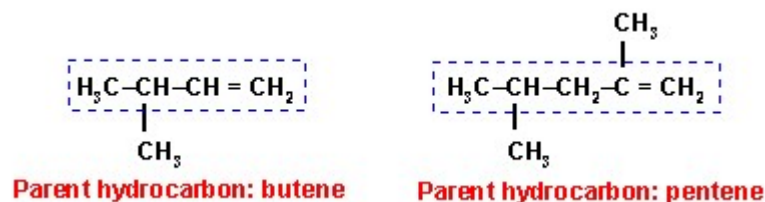
IUPAC system:

The following steps are followed for IUPAC nomenclature of alkenes:

1. Selection of longest continuous chain:

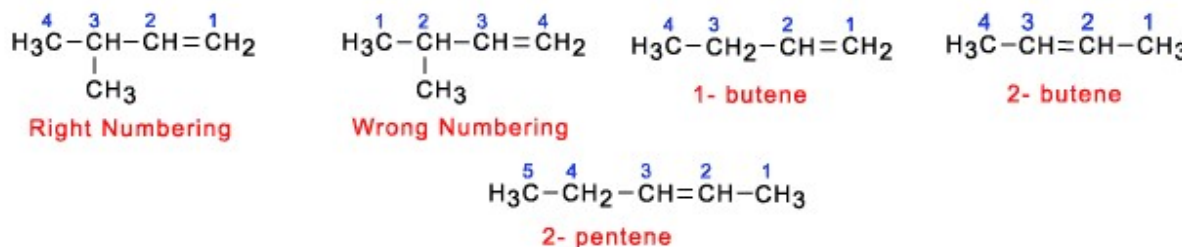
The longest continuous chain of carbon atoms in the molecule containing double bond selected. This is regarded as the **parent chain** and it gives the name of the **parent hydrocarbon**.

The ending 'ane' of the **alkane** corresponding to the longest chain is changed to 'ene'. The other carbon atoms not included in the parent chain (if any) are regarded as the substituents.



2. Numbering the parent chain

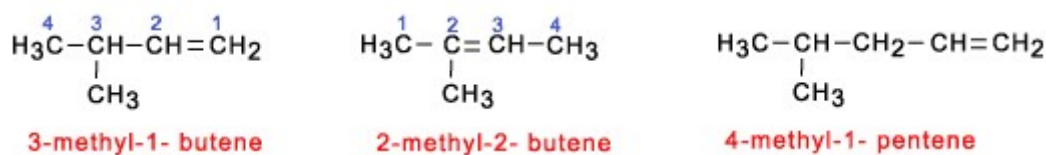
The carbon atoms of the parent chain are numbered from end-to-end in such a way that the double bond gets the smallest possible number (irrespective of the substituents).



3. Naming the substituents:

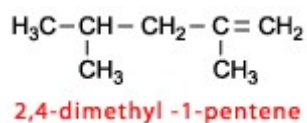
The substituents are alkane molecules with one less hydrogen atom. Hence, they are named by replacing 'ane' in its name by 'yl'.

The position of each substituent is designated by the number of the carbon atom to which it is attached. The position number is written before the name of the alkyl group, which is separated using hyphens. **The substituents are written before the parent name.**



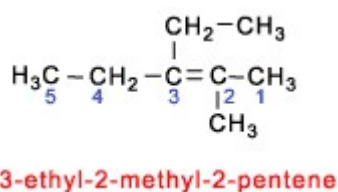
4. Naming similar substituents.

If two or more similar substituents are present, then the prefix di (for 2), tri (for 3), tetra (for 4), etc., are used before the name of the substituents and the position of each substituent is specified and separated by commas.



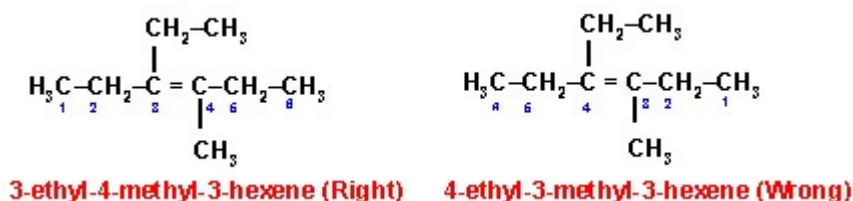
5. Naming different substituents.

If two or more different substituents are present, they are named in the alphabetical order along with their appropriate positions

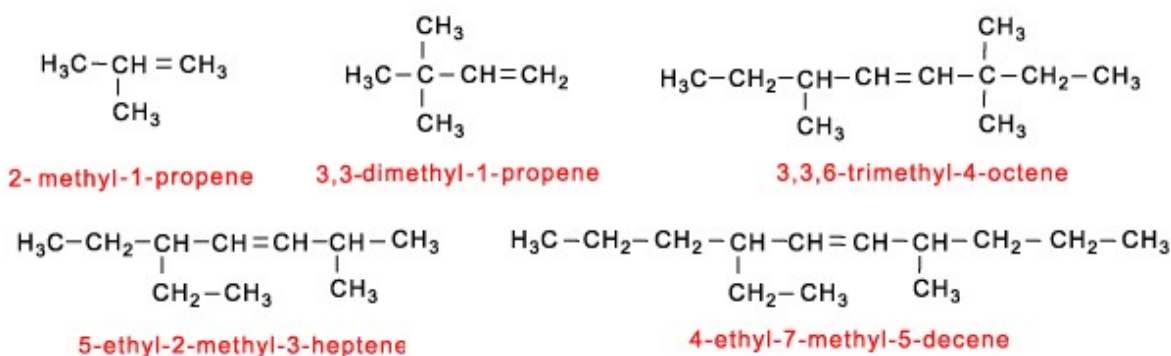


6. Naming different substituents at equivalent positions:

If the compound contains two or more different substituents at equivalent positions from the two ends of the parent chain (from the double bond), they are numbered in such a way that the least possible number is given to the substituent that comes first in alphabetical order.



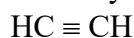
Examples for IUPAC nomenclature of alkenes:



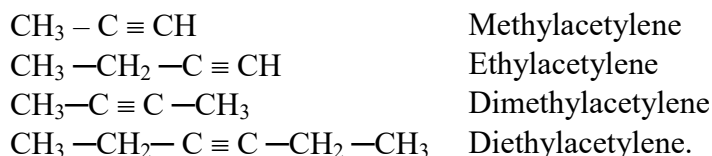
Nomenclature of alkynes:

They are unsaturated hydrocarbons. There is triple bond between two carbon atoms. They have general formula C_nH_{2n-2} . The common names are derived from the corresponding alkanes by replacing 'ane' by 'yne'. e.g.

Common system: The first member of the alkyne family is named as **acetylene**.



The other alkynes are named as substituted **acetylenes** (mono or disubstituted acetylene) e.g.



IUPAC system:

The following steps are followed for IUPAC nomenclature of alkynes:

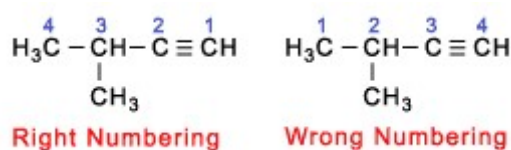
1. Selection of longest continuous chain.

The longest continuous chain of carbon atoms in the molecule containing the triple bond is selected. This is regarded as the parent chain and it gives the name of the parent hydrocarbon. The ending 'ane' of the alkane corresponding to the longest chain is changed to 'yne'. The other carbon atoms not included in the parent chain (if any) are regarded as the substituents.



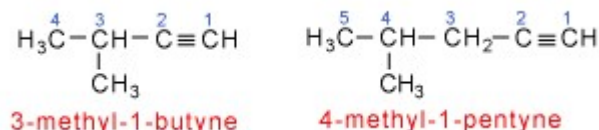
2. Numbering the parent chain

The carbon atoms of the parent chain are numbered from **end-to-end** in such a way that the triple bond gets the smallest possible number (irrespective of the substituents).



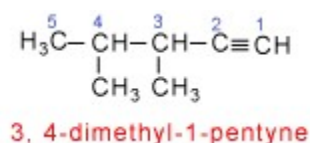
3. Naming the substituents.

The substituents are alkane molecules with one less hydrogen atom. Hence, they are named by replacing 'ane' in its name by 'yl'. The position of each substituent is designated by the number of the carbon atom to which it is attached. The position number is written before the name of the alkyl group, which is separated using hyphens. **The substituent is written before the parent name.**



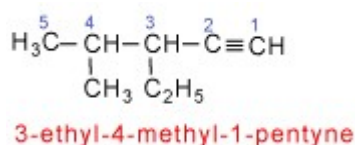
4. Naming similar substituents.

If two or more similar substituents are present, then the prefix di (for 2), tri (for 3), tetra (for 4), etc., are used before the name of the substituents and the position of each substituent is specified and separated by commas.



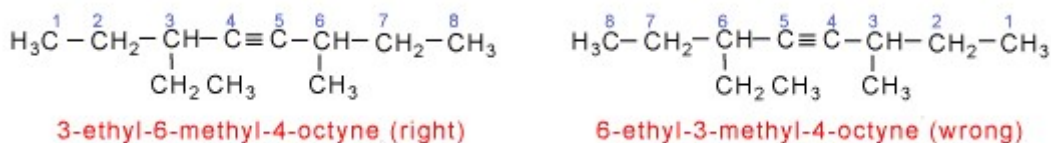
5. Naming different substituents.

If two or more different substituents are present, they are named in the alphabetical order along with their appropriate positions.

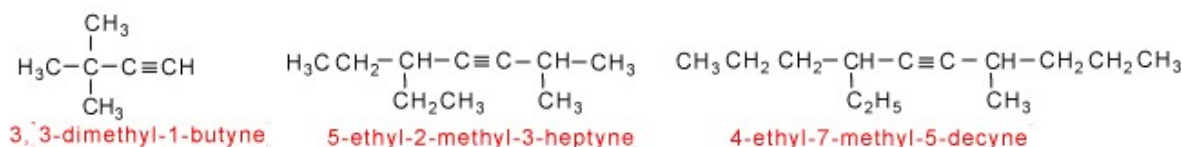


6. Naming different substituents at equivalent positions.

If the compound contains two or more different substituents at equivalent positions from the two ends of the parent chain (and from the triple bond) they are numbered in such a way that the least possible number is given to the substituent that comes first in alphabetical order.



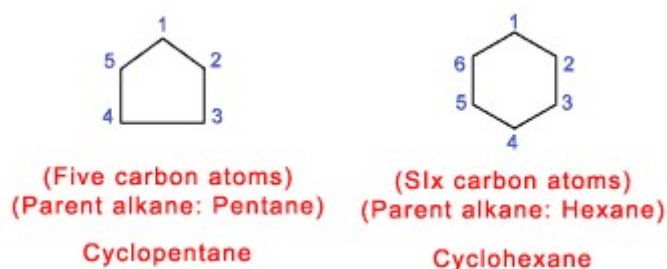
Examples for IUPAC nomenclature of alkynes:



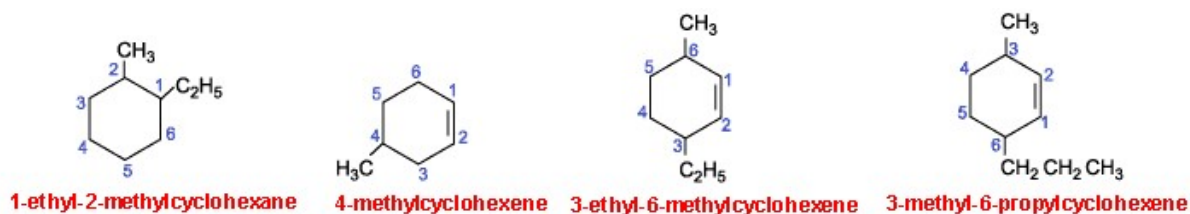
Nomenclature of aliphatic cyclic compounds

The following rules are followed to derive the IUPAC name for an aliphatic cyclic compound:

1. The number of carbon atoms in the ring is counted. The corresponding alkane is the parent alkane. The name of the cyclic saturated compound is obtained by introducing the prefix 'cyclo' to the name of the parent alkane.



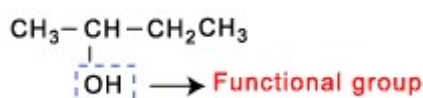
2. Presence of substituents or double/triple bonds is indicated according to IUPAC rules for alkenes/alkynes.



I. Nomenclature of organic compounds containing functional group:

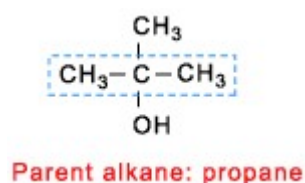
The following IUPAC rules are followed for the nomenclature of organic compounds containing a functional group.

1. Identification of the functional group : The functional group in the molecule is first identified



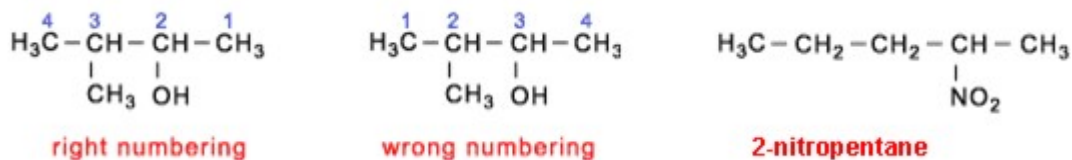
2. Selection of longest continuous chain.

The longest continuous chain of carbon atoms containing the functional group is selected. This is regarded as the parent chain and it gives the name of the parent hydrocarbon. The other carbon atoms not included in the parent chain (if any) are regarded as the substituents.



3. Numbering the parent chain.

The carbon atoms of the parent chain are numbered from end-to-end in such a way that the carbon atom bearing functional group gets the least possible number (irrespective of the substituents).

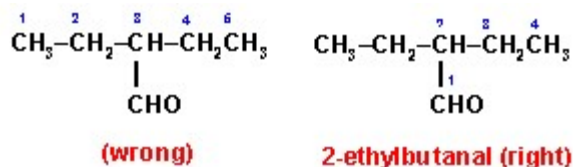


- The functional group along with its position is indicated as a prefix or suffix of the parent alkanes. The prefixes (or suffixes) used for the functional groups is given in the table below:

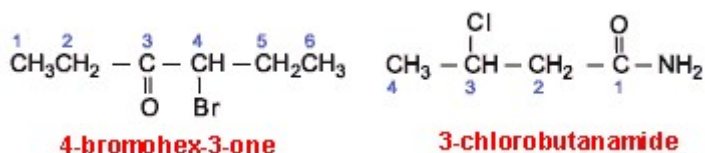
Class of compounds (functional group)	Structure of functional group	IUPAC suffix (s) or prefix (p)	Examples
Alcohol	– OH	– ol(s)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 1 – butanol
Ether	$\begin{array}{c} & & \\ -\text{C} & -\text{O}- & \text{C}- \\ & & \end{array}$	--	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ Ethoxy ethane
Aldehyde	$\begin{array}{c} -\text{C}=\text{O} \\ \\ \text{H} \end{array}$	– al (s)	$\text{CH}_3\text{CH}_2\text{CHO}$ Propanal
Ketone	$\begin{array}{c} -\text{C}=\text{O} \\ \end{array}$	– one (s)	$\text{CH}_3\text{CH}_2-\underset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2\text{CH}_2\text{CH}_3$ 3-hexanone
Carboxylic acid	$\begin{array}{c} -\text{C}-\text{OH} \\ \\ \text{O} \end{array}$	– oic acid(s)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ Butanoic acid
Acid anhydride	$\begin{array}{c} -\text{C}-\text{O}-\text{C}- \\ \quad \quad \\ \text{O} \quad \quad \text{O} \end{array}$	– oic anhydride(s)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2-\text{C} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{O} \\ \quad \quad \quad \diagup \\ \text{CH}_3\text{CH}_2-\text{C} \\ \\ \text{O} \end{array}$ Propanoic anhydride
Amide	$\begin{array}{c} -\text{C}-\text{NH}_2 \\ \\ \text{O} \end{array}$ $\begin{array}{c} -\text{C}-\text{NHR} \\ \\ \text{O} \end{array}$ $\begin{array}{c} -\text{CNR}_2 \\ \\ \text{O} \end{array}$	– amide(s)	$\text{CH}_3\text{CH}_2-\underset{\text{O}}{\underset{ }{\text{C}}}-\text{NH}_2$ Propanamide

Acyl halide	$\begin{array}{c} \text{—C—X} \\ \\ \text{O} \end{array}$	– oyl halide(s)	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{—C—Cl} \\ \\ \text{O} \end{array}$ Propanoyl chloride
Halide	—X (X = F, Cl, Br, I)	Halo (p) or – yl halide(s)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ 1-Chloropropane
Nitro	—NO_2	Nitro – (p)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$ 1-nitropropane
Amine	$\begin{array}{c} \text{—NH}_2, \text{—NH—} \\ \\ \text{—N—} \\ \end{array}$	Amino – (p) or – amine (s)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ 1-aminopropane or 1-propanamine

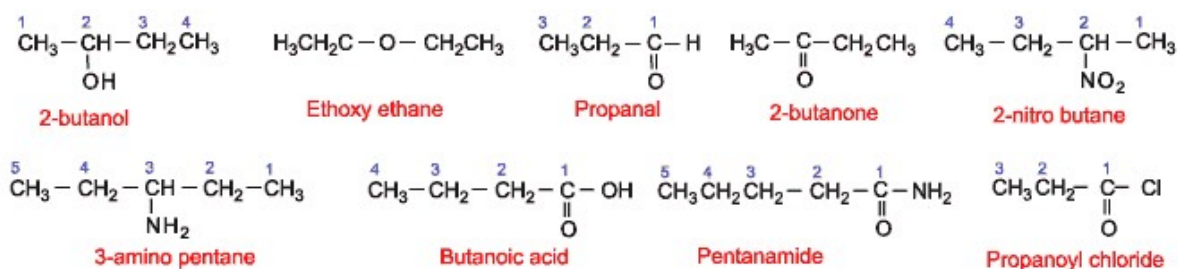
- The rules for naming the substituents are same as that for alkanes.
- If functional groups such as —CHO , —COOH , —COOR , —CONH_2 , —CN etc., which contain a carbon atom and have only one free valency, are present in the molecule, the numbering of the parent chain starts from the carbon atom of the functional group.



