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# Hydro Carbon



#### INTRODUCTION

- Organic compounds made up of hydrogen and carbon atoms are known as hydrocarbons.
- ➤ Hydrocarbons are obtained from fossil fuels like coal, petroleum and natural gases which serve as the primary source of energy for generating heat, electricity and fuel for transportation.
- > The refining of crude oil yields hundreds of hydrocarbons.
- Methane is the most basic hydrocarbon.
- It is the main constituent of natural gas and is commonly found in marshy areas.

#### TYPES OF HYDROCARBONS

Hydrocarbons are classified based on their molecular structure and the types of bonds present between carbon atoms.

They can be categorized into two main groups; aliphatic hydrocarbons and aromatic hydrocarbons.

# Aliphatic Hydrocarbons

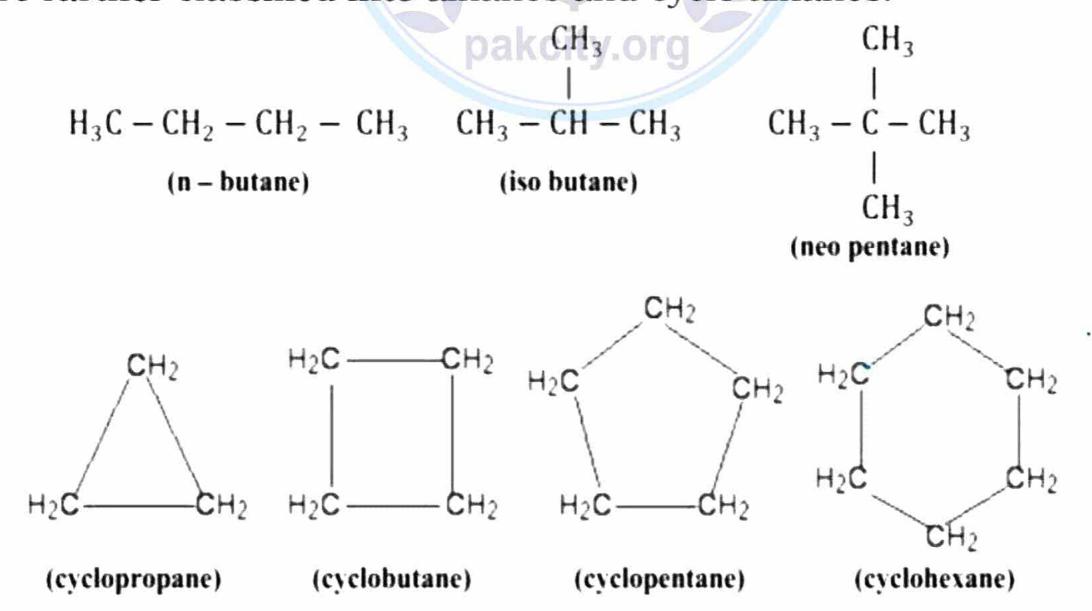
It is a class of hydrocarbon in which carbon atoms are arranged in straight or branched chain through single, double or triple bonds. These are often called as open chain hydrocarbons.

Aliphatic hydrocarbons can be further classified into saturated and unsaturated hydrocarbons. number.

# Saturated Hydrocarbons

"In these hydrocarbons, all carbon atoms are attached to each other by a single bond only".

These are further classified into alkanes and cyclo alkanes.



#### Unsaturated Hydrocarbons

These hydrocarbons contain one or more double or triple bonds between the two adjacent carbon atoms in their structure".

 $CH_2 = CH - CH_3$ 

 $CH_3 - C = C - CH_3$   $CH_2 = CH - CH = CH_2$ 

(1-propene)

(2-butyne)

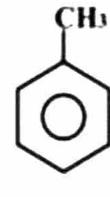
(1,3-buta diene)

#### **Aromatic Hydrocarbons**

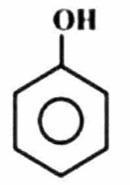
"Aromatic compounds are those which characterized by a cyclic arrangement of atoms that are connected by alternating double bonds they generally follow the Huckle rule  $(4n+2\pi \text{ electrons})$ ".



(Benzene)



(Toluene)



(Phenol)

СООН

(Benzoic acid)

ALKANES AND CYCLO ALKANES

#### **ALKANES**

Alkanes have open-chain or straight chain structures.

# CYCLO ALKANES

Cycloalkanes on the other hand, have a close-ring or cyclic structure.

Cycloalkanes are typically nonpolar similar to alkanes.

Despite both being saturated hydrocarbons, cyclopropane exhibits distinct properties compared to alkanes.

# Physical properties of alkanes

- (i) Alkanes are nonpolar organic compounds that are insoluble in water but soluble in organic solvents.
- (ii) Boiling point of alkanes is very low, it increases with the length of the carbon chain.
- (iii) The boiling point of straight chain alkanes is higher than that of branched chain alkanes because straight chain alkanes are more extended, which allows the greater surface arca.
- (iv) Alkanes which consist of C<sub>1</sub> to C<sub>4</sub> are gases C<sub>5</sub> to C<sub>17</sub> are liquids and above C<sub>17</sub> are waxy solids.

#### Physical properties of cycloalkanes

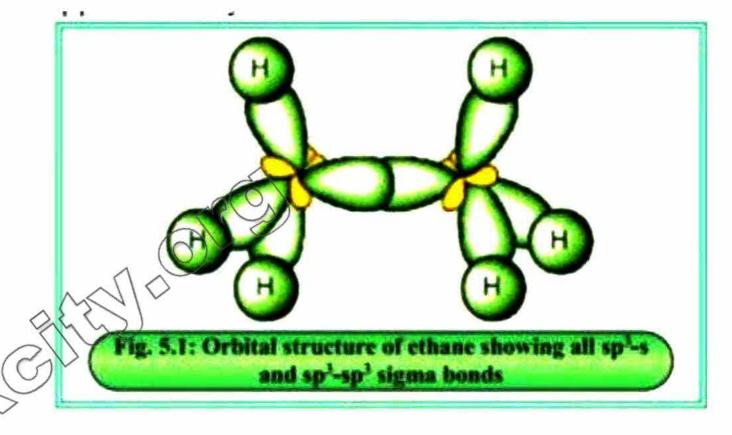
- (i) Cycloalkanes of C<sub>3</sub> and C<sub>4</sub> carbons are gases, while cycloalkanes of C<sub>5</sub> or more carbon atoms are liquids.
- (ii) The boiling point of cycloalkanes is lower than that of straight chain alkanes of comparable molar mass due to the ring strain.

