AROMATIC COMPOUNDS

There are a large number of compounds isolated from natural sources, which have properties quite different from that of aliphatic compounds. They are highly unsaturated and yet very stable. They possess a pleasant odour and therefore called “Aromatic Compounds”. (German, aroma means sweet smelling). Nowadays, all carbocyclic compounds, which contain a benzene ring or nonbenzenoid compounds that show aromatic behavior, have also termed as aromatic compounds.

Analytic studies of aromatic compounds showed that they are derivatives of a hydrocarbon which possess a ring structure. This ring hydrocarbon, known as benzene, possessed a six carbon ring in which the carbon atoms where bonded to each other in a peculiar fashion.

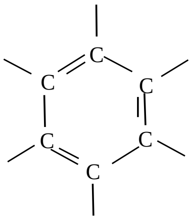


figure : Structural unit present in aromatic compounds

The presence of this structure shows characteristic aromatic properties.

NOMENCLATURE OF AROMATIC COMPOUNDS

Aromatic Compounds have been divided into a number of classes. These include hydrocarbons, halogen compounds nitro compounds, amino compounds, sulphonic acids, hydroxy compounds, aldehydes, ketones, carboxylic acids,etc. All these are assigned names as derivatives of substitution products of benzene, or any other parent hydrocarbon. The parent hydrocarbon benzene,(C_6H_6), has the valence bond structure as shown in Figure.

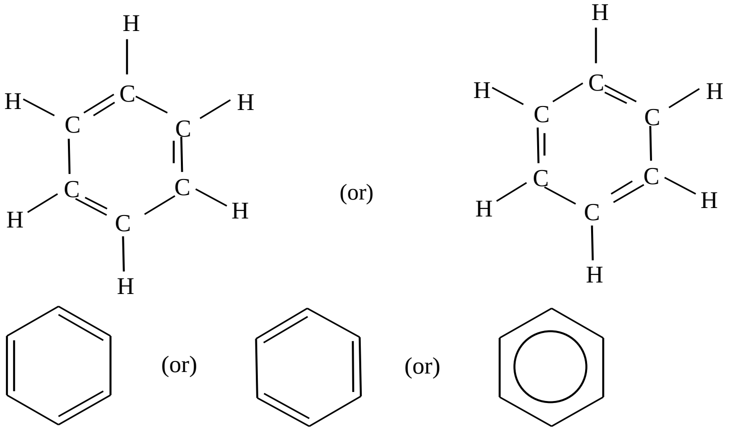
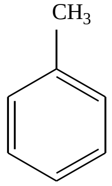


fig : Structural Formula of benzene and its symbolic representation.

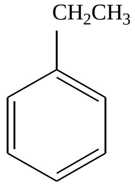
It is always understood that the molecule of benzene is made of six-carbon atoms ring having three double bonds in alternate positions, each carbon carrying one hydrogen atom at each corner of the hexagon.

Naming Benzene Derivatives

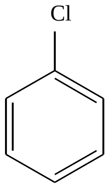
Monosubstituted benzenes are named in a straight forward manner by prefixing the name of the substituent group to 'benzene'. Thus,



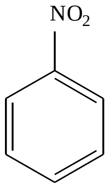
Methyl benzene(Toluene)



Ethyl benzene

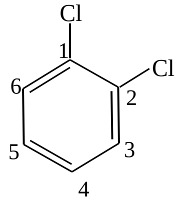


Chloro benzene

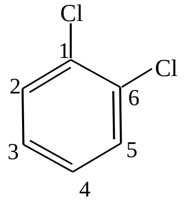


Nitro benzene

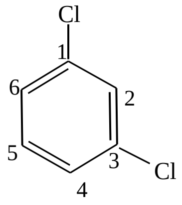
While naming di- and tri-substituted benzenes, the positions are indicated by numbers. One of the carbons carrying a substituent is numbered 1 and the relative positions of the other substituents are denoted by numbering the ring from 2 to 5 either clockwise or anticlockwise whichever gives lower numbers to the substituents. Thus,



1,2-Dichlorobenzene
(clockwise counting)
Right

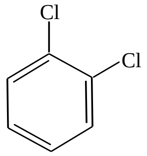


1,6-Dichlorobenzene
(anticlockwise counting)
Wrong

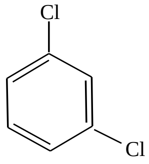


1,3-Dichlorobenzene
Right

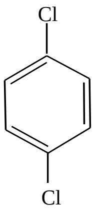
There are only three possible distribution products. They are 1,2-,1,3- and 1,4-distribution products which are often called ORTHO (o-), META (m-) and PARA (p-) derivatives.



1,2-Dichlorobenzene
(O-Dichlorobenzene)

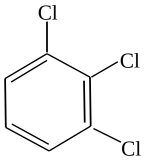


1,3-Dichlorobenzene
(m-Dichlorobenzene)

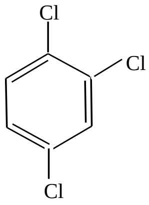


1,3-Dichlorobenzene
(p-Dichlorobenzene)

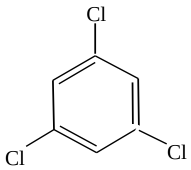
Similarly, the three trichlorobenzenes are named as.



1,2,3-Trichlorobenzene



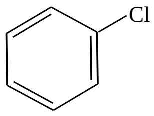
1,2,4-Trichlorobenzene



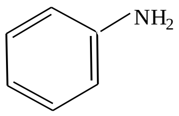
1,3,5-Trichlorobenzene

Naming Monosubstitution Derivatives of Benzenes

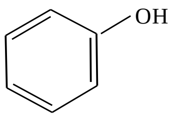
Some monosubstitution derivatives of benzene representing various classes of compounds are listed below.