- If a halogen atom is present in addition to the functional group in the molecule, the halogen is treated as a substituent and is indicated by the prefix 'halo'. e.g.



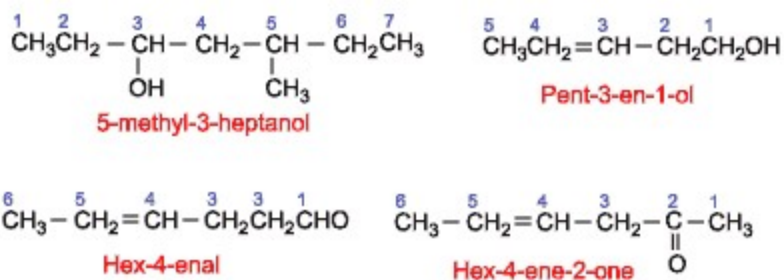
Examples for IUPAC nomenclature of organic compounds containing functional group.



II. Nomenclature for organic compounds containing functional group, multiple bonds and substituents:

In case the organic compound contains a functional group multiple bond and substituent, the naming is done with due preference in the following order:

Functional group > Double bond > Triple bond > Substituent



III. Nomenclature for organic compounds containing more than one functional group:

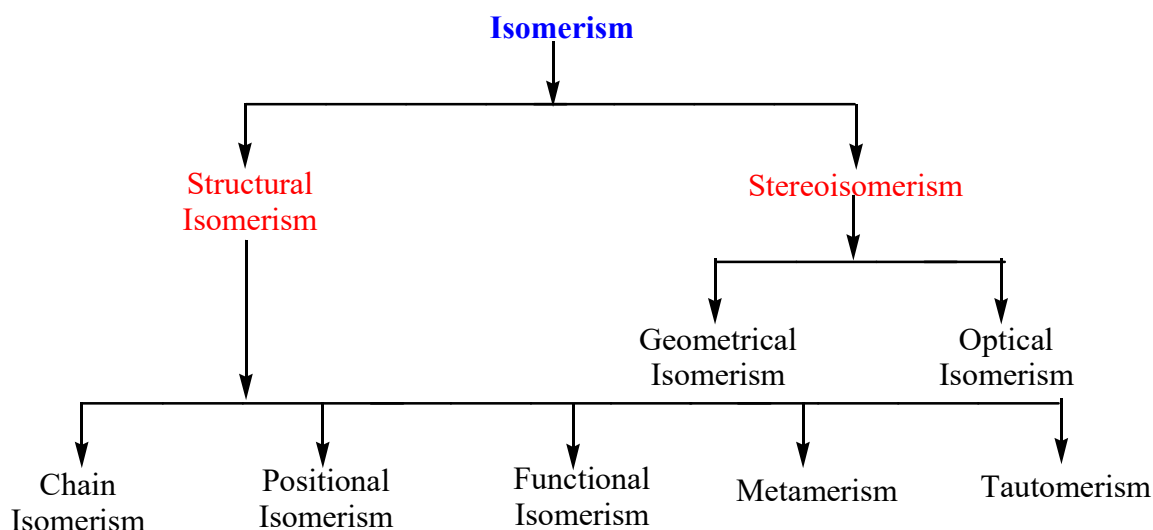
Similar rules as discussed in naming of compounds containing one functional group are applied for naming compounds with two functional groups with slight modifications.

Rules

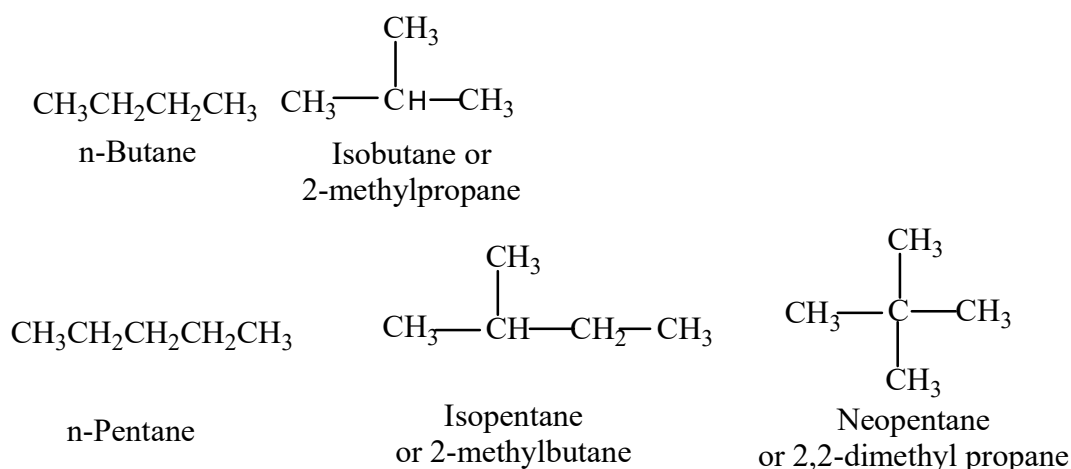
There are two main types of isomerism:

(I) Structural isomerism (II) Stereoisomerism

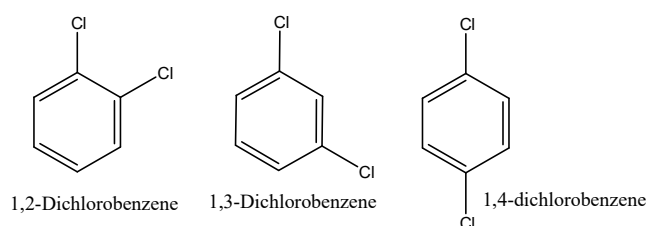
(I) Structural isomerism: Compounds having same molecular formula but different structural formulae. The isomers differ only in the arrangement of atoms or groups within the molecules, without any reference to space are called structural isomers and phenomenon is known as **structural isomerism**. It is further classified into different types:

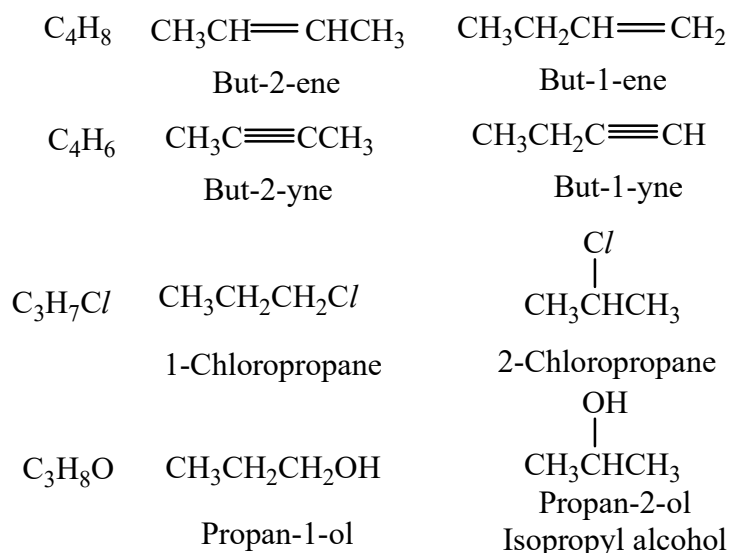


1. Chain or nuclear Isomerism: It is due to difference in the nature of carbon chain(straight or branched) which forms the nucleus of the molecule. It also known as nuclear or skeletal isomerism. Simplest example is butane (C_4H_{10}). It exist two forms. Pentane (C_5H_{12}) exists in three isomers.

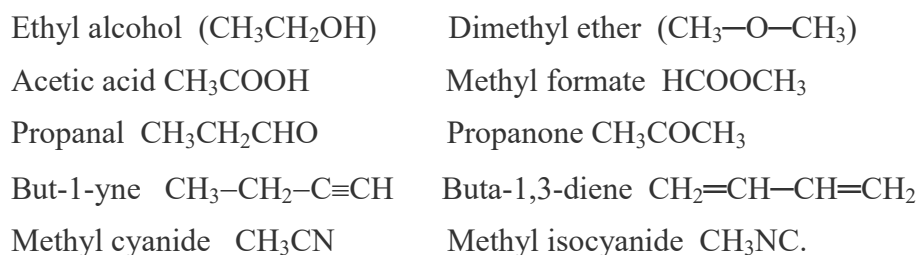


2. Positional Isomerism: It is due to difference in the position occupied by the particular atom or group (substituents) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.



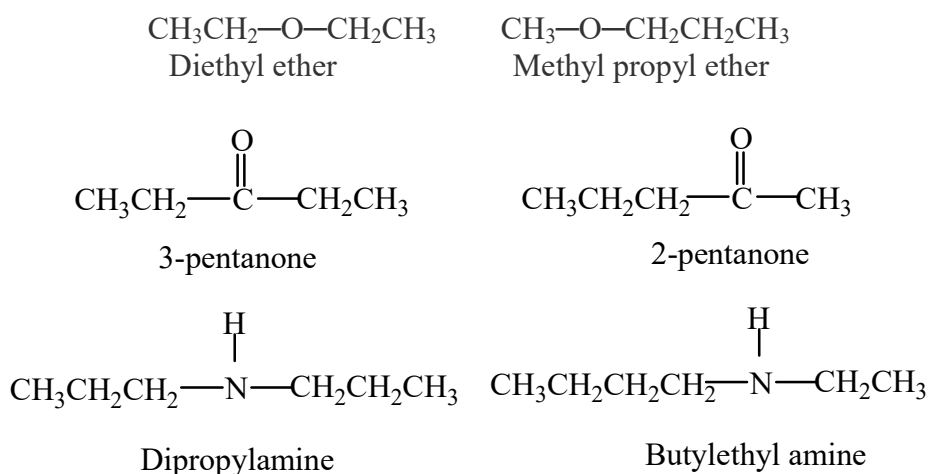


3. Functional Isomerism: Compounds having same molecular formula but different functional groups in their molecules shows functional isomerism and are called functional isomers. Examples;

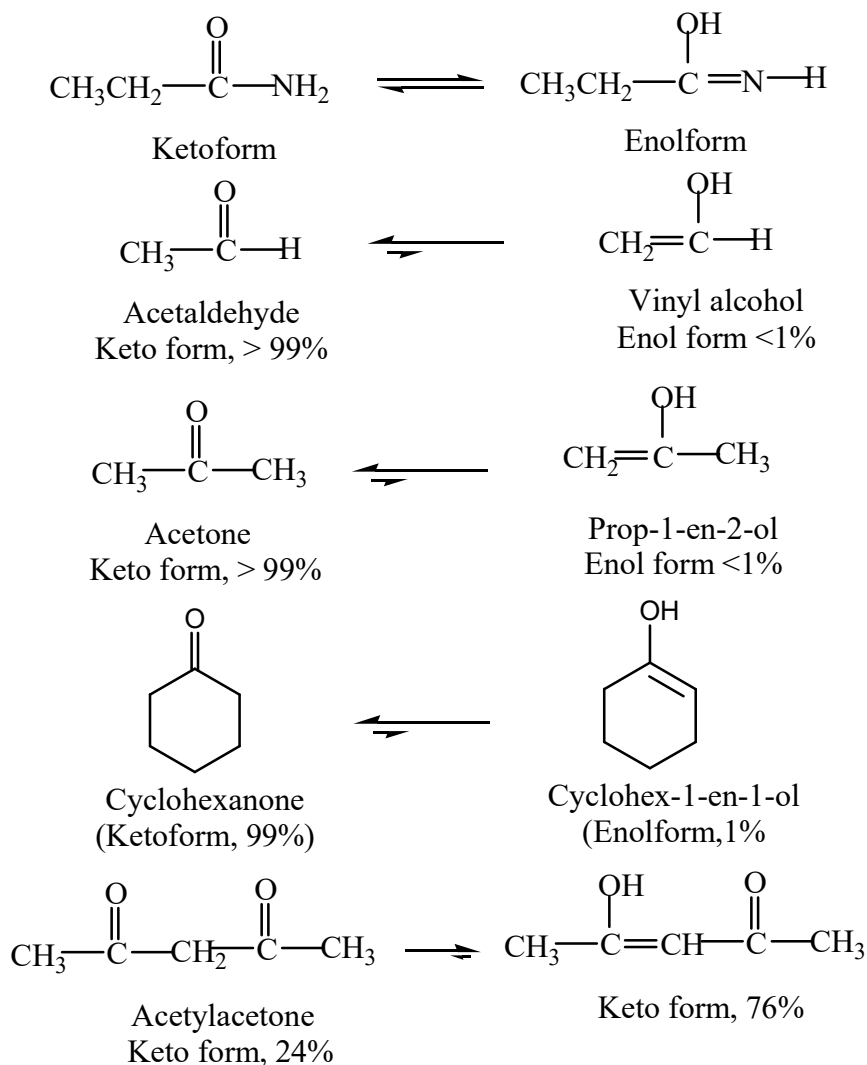


4. Metamerism: It is the isomerism in the same homologous series. It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom (*i.e.*, $-O-$, $-S-$, $-NH-$ and $-CO-$). These isomers have different structural formulae due to different alkyl groups on either side of the functional group are called metamers and phenomenon is called **metamerism**.

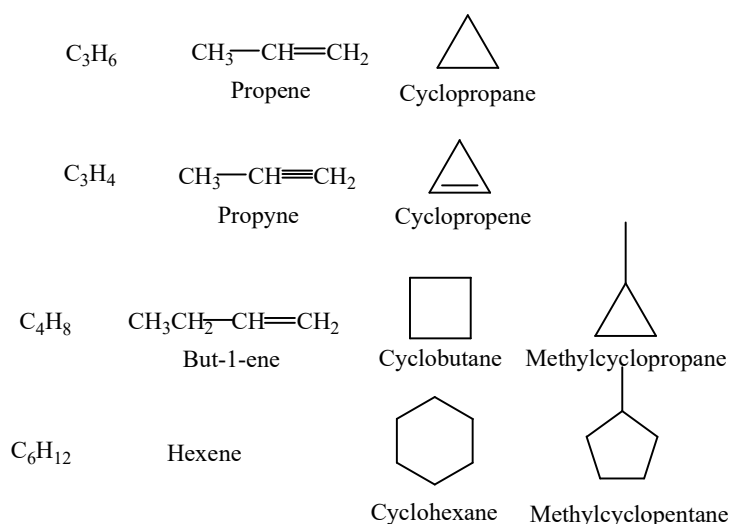
Examples:



5. Tautomerism: It is the one type of isomerism in which a single compound exists in two readily interconvertible different structures leading to dynamic equilibrium is known as **tautomerism** and the different forms are called tautomers. It is caused by the movement (1,2 or mainly 1,3-migration) of hydrogen atom (H ion) between two polyvalent atoms within the same molecule. If the hydrogen atom move between two polyvalent atoms, the system is **dyad** and if the hydrogen atom moves first to third atom the system is **triad**.