#### Structure of Alkanes

Alkanes are open chain saturated hydrocarbons. Each carbon atom in alkanes is tetrahedrally bonded with hydrogen atoms and other carbon atoms.

To illustrate the structure of alkanes, the molecule of ethane is taken as a representative example.

Ethane is composed of two carbon

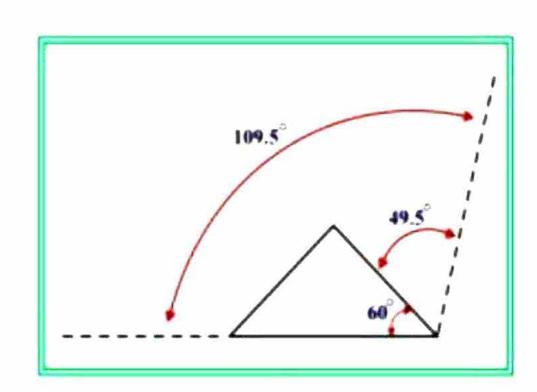


atoms and six hydrogen atoms (CoH<sub>0</sub>). Each carbon atom in ethane is sp<sup>3</sup> hybridized containing four sp<sup>3</sup> hybrid orbitals. These four sp<sup>3</sup> hybrid orbitals are arranged in a tetrahedral fashion. Out of four sp<sup>3</sup> hybrid orbitals of each carbon atom, three sp<sup>3</sup> hybrid orbitals are utilized in the formation of sigma bonds with three hydrogen atoms whereas the remaining sp<sup>3</sup> hybrid orbital of one carbon atom overlaps with the sp<sup>3</sup> hybrid orbital of another carbon atom. The bond length between the carbon and carbon atoms is approximately 1.54 °A, and the bond angle between carbon, carbon and hydrogen atoms is approximately 109.5°.

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# Structure of Cycloalkanes

Cyclopropane is the smallest and simplest cycloalkanes with a ring composed of three carbon atoms and six hydrogen atoms. The carbon atoms in cyclopropane are arranged in a trigonal geometry with an internal angle of 60°, which is quite smaller than the bond angle (109.5°) exist in alkanes.



# Reactivity

#### **Reactivity of Alkanes**

Alkanes are less reactive under normal conditions. This is because they are non polar in nature and hence a polar reagent finds no reaction site. Further, the stronger carbon-carbon bond requires high bond energy for its breaking.

#### Reactivity of Cycloalkanes

Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones - especially cyclopropane. Cyclopropane is much more reactive due bond angle strain in ring structure.

#### RADICAL SUBSTITUTION REACTIONS

#### Homolytic fission

In homolytic fission the bond cleavage takes place evenly, with each atom receiving one of the electron from the bond.

# Heterolytic fission

In heterolytic fission, the cleavage is uneven with one atom receiving both electrons from the bond and the other atom receiving none.

The mechanism of free radical reaction consists of following three steps.

# Step-1: Chain Initiation

The reaction begins with the breaking of the chlorine-chlorine bond in the presence of U.V light producing two chlorine free radicals.

$$CI \stackrel{CI}{\leftarrow} CI \stackrel{U.V. \ light}{\longrightarrow} CI \cdot + CI \cdot$$

# Step-2: Chain Propagation

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The chlorine radical is produced during chain initiation by attacking the methane molecule and abstracting a hydrogen atom. This process results in the formation of a molecule of hydrogen chloride and a methyl free radical.

$$CI \cdot + H : CH_3 \longrightarrow H : CI + \cdot CH_3$$

The methyl free radical then attacks another chlorine molecule, removing a chlorine atom to produce methyl chloride.

$$Cl:Cl + \cdot CH_3 \longrightarrow CH_3:Cl + \cdot Cl$$

# Step-3: Chain Termination

This step leads to the completion of reaction when all free radicals combine to form three possible stable molecules.

In reality, the reaction does not halt after the production of methyl chloride; rather, the remaining three hydrogen atoms in the methyl chloride molecule are substituted by chlorine atoms before the reaction stops.

$$CH_{4} + Cl_{2} \xrightarrow{Sunlight} CH_{3}Cl_{2} + HCl_{2}$$

$$CH_{3} - Cl_{2} + Cl_{2} \xrightarrow{Sunlight} CH_{2}Cl_{2} + HCl_{2}$$

$$CH_{2}Cl_{2} + Cl_{2} \xrightarrow{Sunlight} CHCl_{3} + HCl_{3}$$

$$(Methylene dichloride)$$

$$(Methylene dichloride)$$

$$(Chloroform)$$

$$CHCl_{3} + Cl_{2} \xrightarrow{Sunlight} CCl_{4} + HCl_{3}$$

$$(Chloroform)$$

$$(Carbon tetrachloride)$$

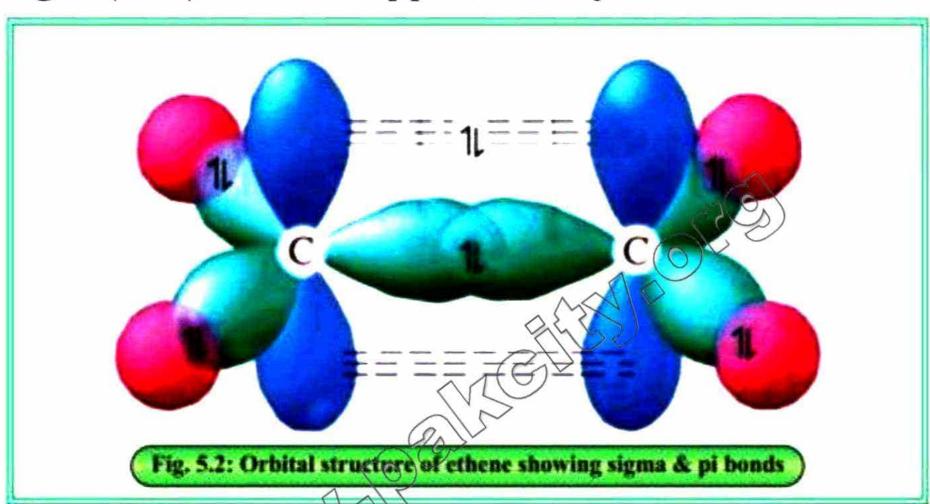
#### **ALKENES**

Alkenes are a class of unsaturated hydrocarbons, they contain one or more carbon-carbon double bonds in the chain.