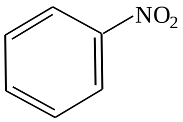
Cholorobenzene
(Phenyl chloride)



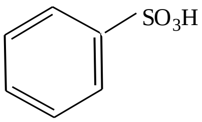
Aminobenzene
(Phenyl amine)
(Aniline)



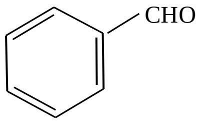
Hydroxybenzene
(Phenyl hydroxide)
(Phenol)



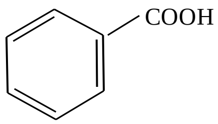
Nitrobenzene



Benzene sulphonic acid



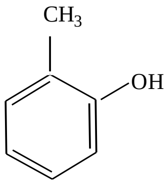
Benzaldehyde



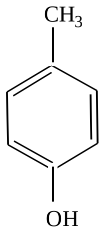
Benzoic acid

Naming Monosubstitution Dervatives of Toluene

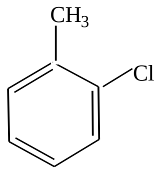
The Monosubstitution Derivatives of Toluene are named by giving the name of tolyl group before the name of the functional group. Thus,



o-Tolyl hydroxide
(2-Hydroxytoluene)
(o-Cresol)



p-Tolyl hydroxide
(4-Hydroxytoluene)
(p-Cresol)



o-Tolyl chloride
(2-Chlorotoluene)

Di-, tri- and higher substitution products are named by assigning positions to substituents in accordance with IUPAC rules.

SOURCES OF AROMATIC COMPOUNDS

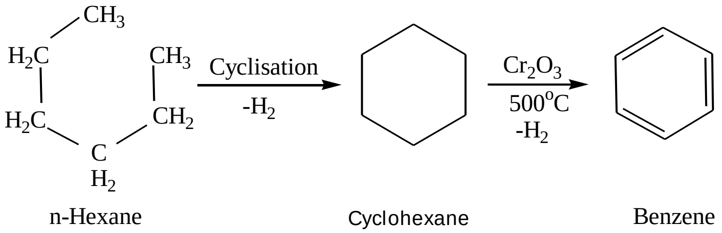
Aromatic compounds occur in both plant and animals. Coal and petroleum are produced by the action of heat and pressure on buried wood and animals beneath earth's surface. Coal and petroleum are the sources of benzene and other aromatic compounds. Many of the aromatic compounds, which were earlier obtained from coal, are now being synthetically produced from petroleum fractions.

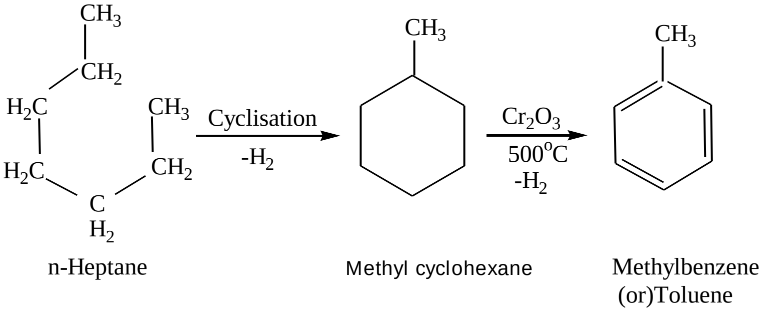
Aromatic from Petroleum

Petroleum contains n-hexane and its related higher homologues. Aromatic compounds are synthetically obtained from open-chain hydrocarbons derived from petroleum.

(a) Aromatization

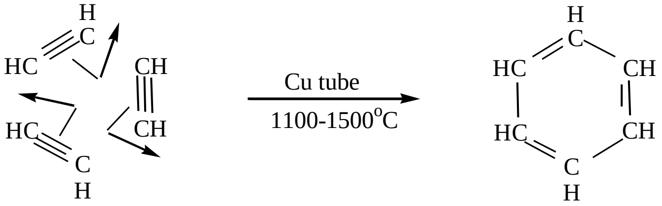
When long chain hydrocarbons are heated in the presence of oxides of Cr, Al and V, aromatic hydrocarbons are formed. The process involves cyclisation and dehydrogenation. Thus,





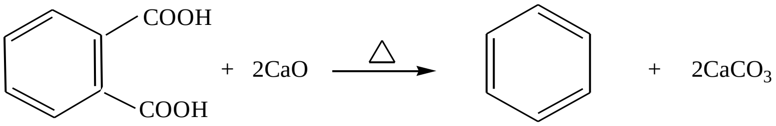
(b) Polymerisation

Acetylene, an important product, obtained from cracking of petroleum when passed through red hot copper tube polymerizes to yield benzene.



Laboratory Preparations of Benzene

1. $C_6 H_5COONa \quad + \quad NaOH(CaO) \xrightarrow{\Delta} C_6H_6 \quad + \quad Na_2CO_3$
2. By heating phthalic acid with calcium oxide



Physical Properties of Benzene

Benzene is a colourless liquid with a distinct gasoline like odour, at boiling $80^{o}C$. It is insoluble in water but it soluble in alcohol and ether. It is highly inflammable and burns with a smoky flame.

Benzene is toxic when taken internally contact with skin harmful continue inhalation of benzene vapour decreases red and white blood cell count. Benzene is considered to be mildly carcinogenic and care must be taken with its use.