6. Ring-Chain Isomerism: This type of isomerism is due to different modes of linking of carbon atoms, *i.e.*, the isomers possess either open chain or closed chain structures.



Stereoisomerism

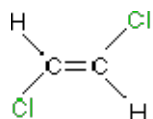
Stereoisomerism is a phenomenon in which compounds having same molecular and structural formula but different relative arrangement of atoms or groups in space (configuration) are called **stereoisomers** and the phenomenon is known as **stereoisomerism**. Stereoisomers have the same connectivity, but different arrangements of atoms in space. It is classified into:

(I) Geometrical isomerism

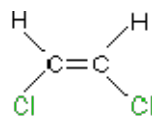
(II) Optical isomerism

(I) Geometrical (or *cis-trans*) isomerism: Compounds having the same molecular and structural formula but different relative arrangement of atoms or groups (or differ in configuration) **around the double bond (i.e., $>C=C<$, $>C=N-$, $-N=N-$)**.

- Geometrical isomerism is possible only when each of the double bonded carbon atoms is attached with two different atoms or groups. ($abC=Cab$).
- Geometrical isomerism is not possible where all the four groups attached to double bonded carbons are different ($abC=Cde$).
- Similar atoms or groups on the same side of the double bonded carbon are called '*cis*' isomers and similar atoms or groups on the opposite side of the double bonded carbon are called 'trans' isomers.

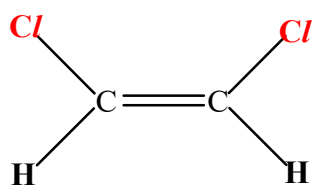


trans-1,2-dichloroethene

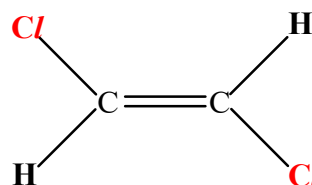


cis-1,2-dichloroethene

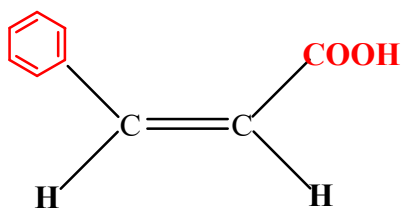
- Geometrical isomerism is also exhibited by compounds containing $>C=N-$ bond (as in aldoxime), $-N=N-$ bond (as in azo compounds), cyclic compounds and dienes.



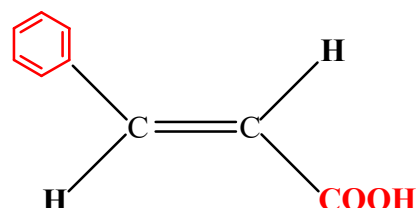
cis- 1,2-Dichloroethene



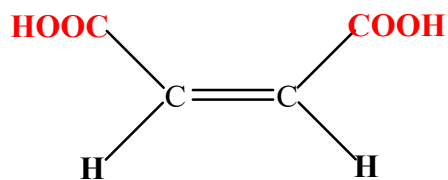
trans- 1,2-Dichloroethene



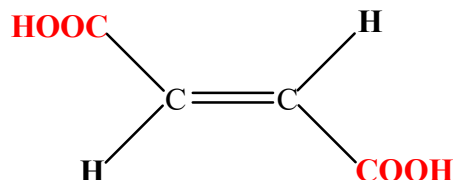
Cinnamic acid
(*cis*)



Cinnamic acid
(*trans*)



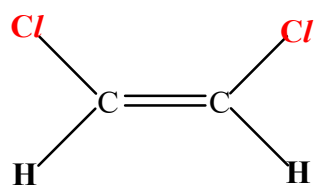
Maleic acid
(*cis*) MP = 403K



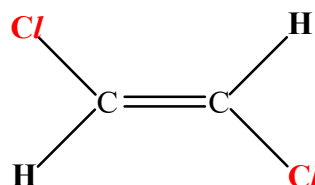
Fumaric acid
(*trans*) MP = 575K

Physical properties of *cis-trans* isomers:

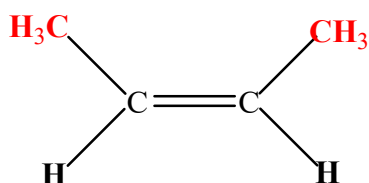
- **Melting Point:** M.P. of *trans*-isomer is more than that of *cis*-isomer.
- **Boiling point:** B.P. of *cis*- isomer is more than that of *trans*-isomer.
- **Solubility:** The solubility, viscosity and refractive index of *cis*-isomer is more than that of *trans*-isomer.
- **Dipole moment:** In general, *cis*-isomer has higher dipole moment than *trans*-isomer.
- **Stability:** In general, *trans*-isomer is more stable but less reactive than *cis*-isomer.
- *Cis-trans* isomers are configuration isomers and called **diastereomers** as they are not mirror image of each other.



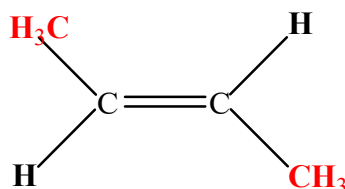
cis- 1,2-Dichloroethene
B.P.= 333K
 $\mu = 1.85\text{D}$



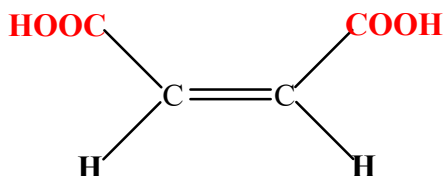
cis- 1,2-Dichloroethene
B.P.= 320.5K
 $\mu = 0.00\text{D}$



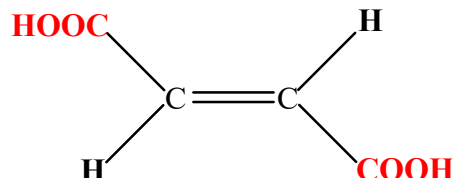
cis- But-2-ene
B.P.= 279 K
 $\mu = 0.33\text{D}$



trans-But-2-ene.
B.P.= 274 K
 $\mu = 0.00\text{D}$

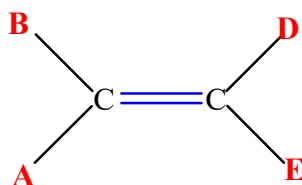


Maleic acid
(*cis*) MP = 403K



Fumaric acid
(*trans*) MP = 575K

***E* and *Z* system of nomenclature:** '*cis*' and '*trans*' designations cannot be used for highly substituted alkenes if four different atoms or groups are attached to the carbon atoms of a double bond i.e., $\text{abC}=\text{Cde}$ type.

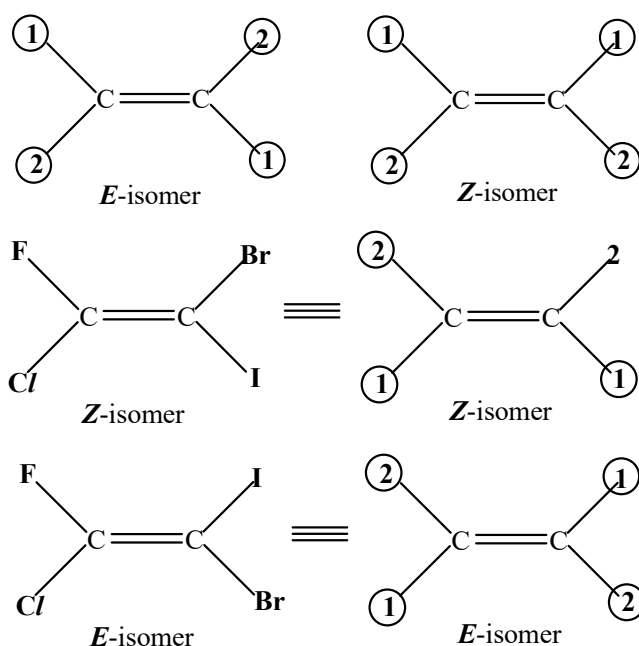


In such cases, *E* and *Z* system of nomenclature is used. This system is based on a priority system developed by **Cahn, Ingold and Prelog**.

In this system, the two atoms or groups attached to each of the doubly bonded carbon are put in order of priority on the basis of sequence rule.

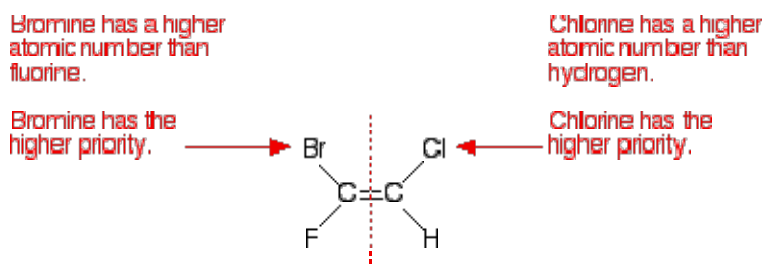
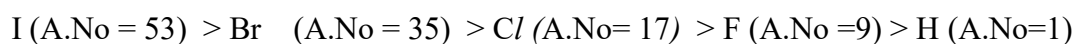
(i) The symbol '*E*' is assigned to an isomer in which the atoms or groups of **higher priority** are on the **opposite side**. *E* (from the German *entgegen*) means "opposed" in the sense of "opposite".

(ii) The symbol '*Z*' is assigned to an isomer in which the atoms or groups of **higher priority** are on the **same side**. *Z* (from the German *zusammen*) means "together".



Sequence rules:

1. Higher priority is assigned to the atoms of higher atomic number. For example, the order of priority in the following atoms



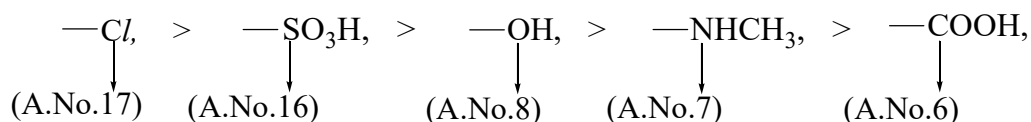
2. If isotopes of same atomic element are attached, the isotope with higher mass number is given higher order of priority. For example, tritium ($^3\text{T}_1$) is given higher priority than deuterium ($^2\text{D}_1$). Deuterium is given higher priority than hydrogen ($^1\text{H}_1$).



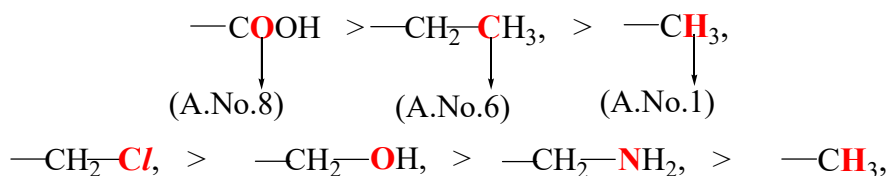
3. In the group the order of priority is also decided on the basis of atomic number of the first atoms of the group. For example, in the following set,



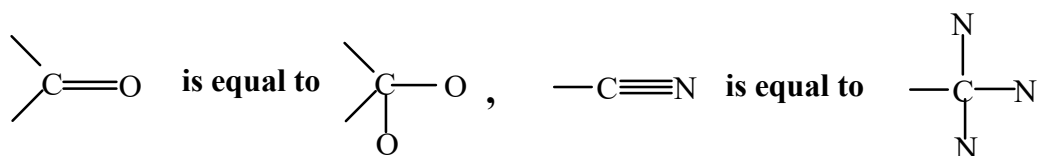
The order of priority is :



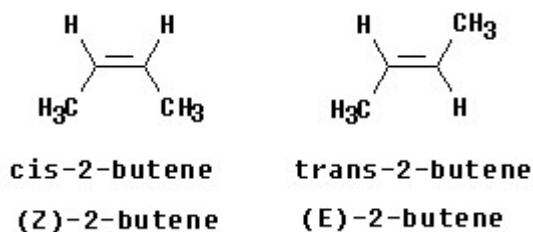
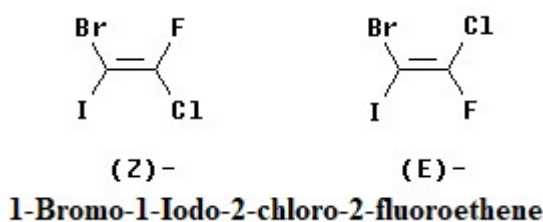
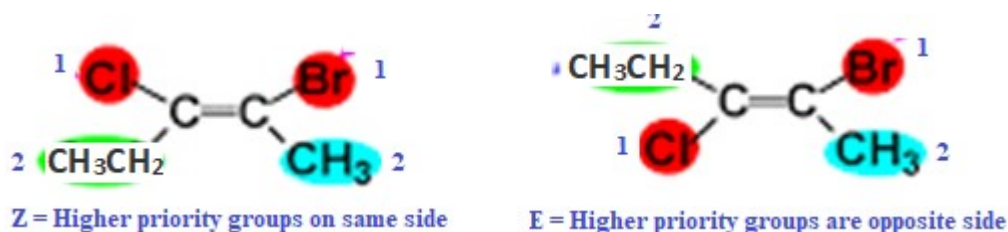
4. When the order of priority of the groups cannot be settled on the first atom, the second atom or subsequent atoms in the groups are considered. For example, in the set $\text{---CH}_2\text{---CH}_3$, ---CH_3 , ---COOH , the order cannot be decided on the basis of first atom as it is same in all the groups. However, in $\text{---CH}_2\text{---CH}_3$, the second atom is carbon, in ---CH_3 , the second atom is hydrogen while in ---COOH , the second carbon is oxygen. Hence, the order of priority is:

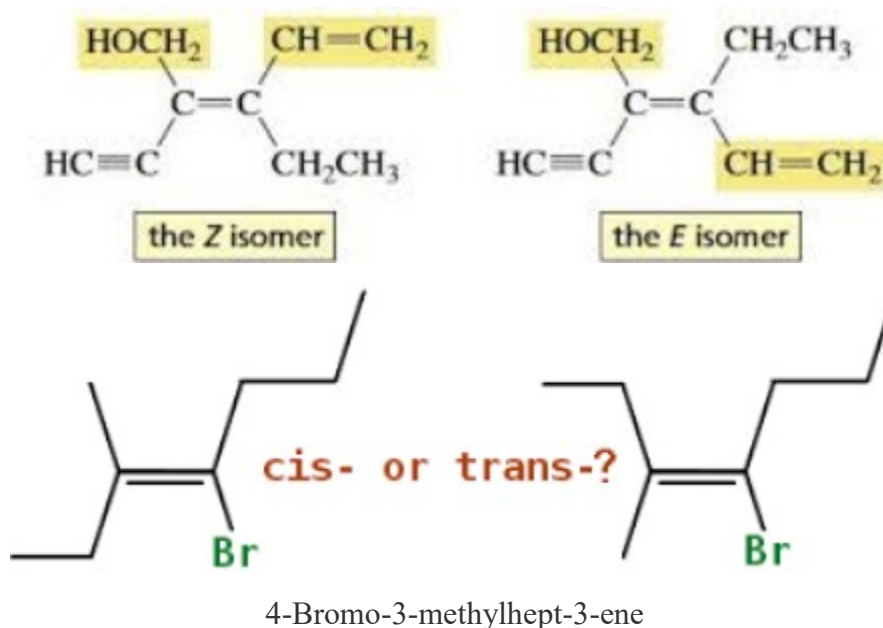


5. A doubly or triply bonded atom is considered equivalent to two or three such atoms. For example:



Examples:





Calculation of geometrical isomers in polyenes:

(a) When the ends of polyene are different:

Number of geometrical isomers = 2^n (n = number of double bonds)

Example 1: $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Br}$ (where $n = 2$) $2^2 = 4$

(b) When the ends of polyene are same:

(i) When n is **even number**, then the number of geometrical isomers = $2^{(n-1)} + 2^{(n/2-1)}$.