Olefins is another term used to refer alkenes. The term olefin derives from Latin oleum meaning oil. This is because some of early discovered alkenes were oil like.

#### Structure of Ethene

The structure of ethene is characterized by two sp<sup>2</sup> hybrid carbon atoms that are arranged in a trigonal planar geometry. The double bond between the carbon atoms is composed of a sigma bond, which arises from the overlap of two sp<sup>2</sup> hybrid orbitals from each carbon atom and a pi bond which forms due to lateral overlapping of two un hybrid p orbitals, one from each carbon atom. Each carbon in ethene is also bonded with two hydrogen atoms through sp<sup>2</sup>-s sigma bonding. The bond length for the C-C single sigma bond is approximately 1.34 °A and bond angle between the two carbon-hydrogen (C-H) bonds is approximately 120°



# Preparation of Alkenes

Alkenes can be prepared by dehydration of alcohol and dehydrohalogenation of alkyl halides.

# Dehydration of Alcohol

When an alcohol is heated in the presence of a dehydrating agent such as concentrated sulphuric acid, it undergoes elimination of water molecule and gives an alkene.

# Dehydrohalogenation of an Alkyl halide

When ethyl halide is treated with an alcoholic solution of potassium hydroxide (KOH), the elimination of a hydrogen and a halogen atom takes place from two adjacent carbon atoms of alkyl halide, giving an alkene.

#### Reactivity of Alkenes

The higher reactivity of alkene as compared to alkane is attributed to the presence of a pi bond between the carbon atoms.

The pi bond relatively weaker and requires less energy to break.

Additionally the electron density associated with the pi bond is distributed above and below the carbon-carbon axis, making the pi electrons more exposed to an Electrophilic species.

Consequently, alkenes readily react with electrophile making them more reactive than alkanes.

#### **Reactions of Alkenes**

Even though alkenes can undergo oxidation and polymerization reactions, the most frequently observed reactions for alkenes are those involving addition reactions.

# Hydrogenation

In this reaction, hydrogen gas (H<sub>2</sub>) is added across a carbon-carbon double bond of alkene. The reaction is carried out in the presence of metal catalyst such as platinum (P), palladium (Pd) or nickel (N)) at a temperature of 250°C to 300 °C.

$$H_2C = CH_2 + H_2$$

$$(ethene)$$

$$250-300^{\circ}C$$
Ni.Pt or Pd
$$(ethane)$$

$$(ethane)$$

# Halogenation

The reaction of ethene with halogen is an addition reaction which gives a dihaloalkane. This reaction takes place in the presence of an inert solvent such as carbon tetrachloride or chloroform.

#### Hydrohalogenation

The addition of a halogen acid (HX) on an alkene to give an alkyl halide is known as hydrohalogenation of alkene.

$$CH_2 = CH_2 + H - Br$$
  $\rightarrow$   $CH_3 - CH_2 - Br$  (ethene) (ethyl bromide)

The addition of halogen acid on an un**symmetri**cal alkene is governed by Markovnikov's rule which states that

"When an unsymmetrical alkene undergoes addition reactions, the negative part of attacking reagent is added to that double bonded carbon atom which holds lesser number of hydrogen atoms while the hydrogen atom is attached to the carbon atom with the highest number of hydrogen substituents".

For example the reaction of propene with hydrogen bromide (HBr) gives 2-bromo propane as a major product.

The order of reactivity of halogen acid HX is HI > HBr > HCl

# Hydration

The addition of water on an alkene to give alcohol is known as hydration of alkene. This reaction is carried out by acid catalysis at 80-100°C.

$$H_2C = CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3 - CH_2 - OH$$
(ethene) (ethyl alcohol)

# Halo hydration

Halo hydration is a reaction in which a halogen reacts with alkene in presence of water and forms halohydrin.

$$CH_2 = CH_2 + Br_2 + H_2O \longrightarrow CH - CH_2 + HBr$$
(ethene)
$$OH$$
(bromohydrin)

# **Epoxidation**

The addition of oxygen to the double bond of an alkene is known as epoxidation. The product of this reaction is an epoxide which is a three membered cyclic ether.

$$CH_{2} = CH_{2} + \frac{1}{2}O_{2} \xrightarrow{\text{Peracetic acid} \atop (CH_{1}CO,H)} CH_{2} \xrightarrow{\text{Peracetic acid} \atop (CH_{2}CO,H)} CH_{2}$$
(ethene) (epoxide)

#### **Ozonolysis**

Ozonolysis is a chemical reaction that involves the cleavage of an alkene or alkyne by ozone in the presence of reducing agent such as zinc. The reaction results in the formation of ozonide intermediates which are unstable and quickly decompose to form an aldehyde.

#### **Polymerization**

Polymerization of alkene involves the linking of many alkene monomers together to produce a polymer chain.

$$nH_2C = CH_2$$

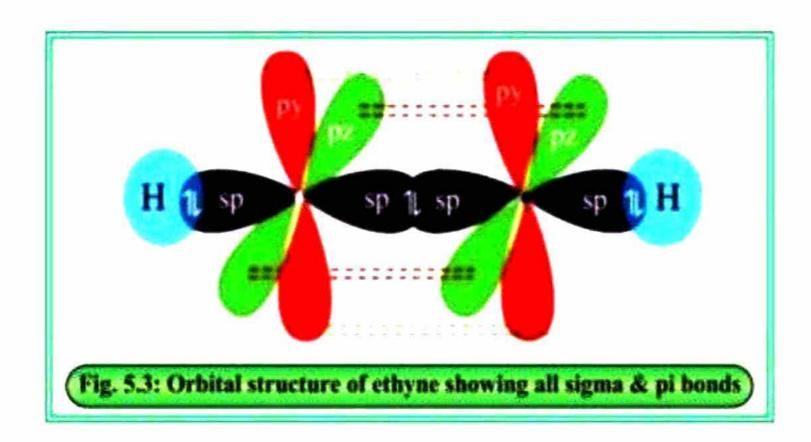
$$\frac{200^{\circ}C}{2000 \text{ atms}} \qquad CH_2 = CH_2$$
(ethene)
(polyethene)

# ALKYNES

Alkynes are hydrocarbons that contain a triple bond between the two carbon atoms.