Chemical properties of Benzene

1. Addition of hydrogen

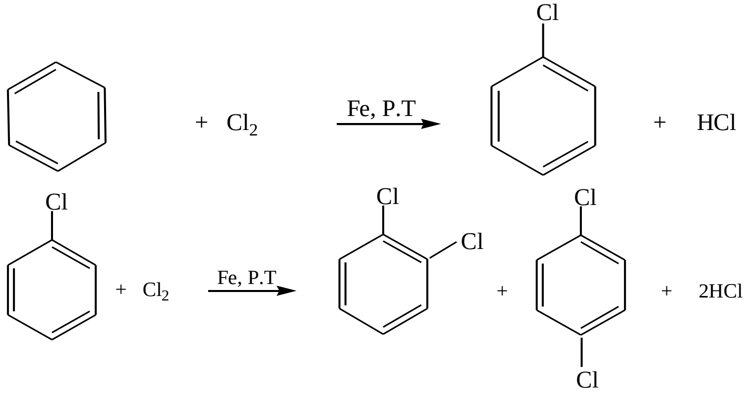
Although ordinary alkene and diene are readily reduced with H_2 in the presence of catalyst, benzene and other aromatic compounds usually undergo this reaction with greater difficulties.

$$C_6H_6 \quad + \quad H_2 \quad \xrightarrow{200^oC} \quad \underset{\text{cyclohexane}}{C_6H_{12}}$$

2. Substitution reactions

Halogenation

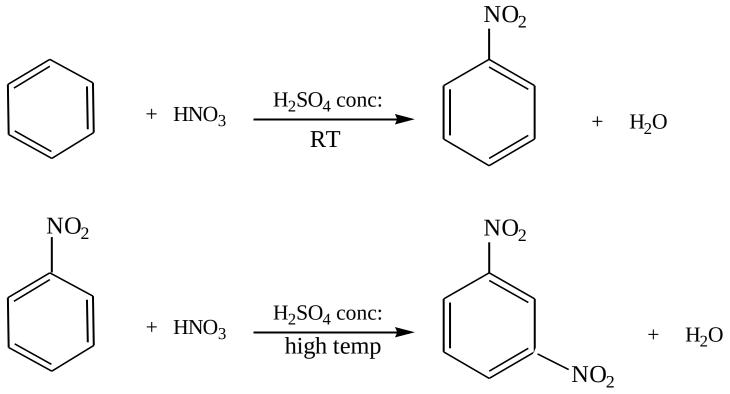
On the other hand chlorine substitution on benzene occur readily to give mainly chlorobenzene. The reaction is catalyzed by iron.



The reaction rate of benzene and halogen is faster than that of chloro benzene and chlorine or bromo benzene and bromine.

3. Nitration

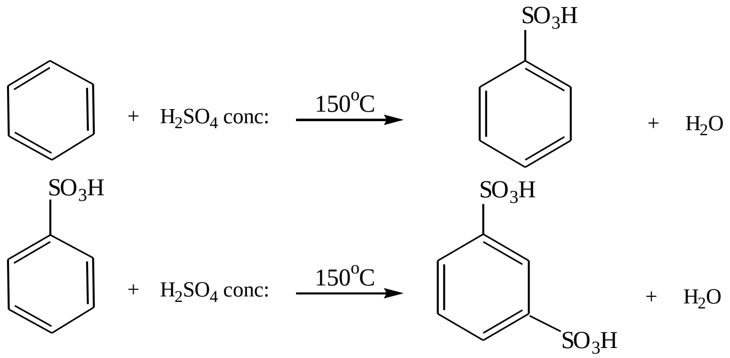
If benzene is treated with a solution containing both conc: H_2SO_4 and conc: HNO_3, substitution being even at RT. A nitro group from nitric acid is substituted onto the ring. This process is termed nitration.



H_2SO_4 is used as catalyst in this reaction. No more nitration will occur. Nitration is an important reaction in the aromatic series. Subsequently reduction of the $-NO_2$ group to $-NH_2$ group can be readily carried out and a great variety of others compounds can be derived from the amine.

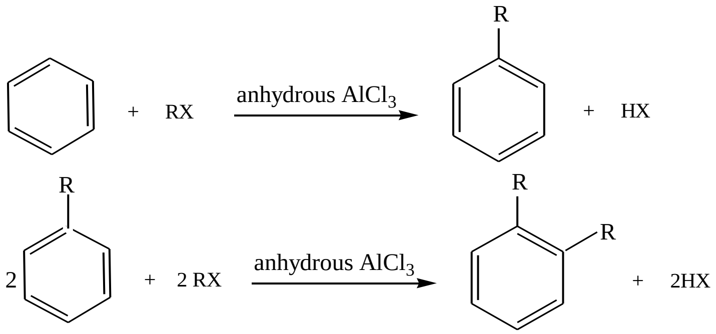
4. Sulphonation

Introducing of $-SO_3H$ group into benzene molecule is known as sulphonation. Conc: H_2SO_4 does not react with benzene at room temp. In fact the two liquids are immiscible. However, if the mixture is heated to moderate temp. (150°C), sulphonation occurs.

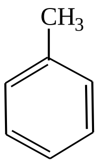


5. Friedel and Crafts alkylation

It is a method of preparing alkyl substituted aromatic compounds. Benzene is treated with alkyl halide in the presence of a traces of Lewis acid such as anhydrous $AlCl_3$, alkylation will occur.



