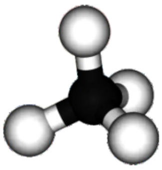
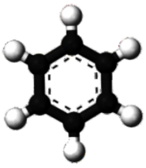
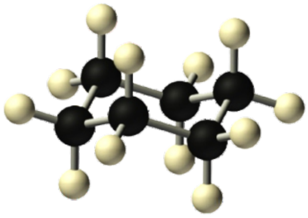
CHAPTER 5

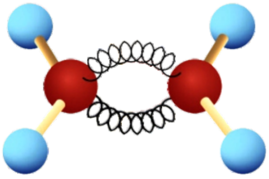
INTRODUCTION TO HYDROCARBONS

Teaching Periods	**22**	**Assessment**	**02**	**Weightage %**	**18**









Students will be able to:

- Classify hydrocarbons as aliphatic and aromatic. (Understanding)
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. (Applying)
- Explain unreactive nature of alkanes towards polar reagents. (Applying)
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. (Remembering)
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. (Understanding)
- Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism. (Understanding)
- Identify chiral centers in given structural formula of a molecule. (Analyzing)
- Analyze glucose molecules by optical activity. (Applying)
- Explain the terms isomerism and structural isomerism with suitable examples. (Remembering)
- Define stereoisomerism (cis and trans) with example of alkene. (Remembering)
- Explain shape of ethene molecule in terms of sigma and pi C-C bonds. (Understanding)
- Describe the structure and reactivity of alkenes as exemplified by ethene. (Applying)
- Draw all possible isomers of molecular formula C_4H_{10}, C_5H_{12}, C_4H_8, C_5H_{10}, C_4H_6, C_5H_8 with their IUPAC names. (Applying)
- Draw all possible isomers of molecular formula C_3H_7OH, C_3H_7Cl, $C_4H_9NH_2$ with their IUPAC names. (Applying)
- Draw all possible isomers of molecular formula C_2H_6O, C_3H_6O, $C_2H_4O_2$ with their IUPAC names. (Applying)
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. (Understanding)
- Describe the chemistry of alkenes by the following reactions of ethene: Hydrogenation, hydrohalogenation, hydration, halogenation, halohydration, epoxidation, ozonolysis, polymerization. (Understanding)
- Explain the shape of benzene molecule (molecular orbital aspect). (Understanding)
- Describe what is meant by the term delocalized electrons in the context of the benzene ring. (Understanding)
- Describe addition reactions of Benzene (with hydrogen and halogen). (Understanding)
- Describe the general mechanism of electrophilic substitution in benzene. (Understanding)
- Discuss the electrophilic reactions of benzene and toluene (nitration, sulphonation, halogenation, Friedel Craft's alkylation and acylation). (Applying)
- Apply the knowledge of positions of substituents in the electrophilic substitution of benzene. (Applying)
- Compare the reactivity of alkanes, alkenes and alkynes. (Analyzing)
- Discuss the shape of acetylene in terms of sigma and pi bonds. (Applying)
- Describe the preparation of alkynes using elimination reactions. (Applying)
- Describe acidity of acetylene. (Understanding)
- Discuss reaction of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonolysis, and reaction with metals. (Understanding)

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.

Hydrocarbons are considered as the mother of thousands of organic compounds since the introduction of functional groups to the basic hydrocarbon chain creates new molecules with different properties and structures.

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. Hexane, heptanes and octane are derived from petroleum and employed as automotive fuel. Parafin wax obtained from petroleum has various uses, including as a component in candles, polishes, lubricants and cosmetics. Ethyne is used for welding purposes, ethene is used for ripening fruits. Cycloalkanes have versatile uses, serving as solvents, lubricants and even fuel sources.

5.1 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. The name aliphatic was given to those compounds that were initially extracted from fat and oil.

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

DO YOU KNOW?

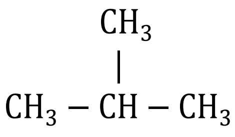
Gasoline is a fuel used in automobiles. It chemically consists of C_5 to C_8 carbon atoms. The grading of gasoline is a measure of its resistance to knocking in an internal combustion engine and is referred as the octane number.

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.