# Structure of Ethyne

Ethyne is the first member of alkynes family in which both carbon atoms are sp hybridized. Each carbon has two sp hybrid orbitals and two unhybrid 'p' orbitals (Py and Pz). Two hybrid orbitals form two sigma bonds, one with carbon and other with hydrogen, whereas two unhybrid orbitals form two pi bonds by parallel overlapping. Hence the shape is linear with an angle of 180° The bond length of the carbon-carbon triple bond (C=C) in ethyne is approximately 1.20 °A



#### **Physical Properties**

- 1. Alkynes are colourless and odourless except for acetylene gas which has garlic like odour.
- 2. Alkynes are insoluble in water but soluble in the organic solvents like acetone, ether, Ethyl acetate etc.
- 3. Melting and boiling points increase with increasing molecular mass of alkynes.
- 4. First three members are gases and next members up to 12 carbons are liquids.

# Preparation of Alkynes by elimination reaction

Alkynes are generally synthesized through elimination reactions, which involve the removal of atoms or groups from two adjacent carbon atoms.

# Dehydrohalogenation of Vicinal dihalide

When vicinal dihalide is heated with an alcohol solution of potassium hydroxide (KOH) to give an ethyne. This reaction involves the removal of two halogens and two hydrogens from adjacent carbon atoms.

# **Dehalogenation of Tetrahalides**

A tetrahalide on heating with zinc dust forms ethyne.

Br Br 
$$H \rightarrow C \rightarrow C \rightarrow H \rightarrow Zn \rightarrow Heat \rightarrow H \rightarrow ZnBr_2$$

Br Br  $H \rightarrow C \rightarrow C \rightarrow H \rightarrow ZnBr_2$ 

Br  $H \rightarrow C \rightarrow C \rightarrow H \rightarrow ZnBr_2$ 

Heat  $H \rightarrow C \rightarrow C \rightarrow H \rightarrow ZnBr_2$ 

Br  $H \rightarrow C \rightarrow C \rightarrow H \rightarrow ZnBr_2$ 

(1,2-dibromoethene) (ethyne)

#### Addition reaction of alkynes

Alkynes undergo addition reactions similar to alkenes however, the reactivity of alkynes towards electrophilic reagents is relatively less than that of alkenes.

#### Hydrogenation

Alkyne reacts with hydrogen in the presence of metal catalysts such as nickel (N), platinum (Pt) and palladium (Pd) to give an alkene which then further reacts with another molecule of hydrogen to produce an alkane.

$$HC \equiv CH + H_{7}$$

$$(ethyne)$$

$$H_{2}C = CH_{2} + H_{2}$$

$$(ethene)$$

$$H_{3}C = CH_{4} + H_{2}$$

$$(ethene)$$

$$H_{4}C = CH_{4} + H_{2}$$

$$(ethene)$$

$$H_{5}C = CH_{5} + H_{2}$$

$$H_{5}C = CH_{5} + H_{5}$$

$$H_{7}C = CH_{7} + CH_{7}$$

$$H_{7}C = CH_{7} + CH_{7}$$

$$H_{7}C = CH_{7} + H_{7}$$

$$H_{7$$

# Hydrohalogenation

The final product of the reaction of an alkyne with hydrogen halide is a dihaloalkane, however, the reaction completes in two steps. The second step involves the Markovnikov's rule.

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#### **Hydration**

When an alkyl halide undergoes reaction with water in the presence of mercurous sulphate and sulphuric acid, it forms an enol. This enol subsequently undergoes rearrangement, resulting in the formation of an aldehyde or ketone.

$$H-C \equiv C-H + H-OH \xrightarrow{\delta^{+}} \xrightarrow{\delta^{-}} \frac{100^{\circ}C}{H_{2}SO_{4}, HgSO_{4}} \xrightarrow{CH_{2} = CH} \xrightarrow{rearrangment} CH_{3} \xrightarrow{C} C-H$$

$$(ethyne) \qquad (vinyl alcohol) \qquad (acetaldehyde)$$

$$H-C \equiv C-CH_{3} + H-OH \xrightarrow{\delta^{+}} \xrightarrow{\delta^{-}} \frac{100^{\circ}C}{H_{2}SO_{4}, HgSO_{4}} \xrightarrow{CH_{2} = C-CH_{3}} \xrightarrow{rearrangment} CH_{3} \xrightarrow{C} C-CH_{3}$$

$$(propyne) \qquad (Enol form) \qquad (acetone)$$

#### **Bromination**

The addition of bromine to an alkyne molecule gives a dibromo alkene which then absorbs another bromine molecule to produce tetrabromo alkane.

# Ozonolysis

Ozonolysis is a reaction in which the pi bonds between carbon-carbon atoms are broken down by the addition of ozone (O<sub>3</sub>). The ozonolysis of an alkyne initially gives an ozonide, which subsequently undergoes oxidation with hydrogen peroxide. This oxidation results in the formation of glyoxal.

$$H-C \equiv C-H + O_3 \longrightarrow H-C-C-H \xrightarrow{H_2O_2} H-C-C-H$$
(ethyne) (ozonide) (glyoxal)

Alkanes	Alkenes	Alkynes
Alkanes are chemically	Alkenes are more	Alkynes display higher
less reactive since the	reactive because the	reactivity than alkanes

Sigma bond between	electron density of pi	but lower reactivity
carbon-carbon requires	electrons spreads above	than alkenes because
high energy to break.	and below the axis	electrons are not
	which offers an	entirely exposed owing
	electrophile to attack on	to the short length of
	the substrate molecule.	triple bond.
They do not oxidized by	They oxidize by KMnO <sub>4</sub> .	They oxidize by KMnO <sub>4</sub> .
KMnO <sub>4</sub> .		

#### **ISOMERISM**

"A wide range of organic compounds studied in organic chemistry exhibit the same molecular formula, yet differ in their structure or sterio chemistry. These compounds are known as isomers and the phenomenon is referred as isomerism".

Isomers are initially classified into following two categories.

(i) Structural isomers (ii) Stereo isomers

#### Structural Isomerism

Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers.

These are further classified into the following types.



#### Chain isomers

"It is a type of structural isomer in which the molecules differ from each other with respect to carbon skeleton".

For example  $C_4H_{10}$  exists in the following two chain isomers.

Similarly C<sub>5</sub>H<sub>12</sub> has the following three possible chain isomers.

#### Position isomerism

"In this type of isomerism, the structural difference is based on the change in the position of functional group".