Toluene



$(C_6H_5CH_3)$

Preparations

1. **Wurtz-fitting reaction**

$$3C_6H_5Br \;+\; 3CH_3I \;+\; 6Na \xrightarrow{\Delta} C_6H_5CH_{3\,(l)} + 3NaI + 3NaBr + C_2H_6$$

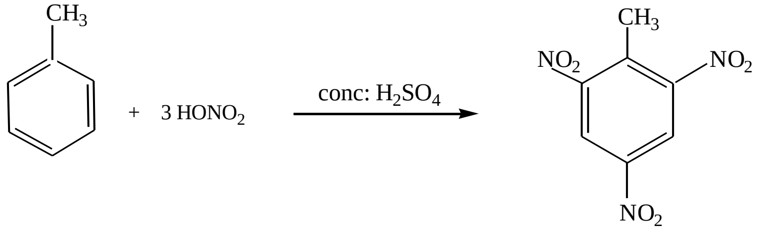
$$C_6H_5 - C_6H_5$$

2. **Friedel and Craft alkylation**

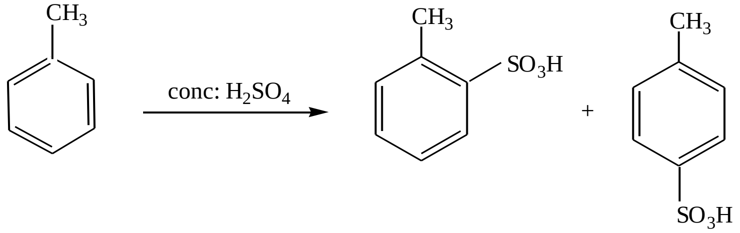
$$C_6H_6 \;+\; CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} C_6H_5CH_3 \;+\; HCl$$

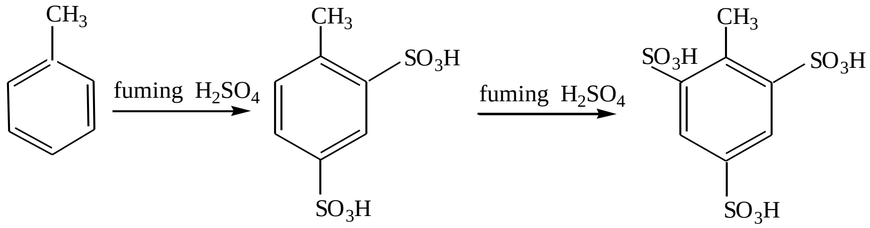
Chemical properties

1. **Nitration**



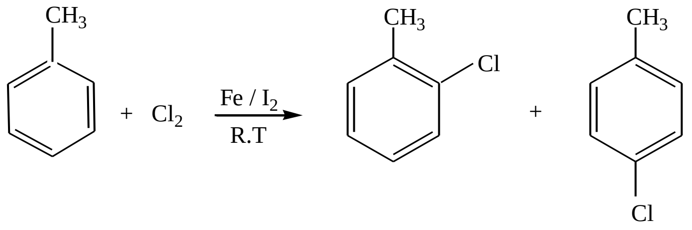
2. **Sulphonation**





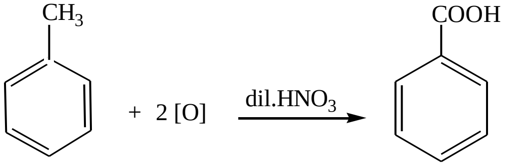
3. Halogenation

Substitution take place on the benzene nucleus at R.T in the presence of a catalyst Fe or halogen carrier I_2.



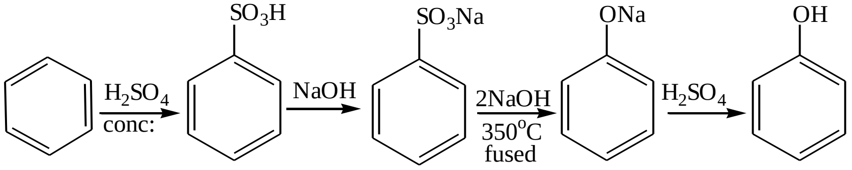
4. Oxidation

Unlike benzene, toluene is easily oxidized even with dilute nitric acid. If toluene is boiled with dilute nitric acid. If toluene is boiled with dilute nitric acid, the side chain CH_3 group is converted into -COOH group.



Phenol

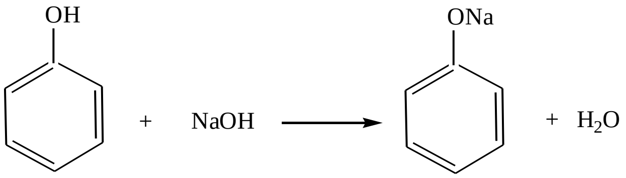
General method of preparation of phenol



Chemical properties

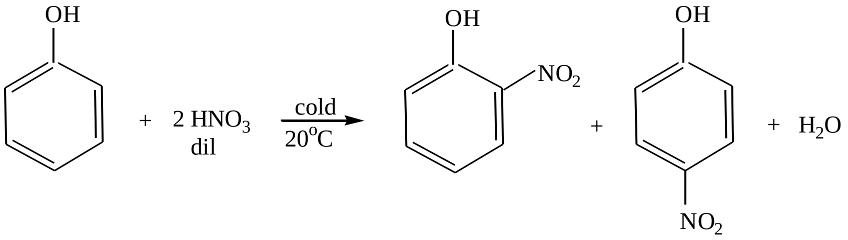
1. Reactivity to the hydroxyl group in phenol

Weak monobasic acid therefore forms soluble salt with caustic alkali.