Example 1: $\text{X}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{X}$ (where $n = 4$; even)

$$\text{Number of G.isomers} = 2^{4-1} + 2^{\frac{4}{2}-1} = 2^3 + 2^1 = 10$$

(ii) When n is an **odd number**, then the number of geometrical isomers:

$$\text{Number of geometrical isomers} = 2^{(n-1)} + 2^{\frac{n-1}{2}}$$

Example 1: $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ (where $n = 3$; odd)

$$\text{Number of G.isomers} = 2^{3-1} + 2^{\frac{3-1}{2}} = 2^2 + 2^1 = 6$$

Optical Isomerism: Compounds having similar physical and chemical properties but differing only in the rotation of plane polarized light are called **optical isomers** and this phenomenon is known as **optical isomerism**.

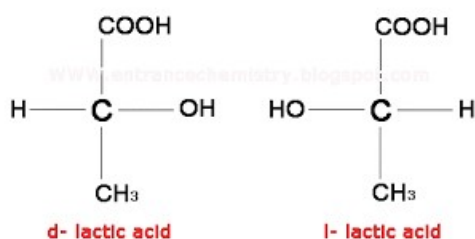
(i) The optical isomer which rotates the plane polarised light to the right (clockwise) is known as **dextrorotatory** isomer (Latin: *dexter* = right) or **d-form** or indicated by **+ve**.

(ii) The optical isomer which rotates the plane polarised light to the left (anticlockwise) is known as **laevorotatory** isomer (Latin: *laevo* = left) or ***l*-form** or indicated by **–ve**.

(iii) The optical power of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive. This equimolar mixture of ***d*-form** and ***l*-form** is termed as **racemic** mixture or ***dl*-form** or (\pm).

Examples:

Optical Isomers of lactic acid: In lactic acid $\text{CH}_3\text{—CHOH—COOH}$, **second carbon is chiral**. There are two optically active isomers of Lactic acid: ***d*-lactic acid** and ***l*-lactic acid**. In addition to these optically active varieties there is an optically inactive form which results when dextro and laevo (levo) varieties are present in equal quantities. It is called racemic mixture or (\pm) lactic acid.

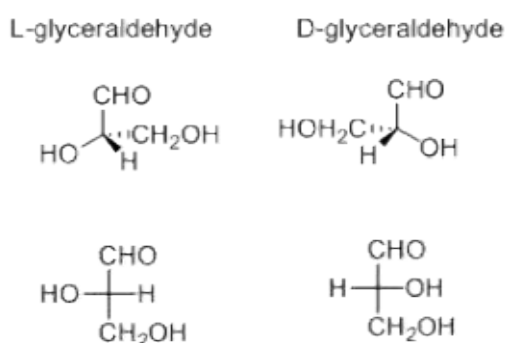


The racemic mixture is **50:50** mixture of ***d*** and ***l*** -isomers and hence have zero optical rotation as the rotation due to one enantiomer cancels the rotation due to the other. That is racemic mixture is optically inactive due to **external compensation**.

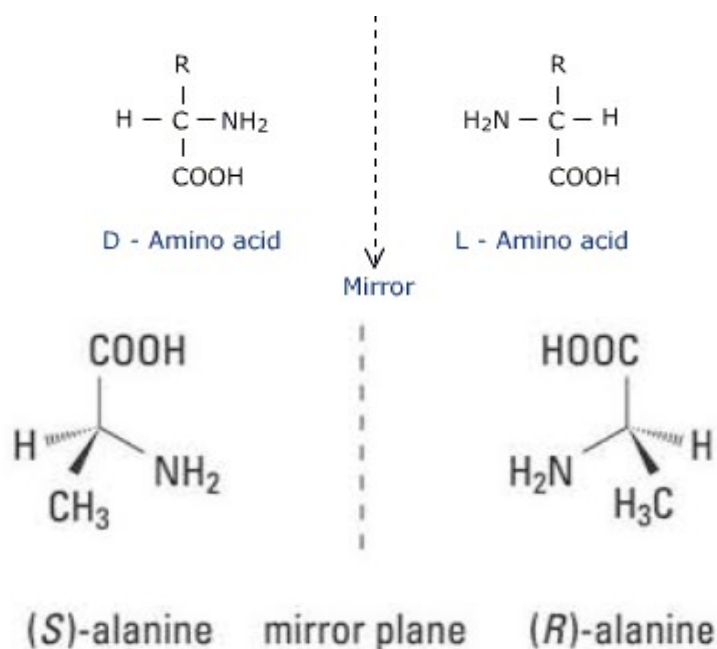
Dextro rotatory lactic acid may be obtained from meat extract and is known as sarcolactic acid. During muscular activity glycogen present in muscles break down to sarcolactic acid. During rest sarcolactic acid is converted back to glycogen.

Leavo rotatory lactic acid may be obtained by the fermentation of sucrose by *Bacillus Acidilactit*. Ordinary lactic acid in sour milk or manufactured by fermentation or by synthetic method is racemic mixture.

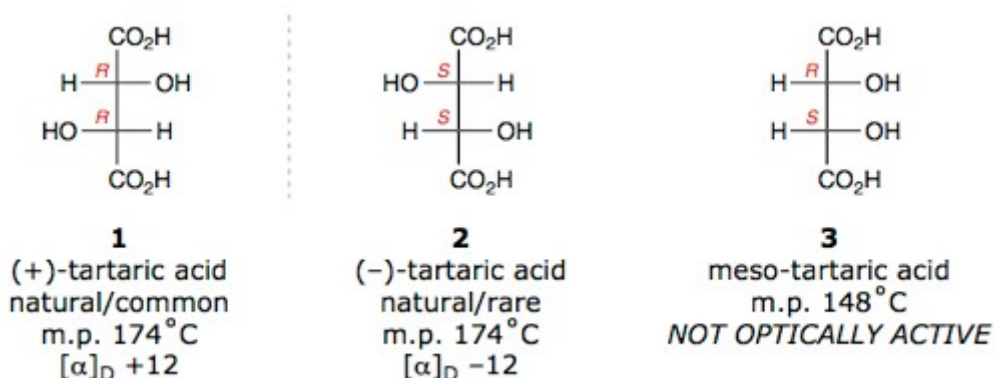
Example 2: Glyceraldehyde:



Example 3: Amino acids:



Optical Isomers of Tartaric acid: Tartaric acid has two asymmetric carbon atoms each lined to the same four different groups. It exists as three stereoisomers (two enantiomers and a meso compound). Crystals of potassium hydrogen (*R,R*)-tartrate are often to be found in the bottom of wine bottles.



(i) Dextro-tartaric acid (*d*-form): This rotates the plane polarised light to the right. Both the asymmetric carbon atoms reinforce each other and cause the rotation of plane polarised light in the same direction, i.e., towards right. It has no plane of symmetry. It occurs in nature and is obtained from tamarind and grapes.

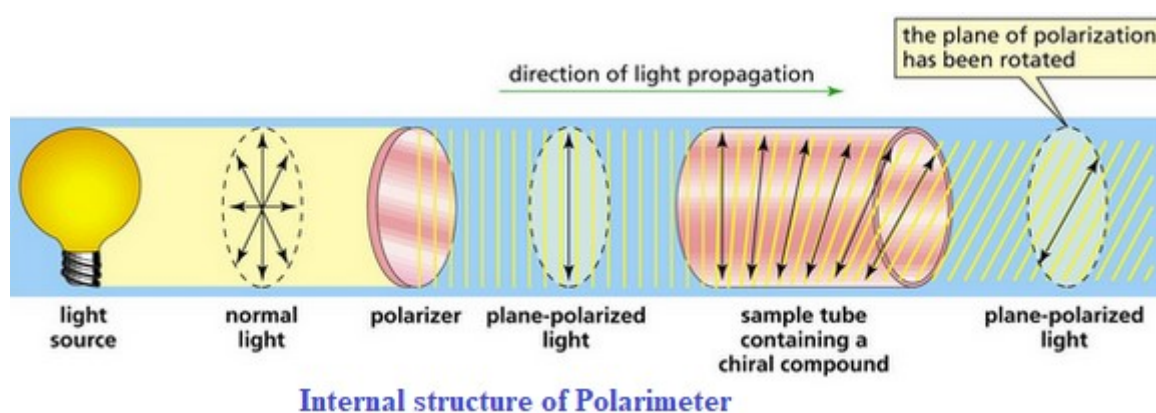
(ii) Laevo-tartaric acid (*l*-form): This rotates the plane polarised light to the left. Both the asymmetric carbon atoms rotate the plane polarised light in the same direction, i.e., towards left. It also has no plane of symmetry. It is obtained by resolving racemic tartaric acid. Both *d*-form and *l*-forms are enantiomers.

(iii) Meso-tartaric acid: It possesses a plane of symmetry and is optically inactive form. One of the asymmetric carbon atom turns the plane polarised light to the right and other to the left and to the same extent. The rotation due to upper half is compensated by the lower half, i.e., internally compensated. It does not occur in nature and cannot be resolved into *d*- and *l*-forms. It is obtained by synthetic methods.

(iii) **Racemic tartaric acid (\pm)**: It is an equimolecular mixture of d- and l-forms. The rotation of the d-form is compensated externally by l-form and hence, it is optically inactive due to external compensation. It can be resolved into d- and l-forms. It is obtained by synthetic methods.

Optical Activity: Ordinary light consists of rays or varying wavelengths vibrating in all possible directions perpendicular to the direction of propagation. When a monochromatic (single coloured) light is passed through a nicol prism (made of calcite, CaCO_3), the vibrations are adjusted in a single plane only. **The light whose vibrations occur only in one plane is termed as plane polarized or simply polarised.** The device that brings polarisation in light is called a **polariser**.

Chiral molecules have ability to rotate the plane polarized light either to the right (clockwise) or to the left (anticlockwise). These chiral molecules are termed as optically active substances and the property is called optical activity. The optical activity of compound is measured by instrument is called **polarimeter**.



The extent or angle of rotation depends on a number of factors:

- Nature of the substance,
- Wavelength of the light used (λ),
- Concentration of the solution (C) in g cm^{-1} ,
- Nature of the solvent used,
- Pathlength (distance travelled by light through the optically active solution),
- Temperature at which the measurements are made.

Specific rotation: It is defined as the rotation produced by a solution of length of 10 centimetre (one decimetre) and unit concentration (1g/mL) for the given wavelength of the light at the given temperature.

$$\text{Specific rotation, } [\alpha]_{\lambda}^{\text{obs}} = \frac{\alpha_{\text{obs}}}{l \times C}$$

Where, α_{obs} is the rotation observed.

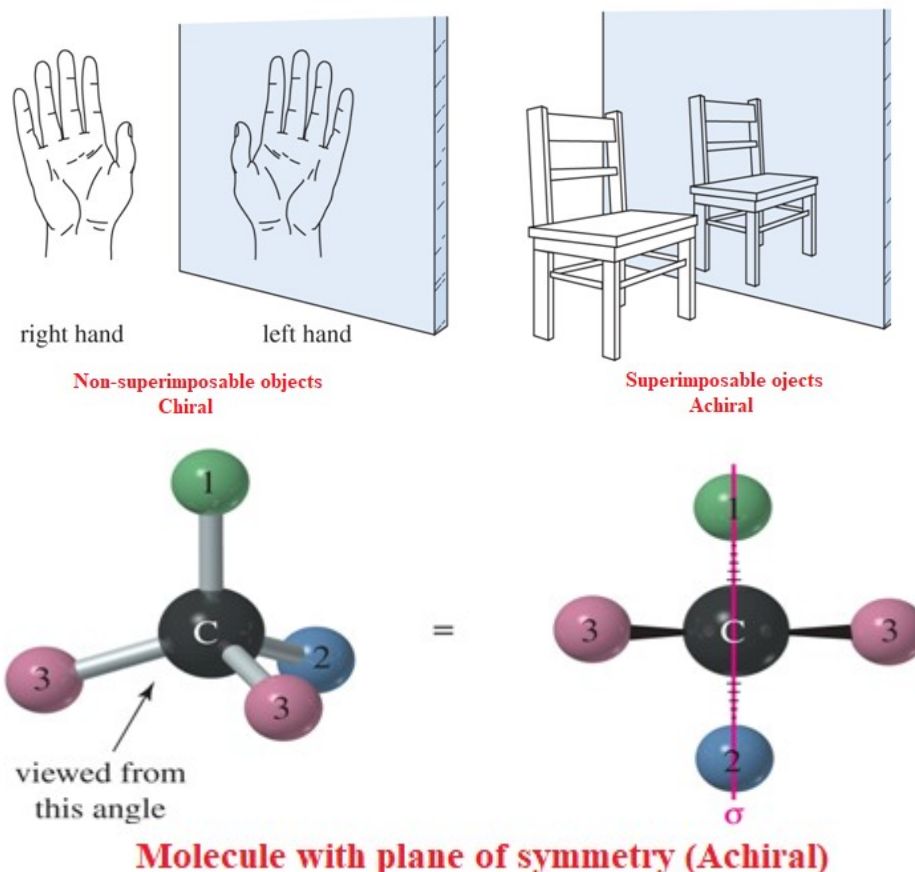
Enantiomers: Compounds which are mirror images of each other and are not superimposable are termed as **enantiomers** (Greek *enantio* = opposite; *meros* = parts:) and phenomenon is described as **enantiomerism**.

(i) A pair of enantiomers have identical physical and chemical properties but differ from each other in the rotation of plane polarized light.

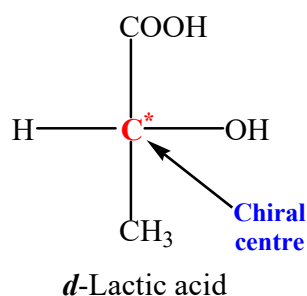
- (ii) In order to exhibit optical activity, an object or molecule must be **chiral**.
- (iii) Chirality or molecular dissymmetry is a necessary condition for the existence of enantiomers.

Chirality: It is a geometric property of some molecules and ions. An object or molecule having no plane of symmetry is called dissymmetric or **chiral**. **An object is chiral if its mirror image is nonsuperimposable on its original object.** “Handedness”: Right-hand glove does not fit the left hand.

A symmetric object or molecule is referred to as **Achiral**. A molecule that has a plane of symmetry is *achiral*. Mirror images that can be superposed are *achiral* (not *chiral*).



A carbon atom which is bonded to four different atoms or groups in the molecule is called **Chiral carbon** or **asymmetric carbon** atom (chiral centre).

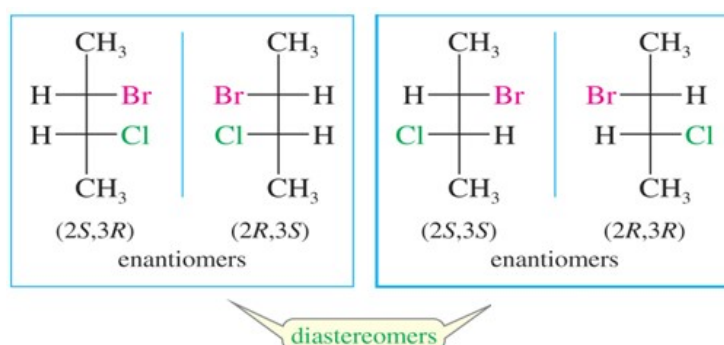


A chiral molecule/ion is non-superposable on its mirror image. The presence of an asymmetric carbon center is one of the main structural features that induce chirality in organic and inorganic molecules.

The mirror images of a chiral molecule or ion are called **enantiomers** or **optical isomers**. Individual enantiomers are often designated as either right-handed or left-handed. The concept is of great practical importance because most biomolecules and pharmaceuticals are chiral.