For example C<sub>4</sub>H<sub>8</sub> has two position isomers.

$$CH_3 - CH = CH - CH$$
,  $CH_3 - CH_2 - CH = CH_2$ 

(2-butene) (1- butane)

Similarly the two possible position isomers of C<sub>3</sub>H<sub>7</sub>Cl are given as.

 $Cl - CH_2 - CH_2 - CH_3$   $CH_3 - CHCl - CH_3$  (1- chloropropane) (2- chloropropane)

# Functional group isomers

"Two molecules having the same molecular formula but differing from each other by the change of functional groups are called functional group isomers",

For example the two possible functional group isomers of  $C_2H_6O$  are given as.

 $CH_3 - CH_2 - OH$   $CH_3 - O - CH_3$  (ethyl alcohol) (Dimethyl ether)

Another example of molecule exhibiting functional group isomerism is

C<sub>3</sub>H<sub>6</sub>O.

 $H_3C-CH_2-CO-H$   $H_3C-CO-CH_3$  (propanal) (2- propanone)

#### Metamerism

"Organic molecule which exhibits unequal distribution of alkyl group on either side of functional group is known as metamerism".

For example two possible metamers of the formula C4Ho0 are.

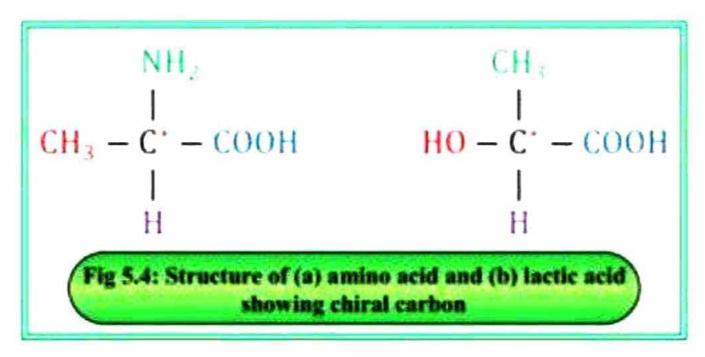
 $CH_3 - 0 - C_3H_7$   $C_2H_5 - 0 - C_3H_5$  (methyl propyl ether) (Diethyl ether)

#### Chiral Centre

"A chiral centre is formed in a molecule when a carbon atom is bonded to four different atoms or groups".

The carbon atom on which these different groups are attached is called chiral carbon and the phenomenon is referred as chirality.

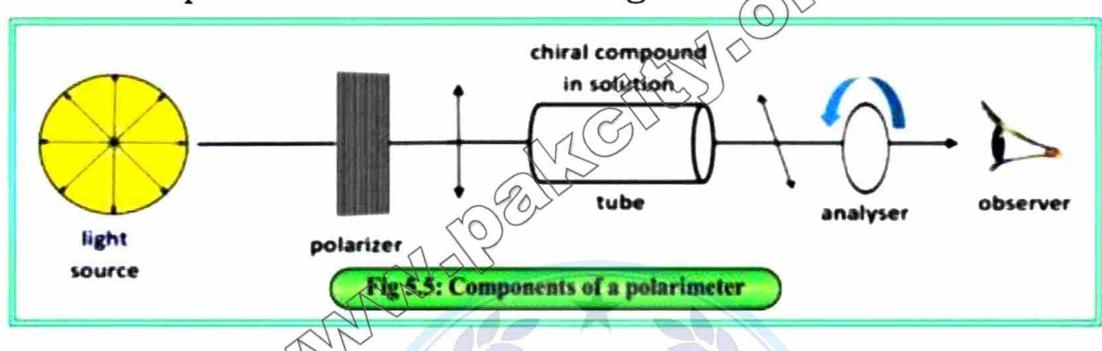
For example, in the molecules of amino acid and lactic acid four different groups are attached with the ∞-carbon as given in figure 5.4.



#### **Optical Activity**

When a plane of polarized light is passed through a solution of organic compound that contain chiral carbon, the light is rotated either clockwise or anticlockwise direction at a certain degree. This property of rotating plane of polarized light when passes through a solution of a compound is known optical activity.

The device used to measure the optical activity is known as polarimeter. The components of a polarimeter is shown in figure

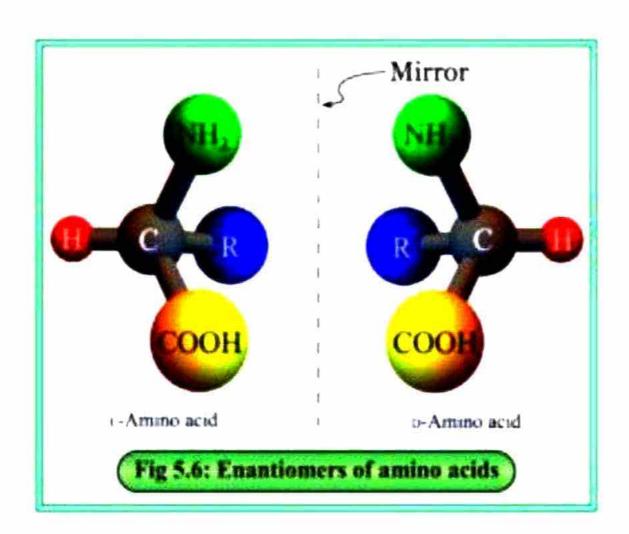


# **Optical Isomers**

Two compounds having the same molecular formula, same structure but differing from each other by the optical rotation of plane of polarized light are enantiomers".

The compound that rotates the plane of polarized light in a clockwise direction is known as dextrorotatory or D-isomer while the compound that rotates the plane of polarized light in anticlockwise direction is referred as levorotatory or L-isomer. These two optical isomers are mirror images to each other but not superimposable and are known as enantiomers.



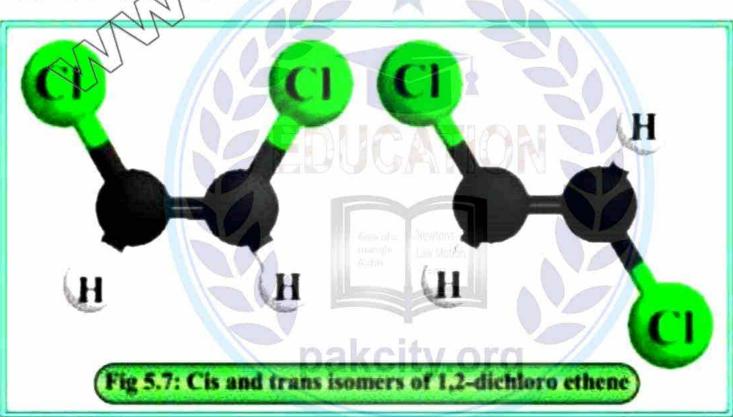


#### Stereoisomerism (Geometrical isomers)

Stereoisomers are a type of isomers that have the same molecular formula and connectivity of atoms but differ in the spatial arrangement of atoms in three-dimensional space, resulting in distinct physical and chemical properties.