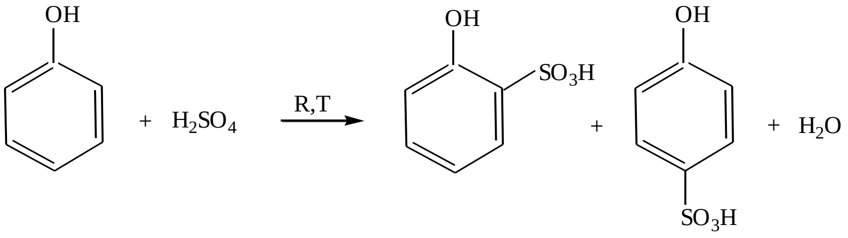
Sodium phenate can be decomposed by weak acid H_2CO_3.

2. Nitration



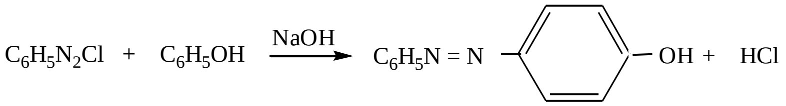
o-nitro phenol p-nitro phenol

3. Sulphonation



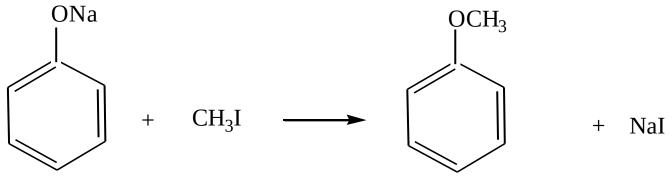
o- phenol sulphonic acid p- phenol sulphonic acid

4. Coupling reaction

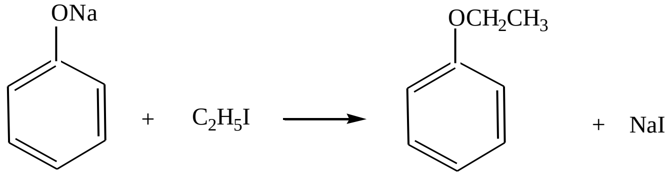


p-hydroxy azo benzene

5. Metallic derivatives of phenol react with alkyl halides to form ethers.



anisole or
methyl phenyl ether



ethyl phenyl ether

ISOMERISM

When two or more compounds have same molecular formula but differ from each other in physical properties or chemical properties, these are called isomers. This phenomenon which revealed the co-existence of compounds whose molecules were made of the same number of like atoms (or parts) was named as isomerism.

There are two types of isomerism

1. When two or more compounds have identical molecular formula but different structure formulas, these are called structural isomers and the phenomenon is referred to as structural isomerism.

Structural isomerism includes,

(i) Skeletal or Chain isomerism
(ii) Positional isomerism
(iii) Functional isomerism
(iv) Metamerism

2. When two or more compounds posses, the same molecular and structural formulas isomerism arises from different arrangements of atoms or groups in space the phenomenon is termed stereoisomerism and the isomers are called stereoisomer or steromers.

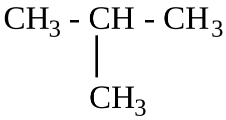
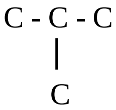
Stereoisomerism includes,

(i) Geometrical or Cis-Trans isomerism
(ii) Optical isomerism

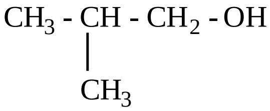
STRUCTURAL ISOMERISM

(i)Skeletal or Chain Isomerism

This type of isomerism caused by different arrangements of the carbon skeletons or chains in the molecule is termed skeletal or chain isomerism. For example, there are two butanes which have the same molecular formula C_4H_{10} but differ is respect of carbon skeletons or chain.

Isomers	**Structural Formula**	**Carbon Formula**
n - butane	$CH_3CH_2CH_2CH_3$	C - C - C - C
Isobutane	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	 $C-\underset{C}{\underset{\vert}{C}}-C$

The chain isomerism is also shown by the other classes or compound e.g.


$CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-OH$

$CH_3CH_2CH_2CH_2$ OH

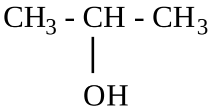
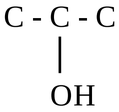
n - butyl alcohol

Isobutyl alcohol

(ii) Positional Isomerism

When two or more compounds have the same structural formulas which differ only in the position of the functional group on the carbon skeleton, they are called positional isomers and the phenomenon is termed positional isomerism.

e.g. Two propyl alcohols C_3H_7OH

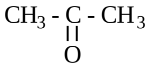
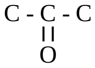
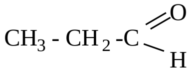
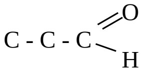
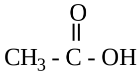
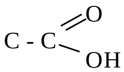
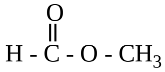
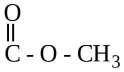
Name	**Structural Formula**	**Skeletal Formula**
n - propyl alcohol	$CH_3CH_2CH_2OH$	C - C - C - OH
Isopropyl alcohol	 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_3$	 $C-\underset{OH}{\underset{\vert}{C}}-C$
1 - butene	$CH_2=CH\ CH_2CH_3$	C = C - C - C
2 - butene	$CH_3\ CH=CH\ CH_3$	C - C = C - C

(iii) Functional Isomerism

When two or more substances incidentally have the same molecular formula but possess different functional groups, they are said to be functional isomers and the phenomenon is termed functional isomerism. Thus dimethyl ether and ethyl alcohol have the molecular formula, C_2H_6O but belong to different classes of compounds, the functional groups being - O - and - OH respectively.