Diastereomers:

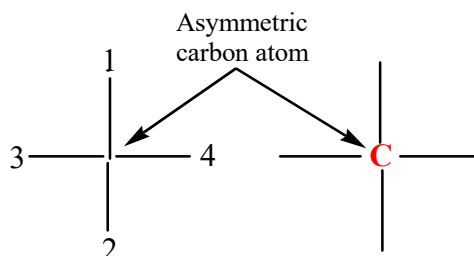
- Molecules with two or more chiral carbons.
- Stereoisomers that are not mirror images.
- Stereoisomers that have different compounds with different physical properties



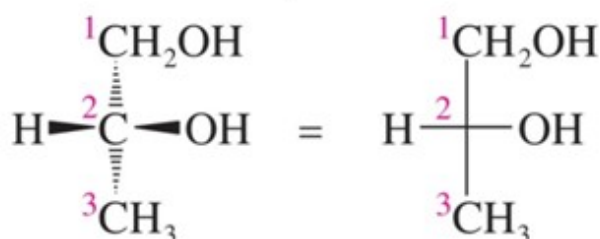
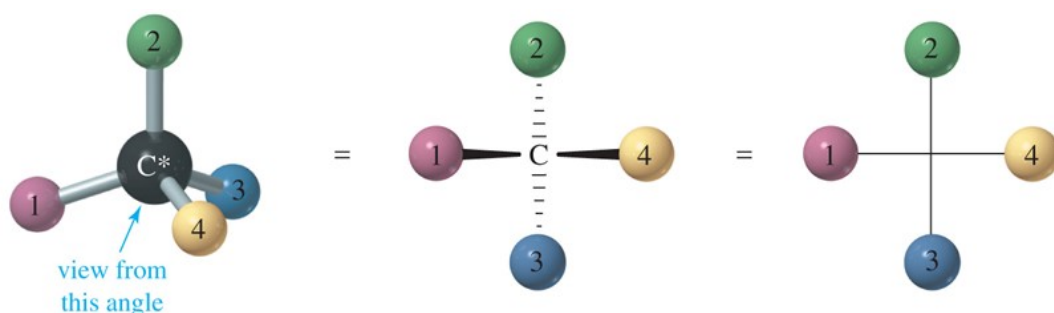
FISCHER PROJECTION:

Emil Fischer (1891) provided an easy method to represent the three dimensional formulae of organic molecules on paper. Thus, **Fisher projection is a planar (two dimensional) representation of the three dimensional structure**. The important rules are:

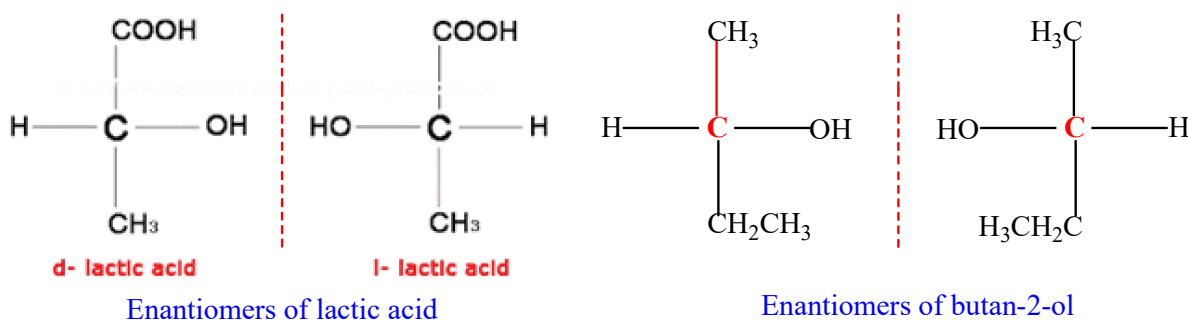
- The carbon chain of the compound is arranged vertically with the most oxidised carbon at the top.
- The asymmetric carbon atom is in the paper plane and is represented at the intersection of crossed lines.



- Vertical lines represent bonds going away from the observer, *i.e.*, groups attached to the vertical lines are present behind the plane of the paper.
- Horizontal lines represent bonds coming towards the observer, *i.e.*, groups attached to the horizontal lines are present above the plane of the paper. Examples:



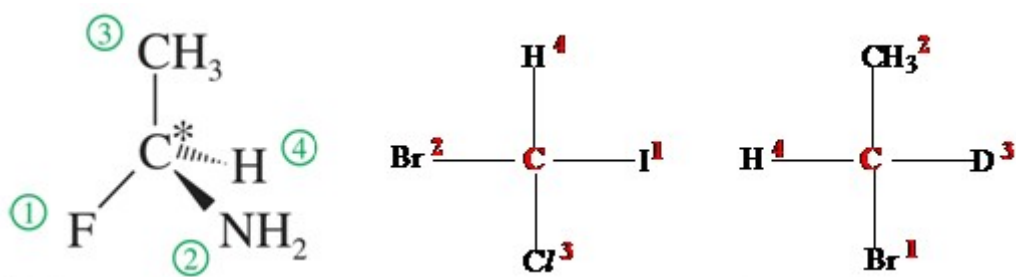
(*R*)-propane-1,2-diol



ABSOLUTE CONFIGURATION (*R* and *S* system of nomenclature):

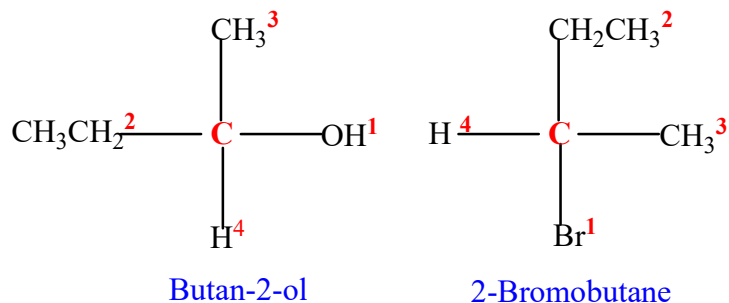
R and *S* system of nomenclature is developed by **Cahn, Ingold and Prelog**. The important features of the system are:

Step 1. Order of Priority: The four different groups attached to the chiral carbon atom are assigned a priority order or 1,2,3 or 4 on the basis of sequence rules as mentioned in *E* and *Z* nomenclature of alkenes. Atoms with higher atomic numbers receive higher priorities. 1 is the highest priority group and 4 is the lowest, (i.e., 1 > 2 > 3 > 4).

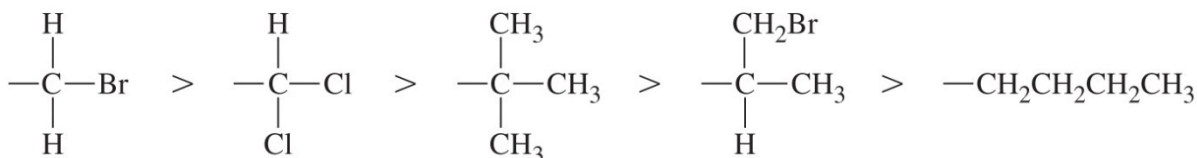




Step 2: If two of atoms attached to the chiral central are same and their priority sequence is unable to be decided on the basis of rule 1, in such cases the relative priorities can be decided by comparing the second (or even third) atom of the respective group as mentioned in *E* and *Z* nomenclature of alkenes..

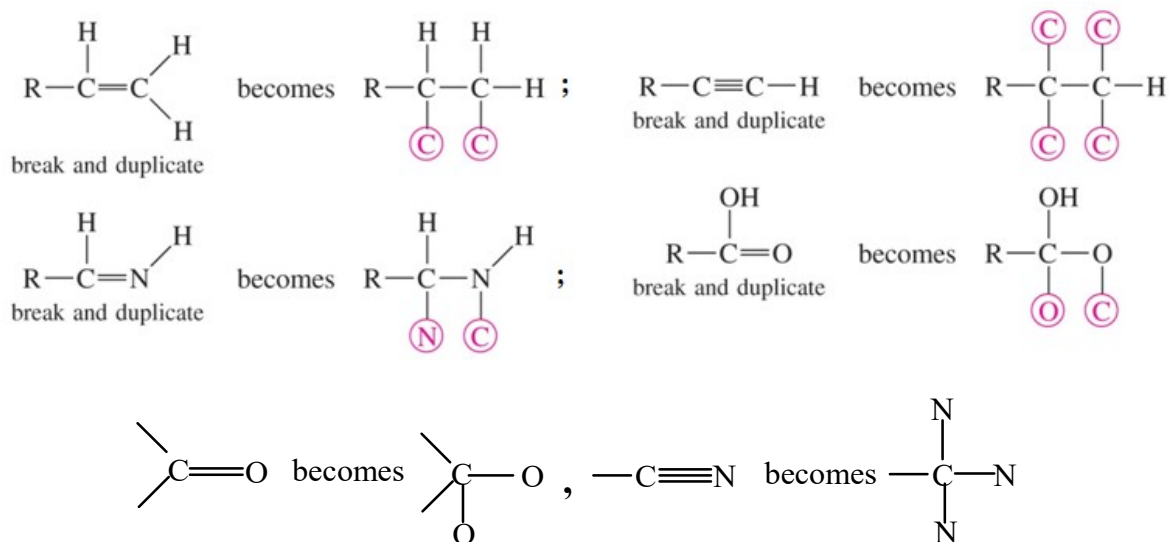


Examples

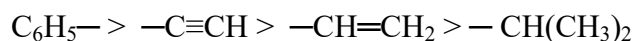


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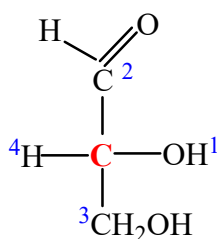
Step 3 : This is an extension of rule II. If the second atom is attached by double bond or triple bond, then double bonds are treated as they have two single bonds and triple bonds have three single bonds respectively. In other words, each double bonded atom is duplicated and triply bonded atom is triplicated. Thus,



If the chiral carbon contains phenyl groups in addition to double bond and triple bonded groups, then the priority order is as follows

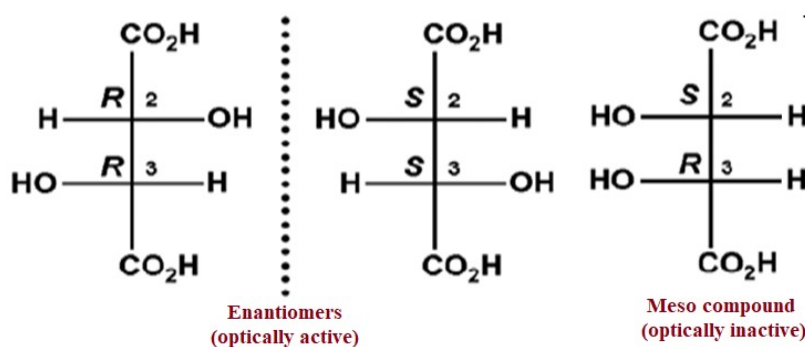
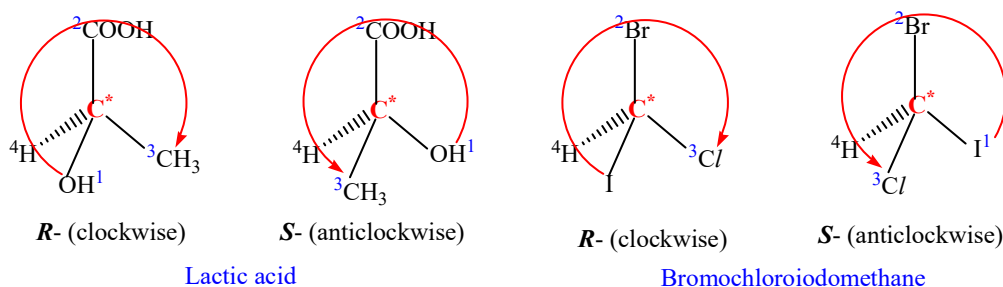


Example: Glyceraldehyde: The order of priority in glyceraldehydes is :



$-\text{OH} = (1), -\text{CHO} = (2), -\text{CH}_2\text{OH} = (3), -\text{H} = (4).$

Step 4: After deciding the priority of four atoms or groups attached to the chirality centre, the molecule (formula) is now rotated so that the group of lowest priority (4) is directed away from the eye (viewer). The arrangement of remaining three groups is viewed in decreasing order of their priorities, i.e., from 1 to 2 to 3. In looking so, if the eye travels in a **clockwise** direction, the configuration is specified as **R** (Latin word *rectus* meaning right), while in case eye travels in the **anticlockwise** direction, the configuration is specified as **S** (Latin word *sinister* meaning left). Examples: Lactic acid, Bromochloriodomethane.



Priority order of important atoms or groups:

$-\text{I}, -\text{Br}, -\text{Cl}, -\text{SO}_3\text{H}, -\text{SH}, \text{F}, -\text{OR}, -\text{OH}, -\text{NO}_2, -\text{NR}_2, -\text{NHR}, -\text{NH}_2, -\text{COOR}, -\text{COOH}, -\text{CONH}_2, -\text{COCH}_3, -\text{CHO}, -\text{CH}_2\text{OH}, -\text{CN}, -\text{CR}_3, \text{C}_6\text{H}_5-, -\text{C}\equiv\text{CH}, -\text{CH}=\text{CH}_2, -\text{CH}_2\text{R}, -\text{CH}_3, -\text{D}$ and $-\text{H}.$

- When the molecule contains more than one chiral centre, the same procedure is applied in each.
- A racemic mixture is designated as (*R*, *S*)

- The direction of rotation of plane polarised light has nothing to do with *R-S* notation. An *R* – or *S* –compound may be either dextrorotatory or laevorotatory.

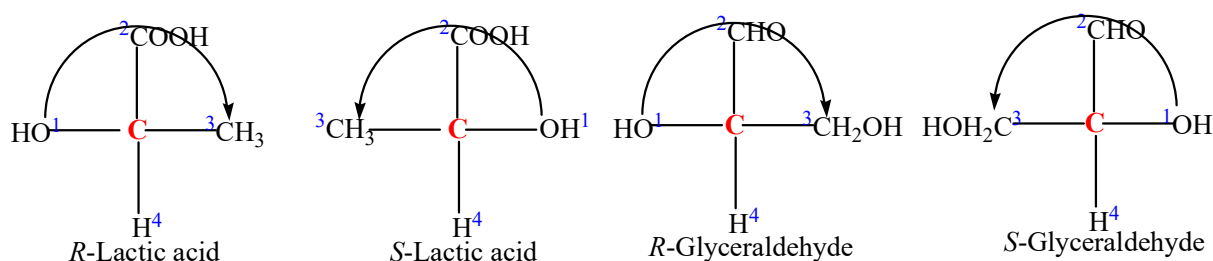
Assigning of *R* and *S* configuration from Fisher Projections containing one chiral centre.

Step1: Assign priorities to the four atoms or groups attached to chiral centre.

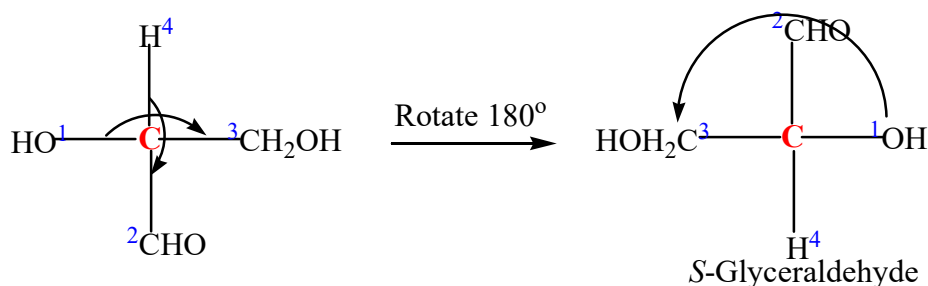
Step2: Apply priority rules. The lowest priority H or group is placed vertically (upward or downward) in the Fischer projection and directed away from the viewer.