"Geometrical isomers are of two types, one is called cis and other is called trans".

If the same groups lie on the same side of molecule, this is called cis isomer where as if the same groups lie on opposite direction in the molecule, this is referred as trans-isomer.



#### BENZENE AND ITS DERIVATIVES

- Benzene is the simplest aromatic compound.
- ➤ It is a colourless, carcinogenic and highly inflammable liquid.
- ➤ It burns with black flames due to the presence of high carbon contents in the molecule.
- $\triangleright$  Its molecular formula is C<sub>6</sub>H<sub>6</sub>.
- ➤ It was first isolated by Michael Faraday in 1825.
- The structure of benzene was suggested by Kekule in 1865.

- According to him "Benzene is a cyclic hexagonal molecule with alternative double bonds".
- ➤ Huckel and certain other chemists studied on Kekule structures of benzene and introduced the term resonance" within the benzene molecule.
- ➤ Hence the additional stability shown by benzene arises from the presence of delocalized pi electrons.

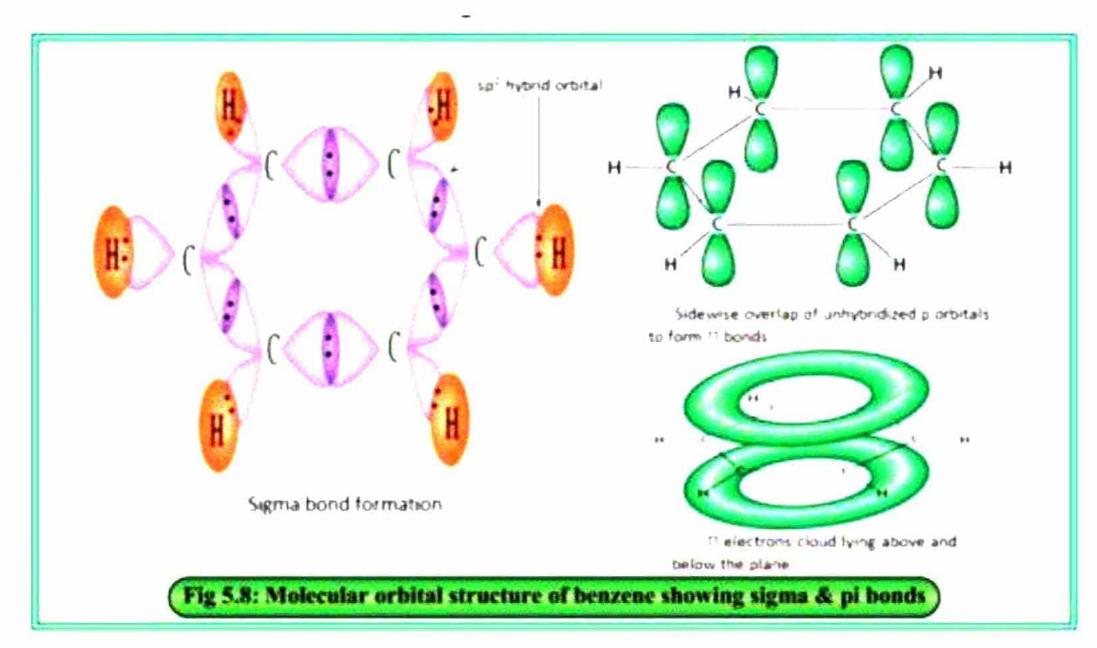
#### **Physical Properties**

- 1. Benzene is a colorless liquid having molecular mass 78 g/mol.
- 2. The melting point of benzene is 5.5°C and boiling point is 80°C.
- 3. The density of benzene is 0.88 g/cm<sup>3</sup>.
- 4. Benzene is insoluble in water but soluble in organic solvents such as ether, acetone and chloroform.

#### Molecular orbital structure of benzene

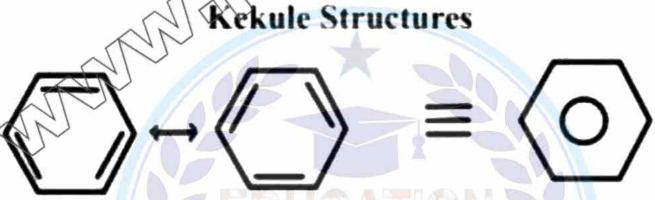
Benzene consists of six carbon atoms in a ring, each carbon is sp<sup>2</sup> hybridized and has three sp<sup>2</sup> hybrid orbitals.

Two hybrid orbitals of each carbon atoms are used to make sigma bond with the adjacent carbon atom, through  $sp^2 - sp^2$  overlapping. The third  $sp^2$  hybrid orbital is involved in sigma bonding with hydrogen atoms through  $sp^2$  S overlapping. All sigma bonds in benzene are coplanar and have bond angle of  $120^\circ$ . In benzene, the carbon-carbon (C-C) bond length as well as carbon-carbon double bond (C = C) length is approximately  $1.39^\circ A$ . The six carbon atoms in benzene possess six non hybridized p orbitals that are oriented perpendicular to the sigma bonds. The side wise overlapping of these p orbitals gives six delocalized pi molecular orbitals where half of them are located above the plane while other half below the plane of sigma bonds. The six electrons present in pi molecular orbitals are delocalized over all six carbon atoms in the molecule.



The molecular orbital structure of benzene provides the following information.

- 1. Benzene is a planar hexagonal molecule,
- 2. Pi electrons of benzene are delocalized and responsible for the extra stability of molecule.
- 3. Actual structure of benzene is a hybrid of two resonating structures described by Kekule.



Two equivalent resonating structures of benzene Re

Resonance hybrid

#### Addition reactions of benzene

Benzene, being an aromatic compound, is highly resistant to addition reactions due to its stability. However, under specific conditions, it can undergo addition reactions. So far only the addition of hydrogen and chlorine to benzene has been observed.