$CH_3\ O\ CH_3$	CH_3CH_2OH
dimethyl ether	ethyl alcohol

Other examples of functional isomers are,

Name	Structural Formula	Skeletal Formula
Acetone	 $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$	 $C-\underset{\underset{O}{\|}}{C}-C$
Propionaldehyde		
Acetic acid	 $CH_3-\overset{\overset{O}{\|}}{C}-OH$	
Methyl formate	 $H-\overset{\overset{O}{\|}}{C}-O-CH_3$	 $\overset{\overset{O}{\|}}{C}-O-CH_3$

(iv) Metamerism

When two or more compounds of the same class with same molecular formular but different due to the unequal distribution of C atoms on either side of the functional group in the molecule are known as metamers and the phenomenon is called metamerism e.g.

$CH_3\,O\,CH_2\,CH_2\,CH_3$	$CH_3\,CH_2\,O\,CH_2\,CH_3$
methyl propyl ether	diethyl ether

both have the molecular formula $C_4H_{10}O$. Metamerism is shown by ether, ketones and amines.

STEREOISOMERISM

There is another kind of isomerism in which the isomers have the same structural formula but differ in the arrangement of atoms or groups in space. This is known as stereoisomerism. Two types of stereoisomerism

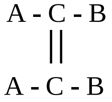
(a) Geometrical or cis-trans isomerism

(b) Optical isomerism

(a) Geometrical isomerism

This type of isomerism is shown by compounds containing a double bonded pair of carbon atoms each of which is attached to two dissimilar atoms or groups. Thus the molecule of (A) (B) C = C (A) (B) can exist in two forms.

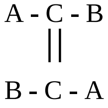
I



$$\begin{array}{c} A-C-B \\ \| \\ A-C-B \end{array}$$

(Cis form)

II



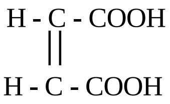
$$\begin{array}{c} A-C-B \\ \| \\ B-C-A \end{array}$$

(Trans form)

The form I is called the cis form (latin cis = on the same side) and the form II is called the trans form (latin trans = across). This type of isomerism is also known as Cis-Trans Isomerism.

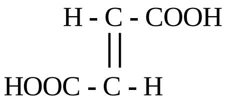
(cis form) (trans form)

(i)



$$\begin{array}{c}\mathrm{H-C-COOH}\\ \|\\ \mathrm{H-C-COOH}\end{array}$$

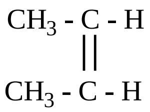
Maleic acid



$$\begin{array}{c}\mathrm{H-C-COOH}\\ \|\\ \mathrm{HOOC-C-H}\end{array}$$

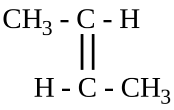
Fumaric acid

(ii)



$$\begin{array}{c}\mathrm{CH_3-C-H}\\ \|\\ \mathrm{CH_3-C-H}\end{array}$$

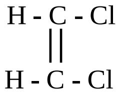
Cis-2-butene



$$\begin{array}{c}\mathrm{CH_3-C-H}\\ \|\\ \mathrm{H-C-CH_3}\end{array}$$

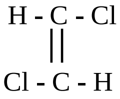
Trans-2-butene

(iii)



$$\begin{array}{c}\mathrm{H-C-Cl}\\ \|\\ \mathrm{H-C-Cl}\end{array}$$

Cis-1,2-dichloro ethene



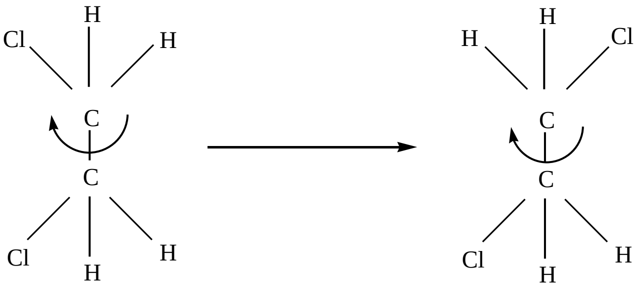
$$\begin{array}{c}\mathrm{H-C-Cl}\\ \|\\ \mathrm{Cl-C-H}\end{array}$$

Trans-1,2-dichloro ethene

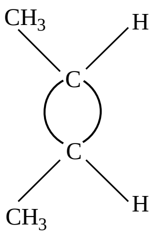
Causes of Geometrical Isomerism

When two carbon atoms are joined together by a single covalent bond, they may rotate freely about this bond independent of one another. In the case of carbon atoms formed by a double bond, however, this rotation is no longer possible.

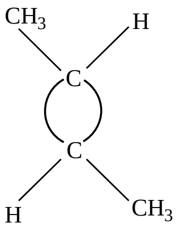
Rotation about single bond makes it identical with the other.



In a compound 2-butene



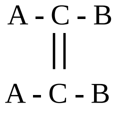
(I)



(II)

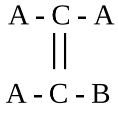
Here second bond between the two carbon atoms restricts their independent rotation. The two carbon atoms are fixed relative to one another. This gives rise to two different arrangements (I) and (II).

When the two atoms or groups attached to a double bonded carbon become similar, the compound does not exhibit geometrical isomerism.