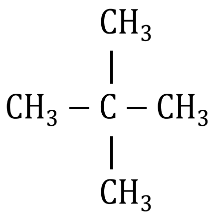
$H_3C-CH_2-CH_2-CH_3$

(n – butane)



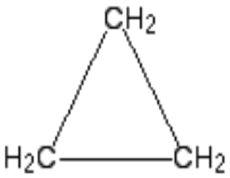
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

(iso butane)

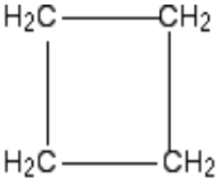


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

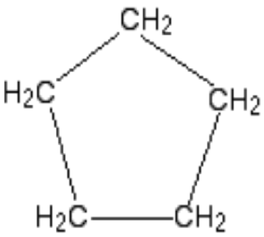
(neo pentane)



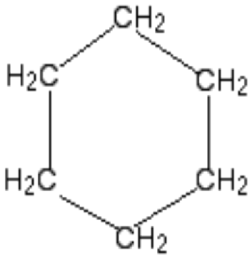
(cyclopropane)



(cyclobutane)



(cyclopentane)



(cyclohexane)

Unsaturated Hydrocarbons

"These hydrocarbons contain one or more double or triple bonds between the two adjacent carbon atoms in their structure". Unsaturated hydrocarbons are generally referred as alkenes and alkynes. The general formulas for their homologous series is C_nH_{2n} and C_nH_{2n-2} respectively.

$CH_2=CH-CH_3$

(1-propene)

$CH_3-C\equiv C-CH_3$

(2-butyne)

$CH_2=CH-CH=CH_2$

(1, 3-buta diene)

Self Assessment

Identify the following hydrocarbons as saturated and unsaturated.
C_3H_6, C_7H_{12}, C_8H_{18}, C_5H_{10}, C_5H_8

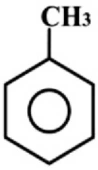
Aromatic Hydrocarbons

"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+2Π electrons)". The term aromatic originates from Greek word "aroma" means fragrant, as these compounds were initially isolated from pleasant smelling plants. The parent member of this class is benzene which is why aromatic compounds are often referred as benzene and its derivatives.

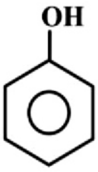
DO YOU KNOW?

Huckel's Rule states that aromaticity is exhibited by planar cyclic compounds with 4n+2 π electrons, where "n" is a non-negative integer. These compounds possess enhanced stability due to the delocalization of π electrons, making them highly aromatic.

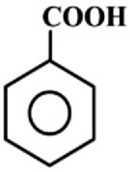
(Benzene)



(Toluene)



(Phenol)



(Benzoic acid)

5.2 ALKANES AND CYCLO ALKANES

Saturated hydrocarbons are represented by both alkanes and cycloalkanes. The fundamental difference between these two lies in the way their carbon atoms are arranged. Alkanes have open-chain or straight chain structures. 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. Cyclocalkanes are named as cyclopropane, cyclobutane, cyclopentane and cyclohexane etc.

5.2.1 Physical Properties

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 area.

(iv) Alkanes which consist of C_1 to C_4 are gases C_5 to C_{17} are liquids and above C_{17} are waxy solids.

Physical properties of cycloalkanes

(i) Cycloalkanes of C_3 and C_4 carbons are gases, while cycloalkanes of C_5 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.

5.2.2 Structure

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 (C_2H_6). Each carbon atom in ethane is sp^3 hybridized containing four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are arranged in a tetrahedral fashion. Out of four sp^3 hybrid orbitals of each carbon atom, three sp^3 hybrid orbitals are utilized in the formation of sigma bonds with three hydrogen atoms whereas the remaining sp^3 hybrid orbital of one carbon atom overlaps with the sp^3 hybrid orbital of another carbon atom. The bond length between the carbon and carbon atoms is approximately 1.54 Å, and the bond angle between carbon, carbon and hydrogen atoms is approximately 109.5°.