Step 3: Determine the direction of rotation while going from priority group 1 to 2 to 3 and assign *R* or *S* configuration. This step is carried out in four different ways:

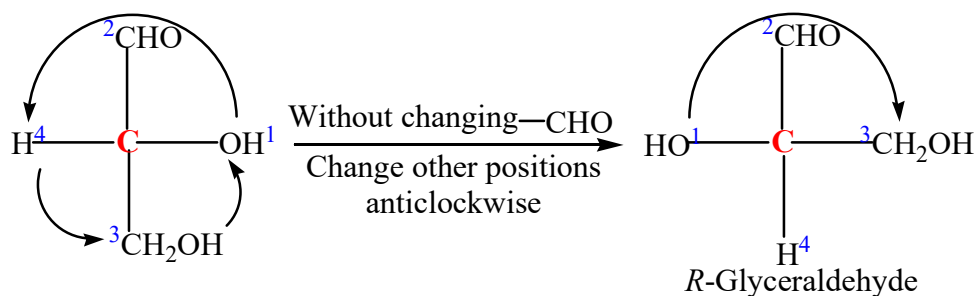
(i) When atom or group of lowest priority is at the bottom of vertical line: Move the eye in order of decreasing priority to determine the configuration.



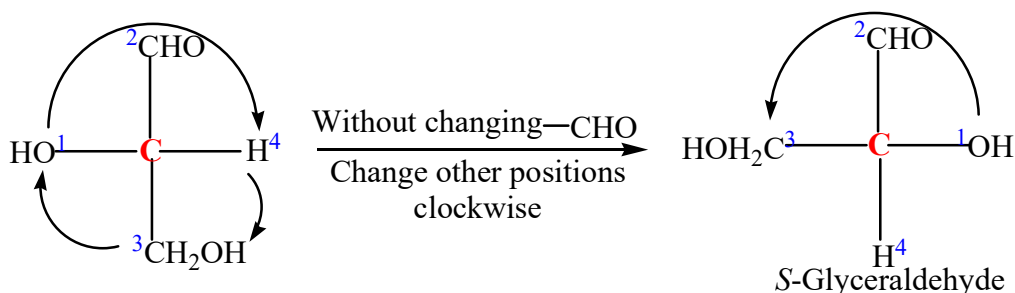
(ii) When atom or group of lowest priority is at the top of vertical line: In this case rotate the entire molecule through 180°, so that the atoms or groups of lowest priority come at the bottom. Now, move the eye in order of decreasing priority to determine the configuration.



(iii) When atom or group of lowest priority is at the left hand side on the horizontal line: In this case without changing the position at the top of vertical line, change the positions of other atoms or groups in anticlockwise direction till the group of lowest priority comes at the bottom of vertical line. Now, note the movement of eye in order of decreasing priority to determine the configuration.



(iv) **When atom or group of lowest priority is at the right hand side on the horizontal line:** In this case without changing the position at the top of vertical line, change the positions of other atoms or groups in **clockwise** direction till the group of lowest priority comes at the bottom of vertical line. Now, note the movement of eye in order of decreasing priority to determine the configuration.



Calculation of number of stereoisomers: The number of optical isomers of a compound depends on its structure and number of asymmetric carbon atoms present in its molecule.

(i) When the molecule cannot be divided into two equal halves, *i.e.*, **the molecule has no symmetry (unsymmetrical)** and n is the number of asymmetric carbon atoms, then

The number of *d*- and *l*- (optical isomers) forms, $a = 2^n$

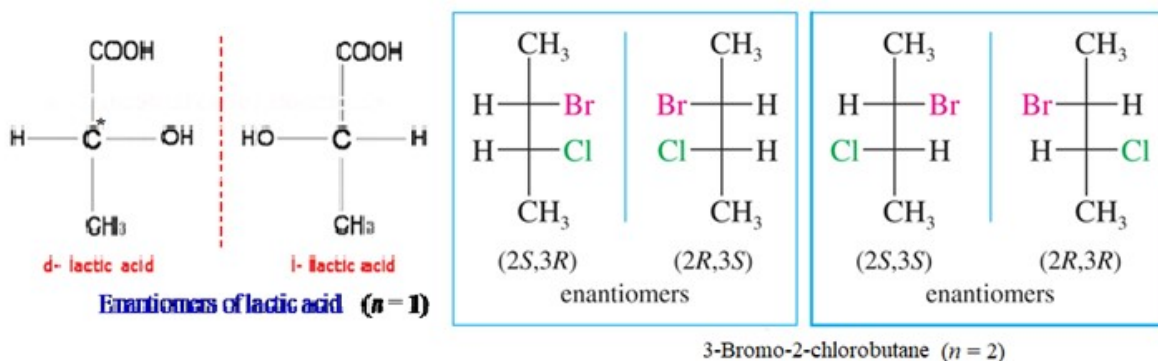
The number of meso-forms, $m = 0$

Total number of optical (stereo) isomers $= a + m = 2^n$

Example: Lactic acid contains one asymmetric carbon centre ($n = 1$).

$$a = 2^1 = 2, \quad m = 0, \quad \text{racemic mixture, } r = 2/2 = 1$$

$$\text{total optical isomers} = 2 + 0 = 2.$$



(ii) When the molecule can be divided into equal halves, *i.e.*, **the molecule has symmetry** and the number (n) of asymmetric carbon atoms is **even**, then

The number of *d*- and *l*- (optical isomers) forms, $a = 2^{(n-1)}$

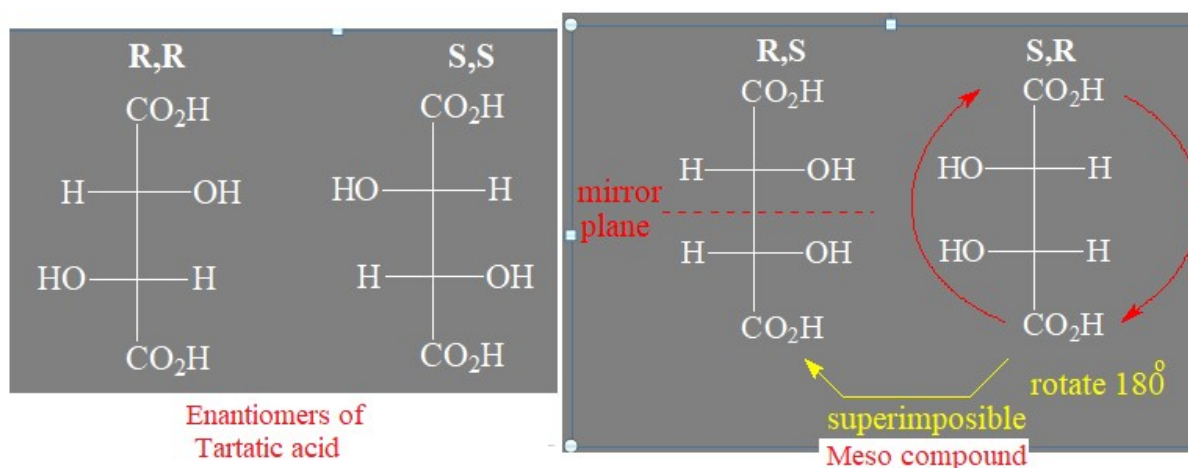
The number of meso-forms, $m = 2^{(n/2)-1}$

Total number of optical (stereo) isomers = $a + m = 2^{(n-1)} + 2^{(n/2)-1}$

Example: Tartaric acid contain two asymmetric carbon centre ($n=2$)

$a = 2^{(n-1)} = 2^{(2-1)} = 2^1 = 2$; Meso forms $m = 2^{(n/2)-1} = 2^{(2/2)-1} = 2^0 = 1$.

total optical isomers = $2 + 1 = 3$.



(iii) When the molecule can be divided into equal halves (**symmetrical**) and the number (n) of asymmetric carbon atoms is **odd**, then

The number of *d*- and *l*- (optical isomers) forms, $a = 2^{(n-1)} - 2^{(n-1)/2}$

The number of meso-forms, $m = 2^{(n-1)/2}$

Total number of optical (stereo) isomers = $a + m = 2^{(n-1)}$

Example : $\text{CH}_2\text{OH}-\overset{*}{\text{CHOH}}-\overset{*}{\text{CHOH}}-\overset{*}{\text{CHOH}}-\text{CH}_2\text{OH}$ ($n = 3$)

, $a = 2^{(n-1)} - 2^{(n-1)/2} = 2^2 - 2^1 = 2$. $m = 2^{(n-1)/2} = m = 2^{(3-1)/2} = 2^1 = 2$

Total optical isomers = $2 + 2 = 4$.

Chapter 6.

Polymer chemistry

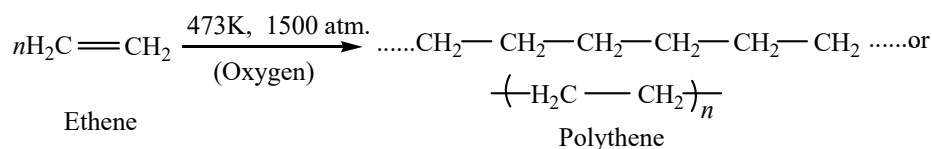
What is a Polymer?

The word **polymer** is derived from the Greek word **Poly** meaning many and **meros** meaning parts. **Polymers** are high molecular mass compounds formed by polymerization of large number of simple repeating chemical units. The simple repeating low molecular mass chemical units are called **monomers** (mono = one). A polymer may be defined as “a number of repeating chemical units held together by covalent bonds.” The process of joining of a large number of simple molecules (monomers) in a regular fashion to make high molecular mass polymer through covalent bonds is termed as **polymerization**, Polymers are also called macromolecules (macro = large), which have very high molecular masses.

What is a Plastic?: A polymer that can be molded when hot and regains its shape when cooled. Smaller species formed by the process of polymerisation of a monomer are referred to **dimer, trimer, tetramer, pentamer** **polymer**, etc depending on the number of monomer units.

Monomer		A
Dimer	Two monomer units	A—A
Trimer	Three monomer units	A—A—A
Tetramer	Four monomer units	A—A—A—A
Pentamer	Five monomer units	A—A—A—A—A
Polymer	Large no. of monomer	(A) _n

Example: High molecular mass (about 20,000) polyethylene can be obtained by heating ethylene under pressure with oxygen. This compound is made up of many ethylene units (monomers) and hence is called polyethylene.



Where **n** is called degree of polymerization.

Homopolymers and Co-Polymers: Polymers are divided into two categories depending upon the nature of the repeating structural units.

(i) Homopolymers (ii) Co-polymers

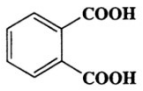
A **polymer** which is made by polymerization of one type of monomer molecule is known as a **homopolymer**. On the other hand, a polymer made from more than one type of monomer molecule is referred to as a **co-polymer**. Few examples of common homopolymers and co-polymers are given in the following tables:

Table-1 HOMOPOLYMERS

S. No.	Name of the homopolymer	Monomer	Uses
1.	Polyethylene	$\text{H}_2\text{C} = \text{CH}_2$ Ethylene	In the manufacture of pipes, toys, bags, wire insulators, squeeze. bottles, etc.
2.	Polypropylene	$\text{H}_2\text{C} = \text{CH}-\text{CH}_3$ Propylene	In the manufacture of toys, bags, carpets, films, bottles, etc.
3	Polyvinyl chloride (PVC)	$\text{H}_2\text{C} = \text{CH}-\text{Cl}$ Vinyl chloride	In the manufacture of sheets, water pipes, hoses, hand bags, plumbing fitting, shower curtains, coats, etc.
4.	Polystyrene	$\text{H}_2\text{C} = \text{CH}-\text{C}_6\text{H}_5$ Styrene	In the manufacture of combs, toys radio and television cabinets, packaging material for shock absorbance'
5.	Polyacrylonitrile (PAN) or Orlon	$\text{H}_2\text{C} = \text{CH}-\text{CN}$ Acrylonitrile.	In the manufacture of orlon (fibre), acrilon films and a substitute for wool, for making cloth and blankets.
6.	Teflon (Polytetrafluoroethene)	$\text{F}_2\text{C} = \text{CF}_2$ Tetrafluoro ethylene	In the manufacture of insulators, gaskets, non-stick cookwares, etc.
7.	Buna rubber	$\text{H}_2\text{C} = \text{CH}-\text{HC} = \text{CH}_2$ Buta-1,3-diene	In the manufacture of tyres, hoses, etc.,
8.	Polyvinyl acetate	$\text{H}_2\text{C} = \text{CHOCCH}_3$ Vinyl acetate	In the manufacture of latex paint.

Table-2. CO-POLYMERS

S. No	Name of the Co-polymer	Monomer	Uses
1.	Synthetic rubber or Styrene butadiene rubber (SBR) or (Buna-S)	$\text{H}_2\text{C} = \text{CH}-\text{C}_6\text{H}_5$ Styrene + $\text{H}_2\text{C} = \text{CH}-\text{HC} = \text{CH}_2$ Buta-1,3-diene	In the manufacture of tyres, belting, hoses and rubber soles.
2	Dacron or Terylene (Polyester)	$\text{HO}-\text{H}_2\text{C}-\text{CH}_2-\text{OH}$ Ethylene glycol +	In the manufacture of fabrics and magnetic recording tapes.

3.	Glyptal (Polyester)	$\text{H}_3\text{COOC}-\text{C}_6\text{H}_4-\text{COOCH}_3$ Dimethyl terephthalate $\text{HO}-\text{H}_2\text{C}-\text{CH}_2-\text{OH}$ Ethylene glycol +  Phthalic acid	In the manufacture of paints and lacquers.
4.	Nylon-6,6 (Polyamide)	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$ Adipic acid + $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ Hexamethylenediamine	In the manufacture of fabrics, tyre cords, ropes, carpets, etc.,
5.	Bakelite (Formaldehyde resin)	$\text{HCHO} + \text{C}_6\text{H}_5-\text{OH}$ Formaldehyde + Phenol	In the manufacture of electrical goods, phonograph records, insulators, fountain pen barrels, combs, etc.
6.	Melamine-formaldehyde resin or Melmac	HCHO Formaldehyde + Melamine	In the manufacture of plastic crockery.
7.	Polyurethane	$\text{HO}-\text{H}_2\text{C}-\text{CH}_2-\text{OH}$ Ethylene glycol + $\text{OCN}-\text{HC}=\text{CH}-\text{NCO}$ Ethylene di-isocyanate	In the manufacture of fibres, paints and heat insulators., etc.,

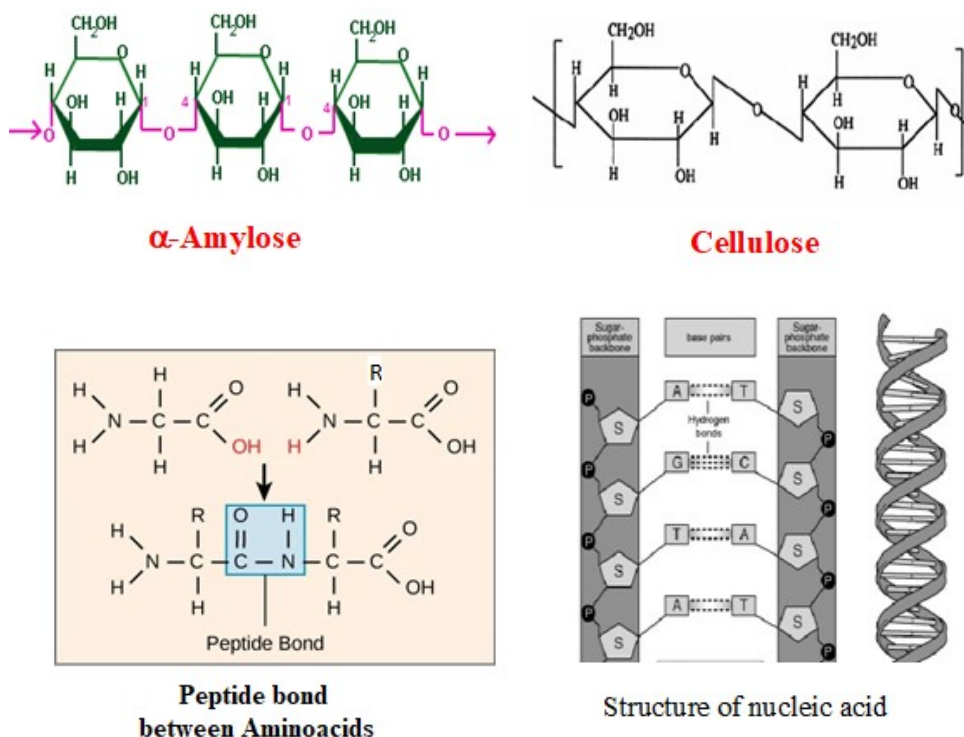
Classification of Polymers: Polymers may be classified in a number of ways as described below.