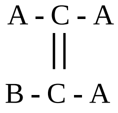
$$\begin{array}{c} A-C-B \\ \| \\ A-C-B \end{array}$$

(I)



$$\begin{array}{c} A-C-A \\ \| \\ A-C-B \end{array}$$

(II)



$$\begin{array}{c} A-C-A \\ \| \\ B-C-A \end{array}$$

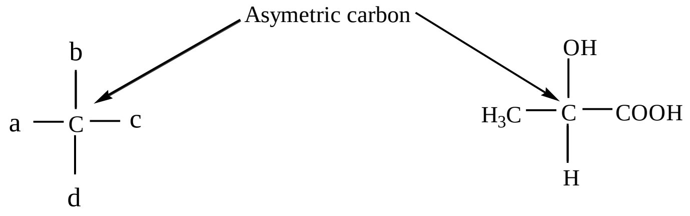
(III)

Exhibits geometrical isomerism Do not exhibit geometrical isomerism

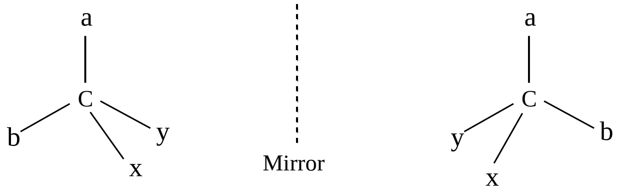
(b) Optical Isomerism

This type of isomerism also arises from the different arrangements in space of the atoms or groups composing a molecule. An organic substance exhibits optical isomerism when its molecule can have two spatial arrangements which are opposite to each other as object to its image in a plane mirror. These arrangements (object and image) give rise to two isomeric forms of the compound which are known as Enantiomorphic forms (Greek enantio = opposite) Enatiomorphs or Antimers.

The cause of optical isomerism is the presence in the molecule of an asymmetric carbon atom (chiral-atom) i.e, a carbon atom whose four valencies are attached to four different atoms or groups

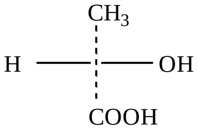


The molecule C_{abxy} could be represented by two space models as,



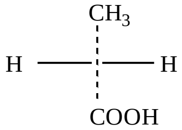
If you may try to superimpose one model over the other a, b, y groups will fall exactly over their identical counterparts of the other model but x groups will go in the opposite directions.

It is noteworthy that a molecule containing an asymmetric carbon atom has no plane of symmetry. i.e, a plane directing the molecule into two similar halves. In fact the absence of plane of symmetry in the molecule is a pre-requisite for optical isomerism. Thus Lactic acid has no plane of symmetry and so it exhibits optical isomerism.



Lactic acid

(Exhibits optical isomerism)

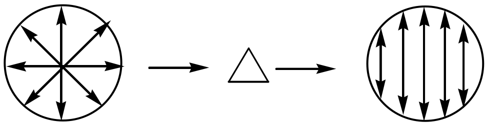


Propionic acid

(Does not exhibits optical isomerism)

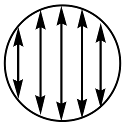
The two optical isomers of a substance have similar physical and chemical properties. They differ only in one respect i.e, their action on plane polarized light or optical activity.

Normally a beam of light consists of waves vibrating in all possible directions. When it is passed through Nicol prism the wave vibrating in other planes except one are blocked or cut off. Thus the beam of light emerging from the prism is made of waves vibrating in one plane only and is said to be plane polarized.

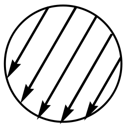


ordinary light waves plane polarized light

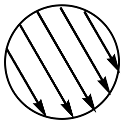
When a plane polarized beam of light is allowed to pass through solution of a substance such as lactic acid ($CH_3CHOH\ COOH$), the direction of its plane is rotated through a certain angle. The rotation may be to the right (clockwise) or to the left (counter clockwise).



Plane polarized light



Plane rotated to the left

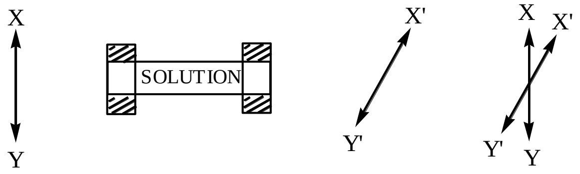


Plane rotated to the right

The property of a substance by virtue of which it can rotate the plane of polarize light is termed optical activity and the substance possessing it is said to be optically active.

A substance which rotates the plane of polarized light in the direction to the right is called Dextro rotatory (latin dexter = right) and designated as d- or by the sign (+). On the other hand, a compound which rotates the plane of polarized light in the direction to the left is known as Levo rotatory (Latin levous = left) and is indicated by l- or (-) sign.

The magnitude of rotation of the beam of polarized light by an optically active substance is measured by the use of instrument named as polarimeter.



Rotation of the plane polarized light by a solution.

If the plane polarized light has its vibrations as XY before entering the solution of a substsance, the direction on leaving it will be changed to say. The angle through which the plane has rotated is called the angle of rotation.

The observed angle of rotation depends on -

(1) the wave length of light used

(2) the length of the solution traversed by light

(3) the concentration of solution

(4) temperature and

(5) nature of the optically active substance.

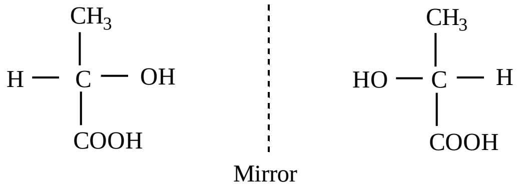
If the first four variables be fixed, the substance under examination will be a definite value of α .

The optically activity of a substance is expressed in terms of specific rotation. Since the determination is done using the wave length of Sodium at room temperature (20), the specific rotation is denoted by [α]. This is defined as the angle of rotation in degrees which the plane of polarized light undergoes on passing through a 1 decimeter (10 cm) column of concentration in grams per mililitre (g/ml) or $[\alpha]_{D}^{20} = \frac{\alpha}{l \, x \, C}$

Where α = observed angle of rotation in degree. l is the length of the solution column in decimeters C is the concentration of the test substance in g/ml .