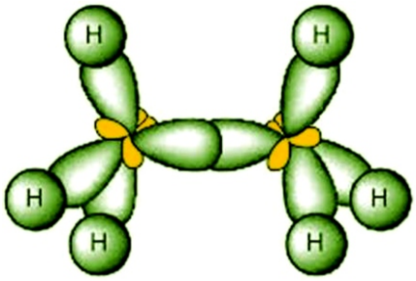
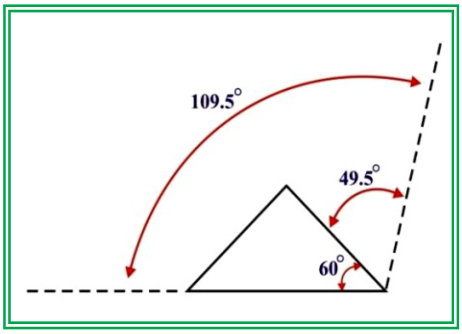


Fig. 5.1: Orbital structure of ethane showing all sp^3-s and sp^3-sp^3 sigma bonds

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.

5.2.3 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. They are often called as paraffin. The term paraffin is said to have originated from the Latin word "parum" meaning "little" and "affin" meaning affinity. However under certain conditions, they undergo halogenations, combustion and cracking which can be used in industrial processes to produce a variety of useful products.

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.

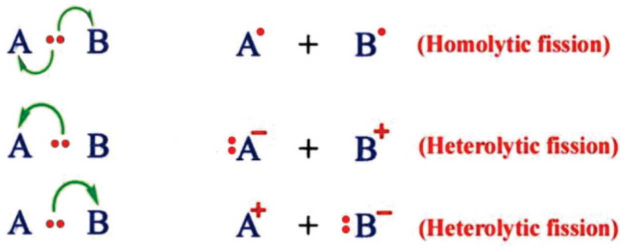
Self Assessment

(i) Draw the structure of cyclopropane and explain the angle strain in it.
(ii) Boiling point of cyclopropane is less than n-propane explain why?

5.3 RADICAL SUBSTITUTION REACTIONS

Before explaining free radical reaction, we need to understand the concepts of homolytic and heterolytic fission.

“The cleavage of chemical bond takes place in the organic molecule either by homolytic fission or heterolytic fission”. In homolytic fission the bond cleavage takes place evenly, with each atom receiving one of the electron from the bond. In heterolytic fission, the cleavage is uneven with one atom receiving both electrons from the bond and the other atom receiving none.



5.3.1 Reaction Mechanism

Free radical substitution reactions are typically carried out by homolytic fission. The reaction between methane and chlorine in U.V light or at high temperature takes place through free radical reaction. The mechanism of free radical reaction consists of following three steps.

Step-1: Chain Initiation

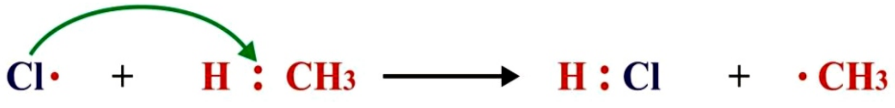
The reaction begins with the breaking of the chlorine-chlorine bond in the presence of U.V light producing two chlorine free radicals.

DO YOU KNOW?

The halogenation of ethane is more difficult than that of methane because of more product formation, firstly due to the presence of six hydrogen atoms in ethane instead of four in methane and secondly because isomerism is possible at the dichlorination step.

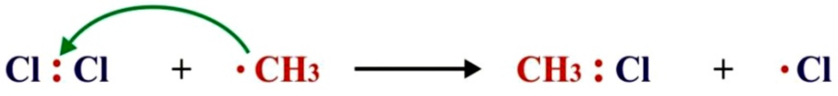
Step-2: Chain Propagation

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.



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

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.

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

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

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

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.

$$\underset{\text{(Methane)}}{CH_4} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Methyl chloride)}}{CH_3Cl} + HCl$$

$$CH_3-Cl + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + HCl$$

$$\underset{\text{(Methylene dichloride)}}{CH_2Cl_2} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Chloroform)}}{CHCl_3} + HCl$$

$$\underset{\text{(Chloroform)}}{CHCl_3} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{(Carbon tetrachloride)}}{CCl_4} + HCl$$

5.4 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.

5.4.1 Structure of Ethene

To describe the structure of alkene, ethene can be taken as a representative example.