# Addition of Hydrogen

Benzene undergoes an addition reaction with hydrogen to produce cyclohexane. It is a catalytic hydrogenation carried out in the presence of Nickel at 200°C and 30 atmospheric pressure.

#### **Addition of Halogen**

Chlorine and bromine are added to benzene under sunlight and at high temperature and pressure.

#### Electrophilic substitution reactions of benzene

Electrophilic substitution reactions type of organic reaction in which an electrophile reacts with an electron-rich compound and replaces an electrophile in the compound.

The proposed general mechanism of Electrophilic substitution reaction of benzene consists of following steps.

# Step-1: Generation of an electrophile

An electrophile (E+) is generated by reaction of catalyst with the reagent.

 $E - Z + Catalyst \rightarrow E^+ + [Z - catalyst]$ 

# Step-2: Formation of Arenium ion

The electrophile attacks on pi system of benzene and forms a carbocation known as arenium ion.

In this attack, one carbon of benzene becomes sp<sup>3</sup> hybridized and hence the aromaticity of benzene has lost.

# Step-3: Abstraction of proton

The unstable non aromatic arenium ion then loses a proton and changes into the product.

$$+ |Z - catalyst| \longrightarrow + |Z - catalyst| + HZ$$

In this stage aromaticity of benzene is restored. Benzene undergoes following types of Electrophilic substitution reactions.

#### 1. Nitration

The reaction of benzene with conc. nitric acid to produce nitrobenzene is known as nitration. This reaction is carried out at 50°C in the presence of conc. sulphuric acid.

In this reaction, one hydrogen of benzene is replaced by a nitronium ion  $(NO_2^+)$ .

Similar to benzene, toluene also undergoes nitration, but the product is a mixture of ortho and para nitro toluene.

#### Sulphonation

Benzene reacts with conc. sulphuric acid at 50 to 60°C to give benzene sulphonic acid.

This reaction may also be carried out at room temperature if fuming sulphuric acid is used.

Sulphonation of toluene gives a mixture of ortho, para methyl benzene sulphonate.

#### Halogenation

Benzene reacts with halogens (Cl<sub>2</sub>, Br<sub>2</sub>) at room temperature in the presence of a Lewis acid (FeCl<sub>3</sub>) to give a halobenzene.

If toluene is allowed to undergo halogenations, it give a mixture of ortho, para chlorotoluene.

#### Friedal Craft Alkylation

Benzene undergoes reaction with an alkyl halide in the presence of a Lewis acid (AlCl;) to produce an alkyl benzene.

The reaction of toluene with an alkyl halide gives a mixture of ortho, para and meta products.

# Friedal Craft Acylation

The reaction of benzene with an acylhalide (RCOCI) in the presence of lewis acid (AlCI<sub>3</sub>) is known as Friedal Craft acylation.

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The attacking electrophile in this reaction is acyl cation (RCO<sup>+</sup>) which is produced by the reaction of acyl chloride with Lewis acid (AlCl<sup>3</sup>). Acylation of toluene give only the para product.

#### **Substituent Effect**

The effect of the first substituent on the incoming electrophilic reagent is known as substitution effect or orientation of benzene.

$$(benzene) + E_1 \longrightarrow (monosubstitude product)$$

$$E_1 \longrightarrow E_2 \longrightarrow E_2 \longrightarrow E_2$$

$$(monosubstitude product) + E_1 \longrightarrow E_2$$

$$(para)$$

#### (i) Ortho, para directing groups

"These substituent groups when attached to benzene ring, direct incoming Electrophilic substituents to the ortho and para positions".

They increase the electron density on ortho and para positions through resonance effect. The increased electron density on these positions make more attraction for the incoming electrophile to attack.

For example the – OH group of phenol is orth0, para director and when reacted with chlorine in presence of ferric chloride (FeCl<sub>3</sub>), it gives a mixture of ortho para chloro phenol.

# (ii) Meta direction group

The presence of these groups in benzene ring decreases the electron density at ortho and para positions due to inductive effect and hence the incoming electrophile attacks on meta position. For example the -COOH part of benzoic acid is meta directing. Thus, when benzoic acid reacts with nitric acid, it produces a meta product.

#### Comparative studies of ortho, para and meta directing group

Ortho para directors	Meta director
They release electron to the aromatic	They withdraw electron from benzene
ring and increasing the electron	ring and decrease the electron
density on ortho para position.	density on ortho para position.
When they attached with the benzene	When they attached with the benzene
rings they allow the incoming	ring, they invite the incoming
electrophilic reagent toward ortho	electrophilic reagent towards meta
and para positions.	positions.
Example are - R, - RCO, - QR, -CY, -	Examples are - COOR, - CHO COOH,
Br, - CH <sub>3</sub> , - OH etc	- NO <sub>2</sub> ,- COCH <sub>3</sub> , - SO <sub>3</sub> H etc

# Preparation of poly substituted benzene

Poly substituted benzene is formed by the replacement of two or more hydrogen atoms of benzene ring with Electrophilic reagents.

These are also called derivatives of benzene.

# Preparation of trinitro toluene (TNT)

Trinitro toluene is an explosive organic material. During its preparation from benzene, the benzene is first converted into toluene and then toluene treated with hot concentrated nitric acid. Since – CH<sub>3</sub> group of toluene is ortho para directing, it invites the NO} group of nitric acid towards ortho and para positions.

#### Preparation of m-nitro toluene

In order to synthesize m-nitro toluene, the first step is to transform benzene into nitrobenzene. Due to the meta directing nature of nitro group of nitro benzene, it directs the incoming – CH3 group towards the meta position.

# **Short Questions**

#### 1. Give three differences between aliphatic and aromatic hydrocarbons

Feature	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Bonding	Single C-C bonds	Alternating single and double C-C bonds in a ring structure
Reactivity	Generally more reactive	Less reactive due to the stabilizing aromatic ring system

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	Methane, Ethane, Propane,	
	Hexane, Cyclohexane,	Benzene, Toluene, Xylene,
Examples	Ethene, Propene, Butyne	Naphthalene, Anthracene

2. Give the mechanism of free radical reaction between methane and chlorine in the presence of sunlight.

Notes

- 3. Complete the following reactions and name the major product formed in each reaction.
  - 1.  $C_2H_5OH \xrightarrow{H_2SO_{4(conc)}170^0C} CH_2=CH_2 + H_2O$
  - 2.  $C_2H_5Br + KOH$  Alcohol, heat  $\xrightarrow{Heat} C_2H_4 + KBr + H_2O$
  - 3.  $CH_3 CH = CH_2 + HBr$   $\longrightarrow CH_3 CH_2 CH_{2Br}$  (major) + CH<sub>3</sub>CHBrCH<sub>3</sub> (minor)
  - 4.  $CH_2 = CH_2 + O_3 \longrightarrow HCOOH + H_2O_2$
- 4. Define a chiral carbon? Give an example to justify your answer. Notes
- 5. Write the equations with all required conditions for the reaction of benzene with the following:
- ()) H<sub>2</sub> (ii) CH<sub>3</sub>COCI (ii) HNO<sub>3(conc.)</sub> (iv) H<sub>2</sub>SO<sub>4(conc.)</sub>
- 6. Bring about the following conversions.
- (i) Toluene to ortho-para nitro benzoic acid
- (i) Benzene to m-nitro toluene **Notes**

Notes

8. Alkanes are generally referred as parafins due to their less reactivity, why are they stable towards chemical reactions?