Optical Isomerism of Lactic Acid

As we have already seen, lactic acid is optically active since it contains one carbon atom linked to four different atoms or groups. It can give rise to two forms of antimers.



$$H - \overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}} - OH \qquad \Bigg\vdots \qquad HO - \overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}} - H$$

In practice, lactic acid is known to exist in three forms.

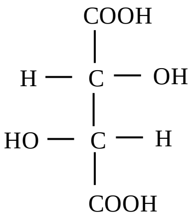
(i) One form of lactic acid named as sarcolactic acid , extracted form muscle tissues with water. It rotates the plane of polarized light to the right. It is called d- lactic acid or (+) lactic acid.

(ii) A second form of lactic acid is obtained by the fermentation of lactose (milk sugar). It rotate the plane of polarized light to the same extent as the first form but to the left. It is designated as l-lactic acid or (-) lactic acid.

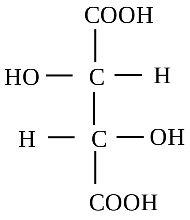
(iii) A third form of lactic acid results from laboratory synthesis and this is optically inactive. It is found to consist of equivalent amounts of the d-and l-isomers and is known as dl-mixture or Racemic mixture (±) lactic acid.

Optical Isomerism of Tartaric Acid

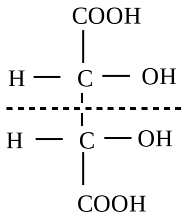
Tartaric acid has two asymmetric carbon atoms in it molecules. It exists in four forms viz d-tartaric acid , l-tartaric acid , dl-tartaric acid and meso or m-tartaric acid. In reality we have only three optical isomers of tartaric acid , d- , l- and m- , while dl- tartaric acid is only a mixture of the first two forms.



d - tartaric acid



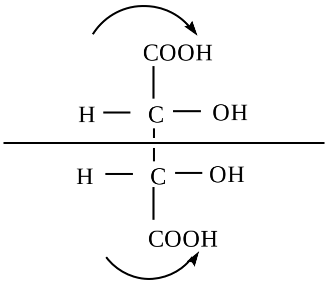
l - tartaric acid



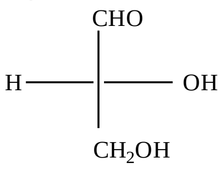
m - tartaric acid

A mixture of d- and l- tartaric acid in equal proportion dl- tartaric acid (racemic mixture)

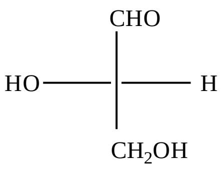
It will be noticed that the formulas of d- and l- acids are mirror images of one another and are optically active. The third form (m-) although it has two asymmetric carbon atoms in the molecule, is optically inactive and also known as m- tartaric acid. Thus, the real cause of optical activity is not the presence of the molecule as a whole. Obviously the molecule of m-tartaric acid has a plane of symmetry (dotted line) and is, therefore optically inactive.



Absolute configuration



D (+) glyceraldehyde

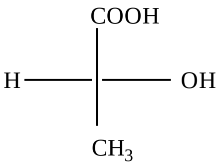


L (-) glyceraldehyde

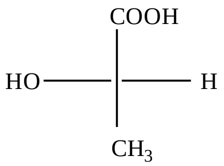
The symbol " D " derived from the Latin dextro, right applies the enantiomer having the ' OH ' group on the right. The symbol ' L ' derived from the Latin Levo, left, applies the enantiomer having the ' OH ' group on the left.

Enantiomers

The chiral molecule is always different from its mirror image like a right hand and a left hand. Such a pair of different mirror images are called enantiomers.



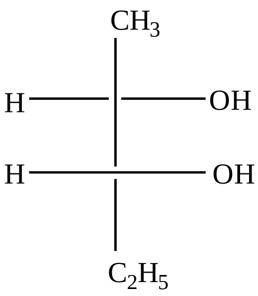
D (+) lactic acid



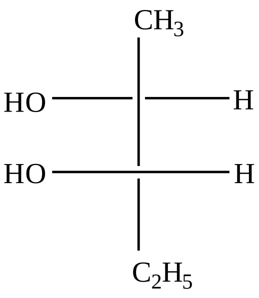
L (-) lactic acid

Diastereomers

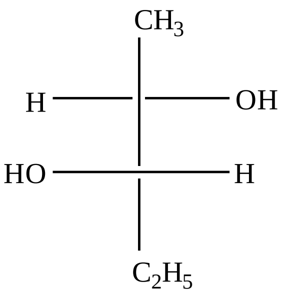
Stereoisomers that are not identical in configuration and are not mirror images are known as diastereomers.



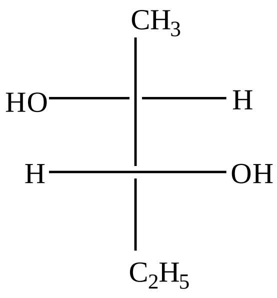
(I)



(II)

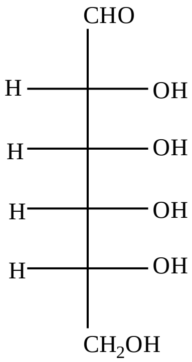


(III)

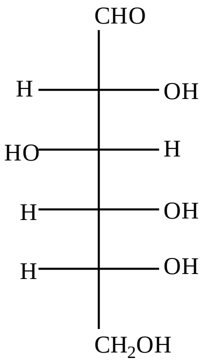


(IV)

Epimers



D (+) allose



D (+) glucose

Isomers which differ only in the configuration at one of several possible optical centers are known as epimers.

* * *