1. Classification based upon source or origin,
2. Classification based upon synthesis,
3. Classification based upon mechanism,
4. Classification based upon structure,
5. Classification based upon molecular forces.

1. Classification based upon source or origin: On the basis of their origin, polymers may be classified into three groups:

(i) Natural polymers (iii) Synthetic polymers

(i) Natural polymers: These are substances of natural origin, *i.e.*, these are found in nature mainly in plants and animals. The well known polymers are proteins (polymers of aminoacids), polysaccharides (polymers of monosaccharides) and rubber (polymer of isoprene *i.e.*, 2-methylbuta-1,3-diene). Silk, wool, starch, cellulose, enzymes, natural rubber, nucleic acids (RNA and DNA) etc., are the examples of natural polymers.

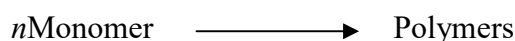


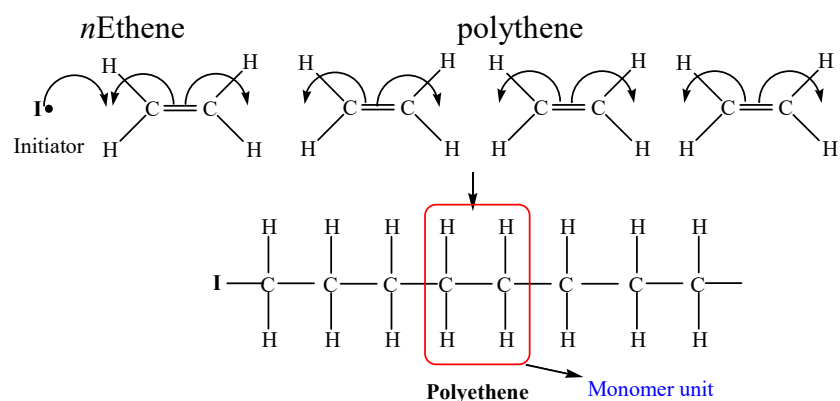
(ii) Synthetic polymers: These are man made polymers, *i.e.*, polymers synthesized in laboratory. A list of synthetic polymers are given in tables 1 & 2.

2. Classification based upon synthesis: On the basis of mode of synthesis, polymers are classified into four types:

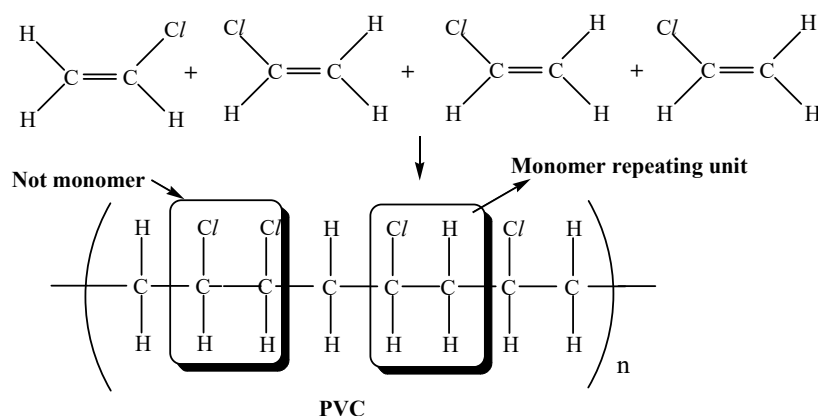
- (i) Addition polymerization (or Chain growth polymers)
- (ii) Condensation polymers (or Step-growth polymers)
- (iii) Co-Ordination polymerisation.
- (iv) Ring-Opening polymerisation (ROP)

(i) Addition polymerization (or Chain growth polymers): These are polymers formed by the addition of molecules of the monomers to form macromolecules without elimination of anything. The addition polymers are formed by monomers which are unsaturated compounds, *e.g.*, ethene and its derivatives. The key feature of addition polymerization is that monomers add to one another in such a way that the polymeric product contains all the atoms of the starting monomers. Ethene, vinyl chloride and vinyl cyanide are some of the examples which undergo addition polymerization.





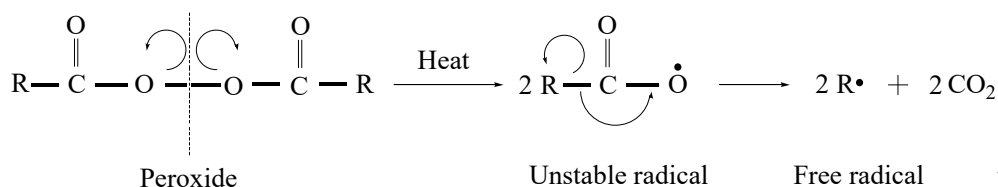
Polymerization of vinylchloride gives polyvinylchloride (PVC)



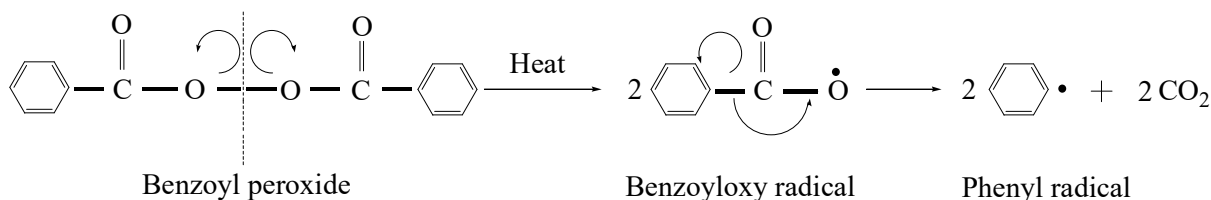
(i) Chain growth addition polymerization: It involves a series of reactions each of which consumes a reactive particle and produces another similar one. The chain growth polymerisation initiate either by **free radicals** or **ions (cations or anions)** to which monomers get added by a chain reaction. Molecular weight increases by successively adding monomers to a reactive polymer chain end. The polymers thus, formed are known as chain growth polymers. It is an important reaction of alkenes and conjugated dienes. Polythene, polypropylene, teflon (PTFE), polyvinyl chloride (PVC), polystyrene, are some examples of chain growth addition polymers.

(a) Free radicle mechanism: Free radical polymerization is initiated by organic peroxide or other reagents which decompose to give radicals. The reaction involve the following steps:

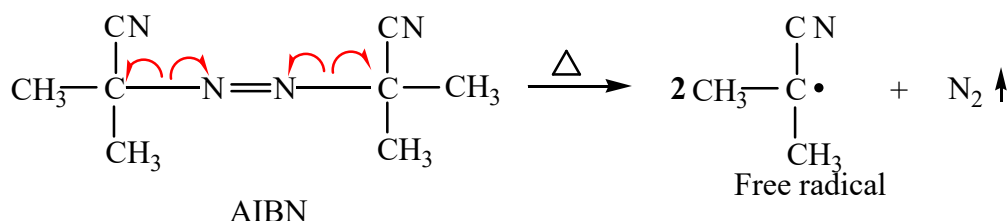
(i) Chain initiation: Organic peroxides undergo homolytic fission in the presence of light or heat to form free radicles. The important peroxide which generate free radicals are alkyl peroxides, bezoyl peroxide and azobisisobutyronitrile (AIBN).



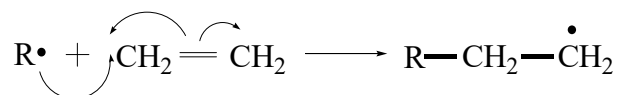
In case of benzoyl peroxide, the free radical formed is benzoyloxy radical and then phenyl free radical.



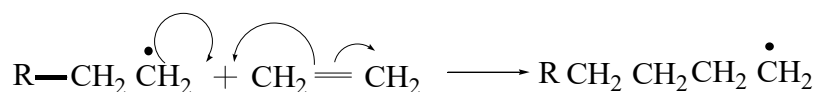
Azobisisobutyronitrile (AIBN) is another common reagent for the initiation of radical reactions. AIBN decomposes at temperatures above 60°C to form isobutyronitrile radicals, which initiate radical polymerisation.



(ii) Chain propagation: Free radicals add to an alkene (ethene) molecule to form a new alkyl radical.

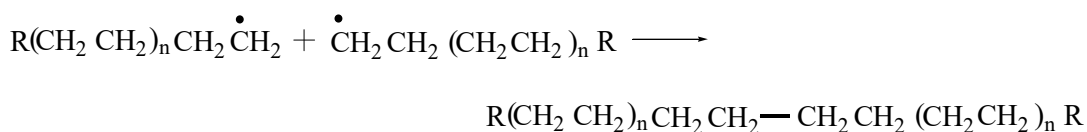


The alkyl free radical formed attacks another alkene molecule and the process continues in building a long chain.

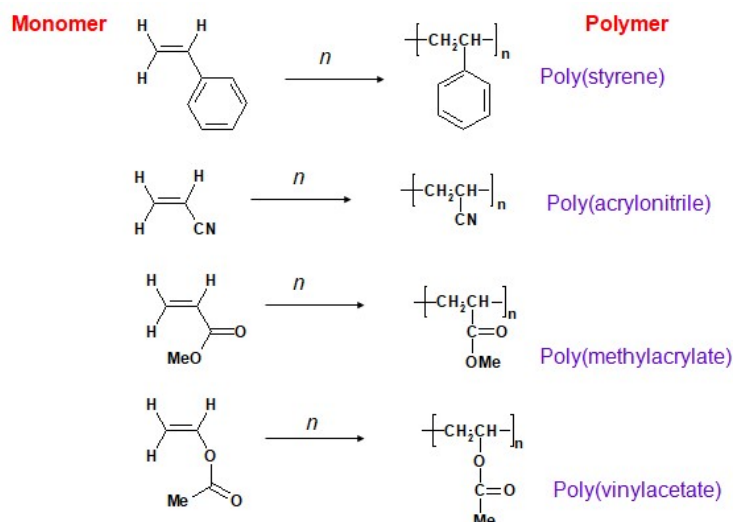


(iii) Chain termination: The chain reaction comes to stop when two radical chains combine (coupling of two radical chains) or chain termination occurs by disproportionation.

(a) Coupling : Coupling of two polymer radical chains stops the reaction.

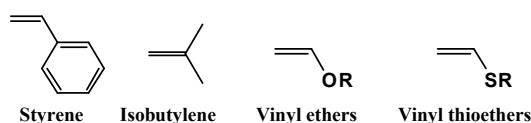


Examples of polymers prepared by radical polymerisation are:



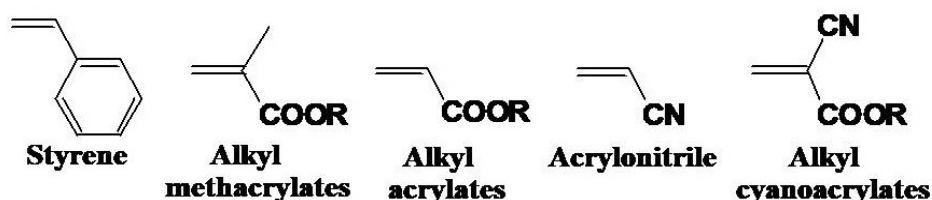
(b) Cationic addition polymerizations mechanism: It is initiated by use of strong Lewis acids such as H_2SO_4 , HF , AlCl_3 , SnCl_4 , TiCl_4 or BF_3 in H_2O . The mechanism of cationic addition polymerization is best illustrated by the polymerization of isobutylene using BF_3 as a catalyst and water as a co-catalyst.

Cationic polymerizations are most common with monomers with **electron-donating** groups.



Some common examples of alkenes (monomers) undergoing cationic polymerization are ethylene, propylene, isobutylene, styrene, vinyl ethers and butadienes, etc.

(C) Anionic addition polymerisation: It is initiated by strong bases such as butyl lithium $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$, sodamide (NaNH_2), Grignard reagents (RMgX). Monomers having electron withdrawing groups such as cyano ($-\text{CN}$), esters ($-\text{COOR}$), nitro ($-\text{NO}_2$) etc increase the rate of anionic addition polymerization. Because these groups decrease the electron density across double bond and facilitate the attack of nucleophile.

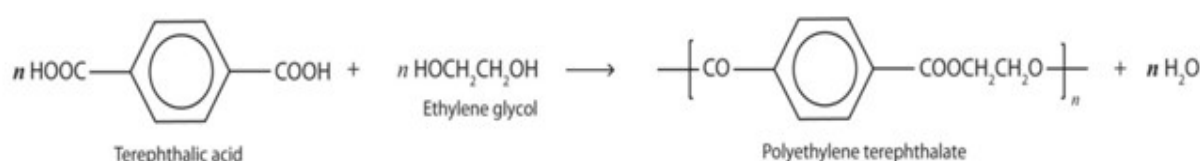


(ii) Condensation polymers (or Step-growth polymers): Condensation polymers are formed by the condensation of monomers with the elimination of simple molecules such as water, alcohol, NH_3 , HCl , CO_2 , etc. Condensation polymers are generally formed by reaction between polyfunctional monomers. Proteins, starch, cellulose etc., are the examples of natural condensation polymers. Amongst the synthetic polymers, two main types of condensation

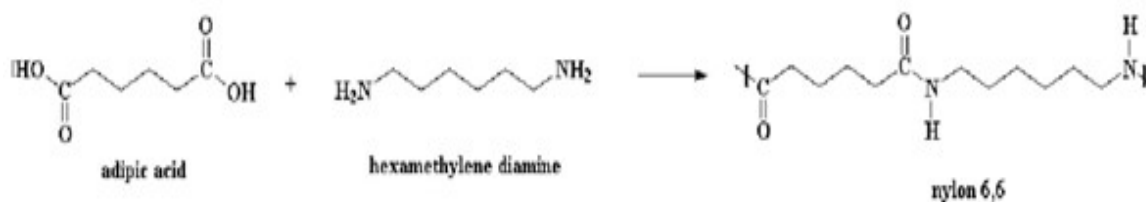
polymers are: polyesters and polyamides. These are also called **step-growth polymers** since they are formed as a result of stepwise reaction.

Some important condensation or step-growth polymers are tereylene (Ethylene glycol + Dimethyl terephthalate), Nylon-66 (Adipic acid + Hexa methylene diamine), Bakelite (phenol + formaldehyde), Melamine-formaldehyde resin), Polyurethane (Ethylene glycol + Ethylene di-isocyanate), alkyl resin (Ethylene glycol + Phthalic acid), silicones, etc.

Polyester: Polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:



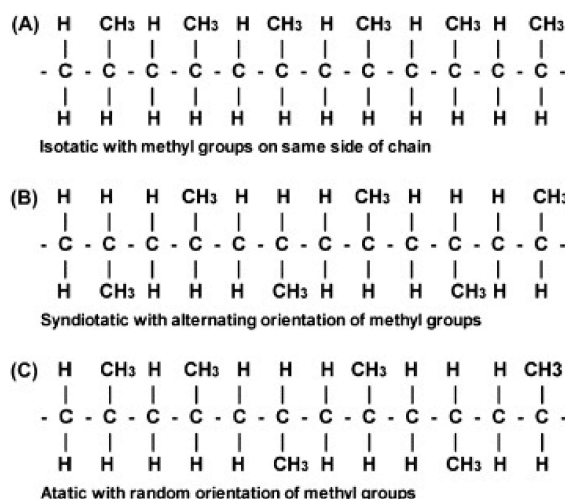
Polyamide: Nylon-66: This polymer is formed by condensation of adipic acid with hexa methylene diamine. It has 12 carbon atoms in its polymer structure, 6 from each of the two monomers; Hexamethylene diamine and adipic acid. Hence it is referred to as Nylon 6,6.