Alkanes are generally referred to as paraffins due to their low reactivity, which is attributed to several factors:

- 1. Strong covalent bonds:
  - Alkanes have strong carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds, which require a significant amount of energy to break.
- 2. Non-polarity:
  - Alkanes are non-polar molecules, meaning they have an even distribution of electrons and no significant positive or negative charges.
- 3. Saturated carbon atoms:
  - Each carbon atom in an alkane has four single bonds, which means it has achieved a full octet of electrons.

- 4. Lack of functional groups:
  - Alkanes are hydrocarbons that only contain carbon and hydrogen atoms.
- 5. High kinetic stability:
  - Alkanes have a high activation energy, which is the minimum amount of energy required for a chemical reaction to occur.

# **Descriptive Questions**

- 1. Draw the orbital structures of the following hydrocarbons.
- (i) Ethane (i) Ethylene (ii) Acetylene

**Notes** 

- 2. Write the equations of the following chemical processes.
- (i) Ethylene is heated at high temperature and pressure.

 $nC_2H_4 \rightarrow (-CH_2-CH_2-)n$  (Polyethylene)

(ii) Ethene is burnt in air in the presence of per acetic acid.

 $C_2H_4 + 3O_2 + CH_3COOOH \rightarrow 2CO_2 + 4H_2O + CH_3COOH$ 

(iii) 1,2-di bromo butane is heated with alcoholic potassium hydroxide.

 $C_4H_8Br_2 + 2KOH (alc.) \rightarrow C_4H_8 + 2KBr + 2H_2O$ 

(iv) 1,1,2,2 tetra bromo ethane is heated with zinc powder.

 $C_2H_2Br_4 + 2Zn \rightarrow C_2H_2 + 2ZnBr_2$ 

(v) Reaction of chlorine with acetylene

 $C_2H_2 + Cl_2 \rightarrow C_2H_2Cl_2$  (1, 1 dichloroethene)

3. Ethene is more reactive than ethane but less reactive than ethyne, how can you explain this behavior?

The different reactivities of ethane (C2H6), ethene (C2H4), and ethyne (C2H2) can be explained by the different types of bonds present in their molecules:

#### 1. Types of bonds:

- Ethane: Contains only single C-C and C-H bonds. These are strong covalent bonds but are less reactive due to their stability.
- Ethene: Contains one double C=C bond and four single C-H bonds. The double bond is composed of a stronger sigma bond and a weaker pi bond. The pi bond is more susceptible to attack by other molecules and is responsible for the increased reactivity of ethene compared to ethane.
- Ethyne: Contains one triple C≡C bond and four single C-H bonds. The triple bond consists of one sigma bond and two weaker pi bonds. These pi bonds are even more vulnerable to attack than the pi bond in ethene, making ethyne the most reactive of the three hydrocarbons.

#### 2. Bond strength and stability:

- Single bonds are the strongest and most stable type of bond.
- Double and triple bonds are weaker than single bonds but are still relatively strong.
- The presence of pi bonds, especially multiple pi bonds, makes the
  molecule more reactive because the electrons in the pi bonds are less
  tightly held and are more easily attracted to other molecules.

#### 3. Availability of electrons:

- Ethane has all its electrons involved in strong single bonds, making them less available to participate in chemical reactions.
- Ethene and ethyne have pi bonds where the electrons are not as tightly held, making them more accessible and reactive.

#### 4. Hybridization:

- Ethane has sp3 hybridized carbon atoms, which means the electron orbitals are arranged in a tetrahedral geometry, making it difficult for other molecules to approach and react with them.
- Ethene and ethyne have sp2 and sp hybridized carbon atoms, respectively, which result in a more linear geometry, making the carbon atoms more accessible for attack by other molecules.

#### In summary:

- The presence of pi bonds, especially multiple pi bonds, increases reactivity due to the weaker electron density and greater accessibility of the electrons.
- The stronger the bond, the less reactive the molecule.
- The availability of electrons for participation in reactions plays a crucial role in determining reactivity.
- The hybridization of carbon atoms also influences the accessibility of the molecule for reaction.

Therefore, the trend in reactivity from least to most reactive is:

#### Ethane < Ethene < Ethyne

4. What is meant by isomerism? Explain four different types of structural isomers and give one example of each.

Notes

5. Explain the following with suitable examples. (a) Optical isomers (b) Geometrical isomers

Notes

6. Describe the molecular orbital structure of benzene.

Notes

7. Give the mechanism of following Electrophilic substitution reaction of benzene.

- (a) Nitration (b) Acylation (c) Chlorination
- 8. What is meant by ortho, para and meta directing groups. Explain the influence of substituent of benzene to the incoming Electrophile.

Notes

9. Why ethyne terminal hydrogen is acidic in nature? Give two reactions of ethyne to show their acidic behavior.

Ethyne's Terminal Hydrogen is acidic due to:

- 1. High s-character in sp-hybridized carbon:
- 2. Stability of the conjugate base (acetylide ion):

Reactions of Ethyne demonstrating its acidity:

- 1. Reaction with strong bases:
  - Ethyne reacts with strong bases like sodium metal or sodium amide to form sodium acetylide and release hydrogen gas.

$$C_2H_2 + 2Na \rightarrow C_2H_2Na_2 + H_2$$
  
 $C_2H_2 + NaNH_2 \rightarrow C_2H_2Na + NH_3$ 

- 2. Reaction with Grignard reagents:
  - Ethyne reacts with Grignard reagents (R-MgX) to form addition products with the acetylide ion.