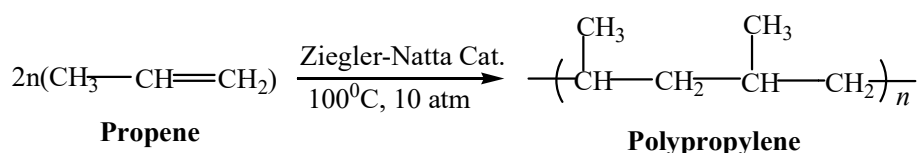
(iii) Coordination Polymerization. Before the development of Ziegler – Natta catalyst nearly all addition polymerisation reactions, are carried out by free radical polymerization. The reactions are conducted at high temperature and pressure. As a result of this, highly branched polymers with irregularly oriented bulky side groups without any stereochemistry are produced. Such type of polymers are called **atactic** polymers. These polymers are unable to arrange each other in regular order because of irregularly oriented bulky groups (due to steric reasons). Consequently, they have low crystallinity, amorphous in nature, low melting and low tensile strength.

In contrast, polymerization by the use of Ziegler – Natta catalyst proceeds under mild conditions and produces unbranched, highly compact (ordered) and stereoregular polymers called **isotactic** polymers. The reaction proceeds via **Coordination polymerization**.

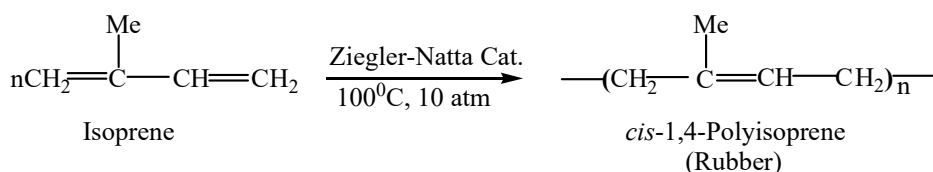
Ziegler – Natta catalysts are a combination of organometallic which consist of a complex of triethyl aluminium, $(\text{CH}_3\text{CH}_2)_3\text{Al}$ and transition metal chloride (TiCl_4). The catalyst catalyses polymerisation of alkenes at low temperature and pressure. The reaction proceeds via **coordination polymerization**. The three types of polypropylene are shown below.



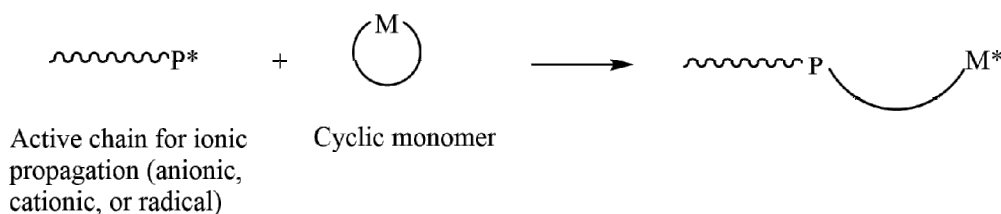
Example 1. Polymerisation of propylene using Ziegler – Natta catalyst give high density polypropylene (HDPE).



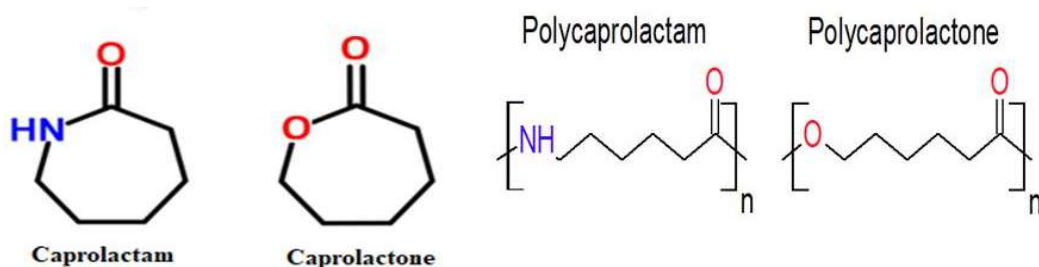
Example 2. Isoprene was polymerized by Ziegler catalyst to a substance identical with natural rubber.



(iv) Ring–Opening polymerization (ROP): A reaction in which a cyclic monomer can react by opening its ring system and form a longer polymeric chain is called Ring-opening polymerization. The reaction is initiated by radicals or anionic or cationic method.

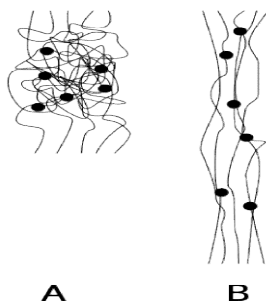


A ROP is another form of chain-growth polymerization in which the terminal end group of a polymer chain acts as a reactive center. Typical cyclic monomers that can be polymerized via ROP are di-functional monomers that carry two different reactive groups like one amine or alcohol and one carboxylic acid that have undergone a cyclization reaction. Two examples are caprolactam and caprolactone:



5, Classification of polymers based upon molecular forces: Polymers have been classified into four types on the basis of the magnitude of intermolecular forces present in them.

(i) Elastomers: A polymer with both viscous and elastic properties is known as an **elastomer**. Elastomers have **very weak intermolecular forces** of attraction between the polymer chains. The weak forces permit the polymer to be stretched out about 10 times their normal length. Few chemical bonds are introduced between the randomly coiled polymer chains which act as cross-links. These cross-links help the polymer to come to its original position after the force is released. Elastomers thus, possess elastic character. Vulcanized rubber is a very important example of an elastomer and other examples are natural rubber, Buna-S or SBR (a copolymer of butadiene 75% and styrene 25%).



(A) is an unstressed polymer; (B) is the same polymer under stress. When the stress is removed, it will return to the A configuration. (The dots represent cross-links)

ii) Fibres: These are the polymers which have quite **strong intermolecular forces** such as hydrogen bonding. These polymers can be used for making fibre as their molecules are long and thread like. Nylon-6,6 polymer, terylene or Dacron and polyacrylonitrile (orlon), etc., are some important examples of this type.

(iii) Thermoplastics: These are the polymers in which the intermolecular forces of attraction are neither very strong nor very weak and there are no cross-links between the chains. These can be easily moulded by heating *i.e.*, a thermoplastic polymer is one which softens on heating and becomes hard on cooling. Because their bonds are weak, thermoplastic polymers readily

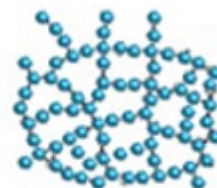
soften when heated, and can be moulded into a wide range of shapes. Thus, thermoplastic polymers are **highly recyclable**. Polyethylene, polypropylene, polystyrene, PVC, and Teflon are the examples of this thermoplastics. In addition to this, some adhesives, including acrylates, cyanoacrylates and epoxy are thermoplastic polymers



Thermoplastic



Elastomer



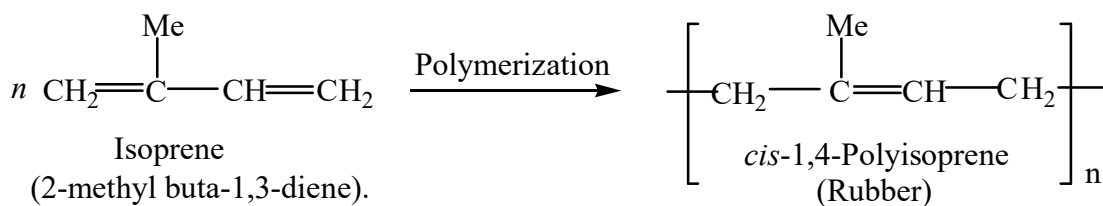
Thermoset

Difference between thermoplastic and thermosetting polymers

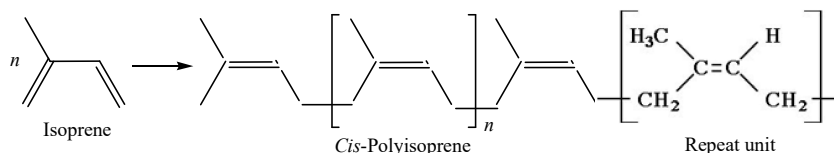
S. No	Thermoplastic polymers	Thermosetting polymers
1.	These soften heating and regain same shape on cooling	These do not soften on heating but rather become hard. In case prolonged heating is done, these start burning.
2.	These can be remoulded, recast and reshaped and recycled.	These cannot be remoulded, recast, reshaped and recycled
3.	These are ductile and soluble in some organic solvents.	These are more brittle and insoluble in organic solvents.
4.	These are formed by addition polymerization.	These are formed by condensation polymerization.
5.	These have usually linear structures.	These are branched or cross-linked polymers.
6.	Examples: Polyethylene, PVC, Teflon, Nylon, etc.	Examples: Bakelite, Urea-Formaldehyde, Resin, Terylene, etc.

iv) Thermosetting polymers: These are polymers in which extensive cross-links are formed between polymer chains on heating. A thermosetting polymer becomes hard on heating. Such polymers are prepared in two steps. The first step is the formation of long chain molecules which are capable of further reaction with each other. The second step is the application of heat which causes a reaction to occur between the chains, thus, producing a complex cross-linked polymer. Bakelite, vulcanised rubber are examples of thermosetting polymer

Phenol- formaldehyde resin (Bakelite): It is obtained by a step-growth polymerization of phenol and formaldehyde in the presence of basic catalyst. The reaction involves the formation of methylene bridges in *ortho*, *para* or both *ortho* and *para* positions. The initial product is a linear polymer called **Novolac** which is used in paints

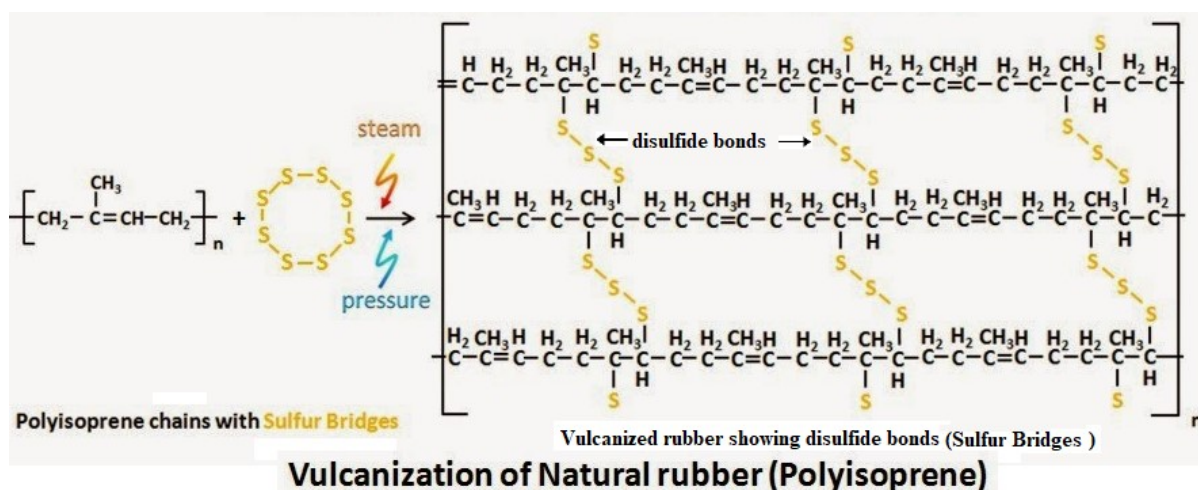


- Natural rubber is a linear 1,4-addition polymer of isoprene. On the average, it contains 5000 isoprene units. **Natural rubber is *cis* 1,4-polyisopren** and has only *cis* configuration about the double bond as shown below:



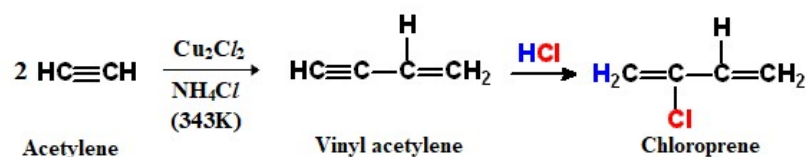
- There are weak van der Waals' forces and therefore, it is elastic and non-crystalline. **Gutta-Percha** (*getah* means gum and *percha* means tree) is naturally occurring isomer of rubber in which all the double bonds are ***trans***. So, **Gutta-Percha is all *trans*-polyisoprene**. It is non-elastic and non-crystalline

Vulcanization of Rubber: Natural rubber is soft and sticky and therefore, in order to give strength and elasticity natural rubber is vulcanized. Vulcanization is a process of treating natural rubber with sulphur or hydrogen sulphide, or some compounds of sulphur (like SF₆) under heat as to modify its properties, i.e., to render it non-plastic and to give greater elasticity and ductility. The sulphur reacts with the polymer molecules forming a cross-linked network. This cross-linking gives mechanical strength to the rubber.

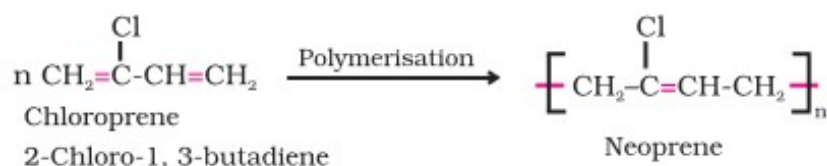


Synthetic Rubber: They are more flexible, tougher and durable than natural rubber. Neoprene, Buna-S and *Cis*-polybuta-1,3-diene are some examples of synthetic rubber.

(a) Neoprene: It was the first synthetic rubber manufactured on large scale. It is also called **dieprene**. Its monomer, chloroprene (2-chlorobuta-1,3-diene) is prepared from acetylene.



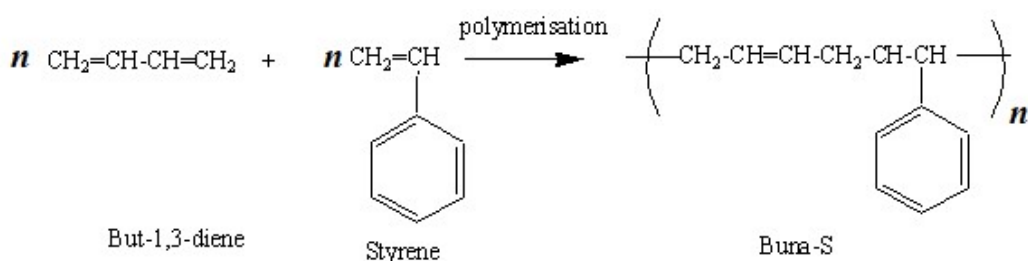
Chloroprene undergoes free radical polymerization to form neoprene (polychloroprene). It polymerizes very rapidly (700 times faster than isoprene) and the reaction occurs by 1,4-addition of one chloroprene molecule to the other.



Many of the properties of neoprene are similar to natural rubber, but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone, and heat. It is non-inflammable.

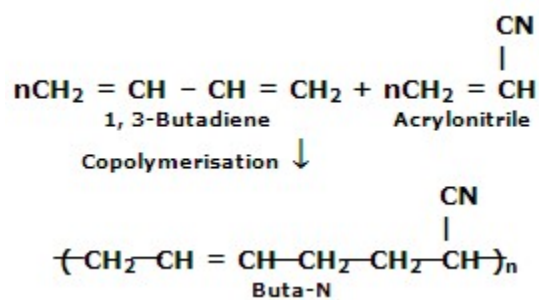
It is therefore, used for making automobile and refrigerator parts, petrol and oil containers, insulation of electrical wires and conveyor belts.

(b) Buna-S (SBR – Styrene butadiene rubber): Buna-S rubber is a co-polymer of three moles of butadiene and one mole of styrene. In Buna-S, ‘Bu’ stands for butadiene, ‘na’ for symbol of sodium (Na) which is polymerizing agent and ‘S’ stands for styrene. It is an elastomer.



Buna-S is generally compounded with carbon black and vulcanized with sulphur. It is extremely resistant to wear and tear and therefore, used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical co-polymerization of its monomers.

(c) Buna-N: It is obtained by co-polymerization of butadiene and acrylonitrile,



It is resistant to the reaction of petrol, lubricating oil and organic solvents. It is utilized in making oil seals, tank lining etc.