The structure of ethene is characterized by two sp^2 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^2 hybrid orbitals from each carbon atom and a pi bond which forms due to lateral overlapping of two unhybrid p orbitals, one from each carbon atom. Each carbon in ethene is also bonded with two hydrogen atoms through sp^2-s sigma bonding. The bond length for the C-C single sigma bond is approximately 1.34 Å and bond angle between the two carbon-hydrogen (C-H) bonds is approximately 120 degrees.

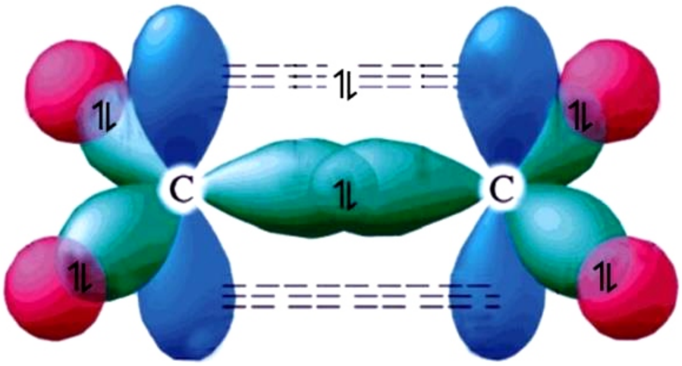


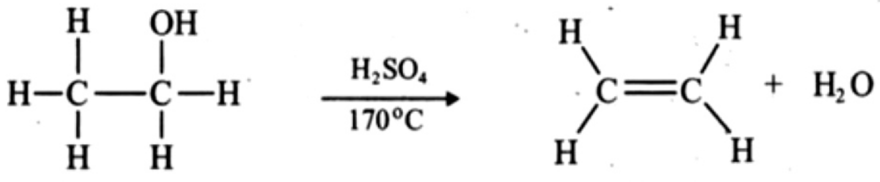
Fig. 5.2: Orbital structure of ethene showing sigma & pi bonds

5.4.2 Preparation of Alkenes

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

5.4.2.1 Dehydration of Alcohol

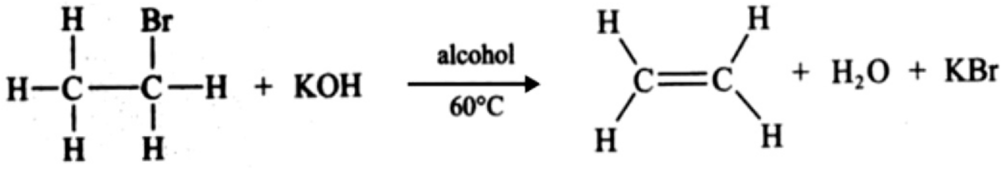
When an alcohol is heated in the presence of a dehydrating agent such as concentrated sulphuric acid, it undergoes elimination of water molecule and gives an alkene.



(alcohol) (ethene)

5.4.2.2 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.



(ethyl bromide) (ethene)

5.4.3 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 is 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.

5.4.4 Reactions of Alkenes

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

5.4.4.1 Hydrogenation

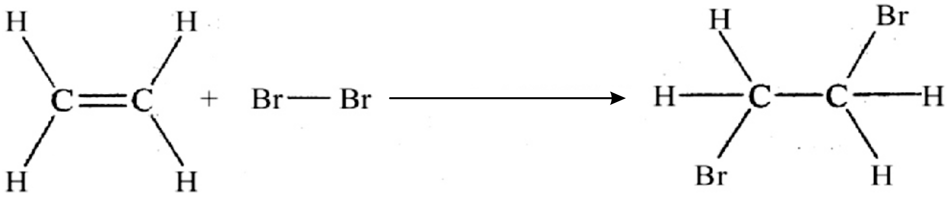
In this reaction, hydrogen gas (H_2) is added across a carbon-carbon double bond of alkene. The reaction is carried out in the presence of metal catalyst such as platinum (Pt), palladium (Pd) or nickel (Ni) at a temperature of 250 to 300°C.

$$H_2C=CH_2 + H_2 \xrightarrow[\text{Ni,Pt or Pd}]{250\text{-}300^\circ C} CH_3-CH_3$$

(ethene) (ethane)

5.4.4.2 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.



(ethene) (1,2-dibromo ethene)

5.4.4.3 Hydrohalogenation

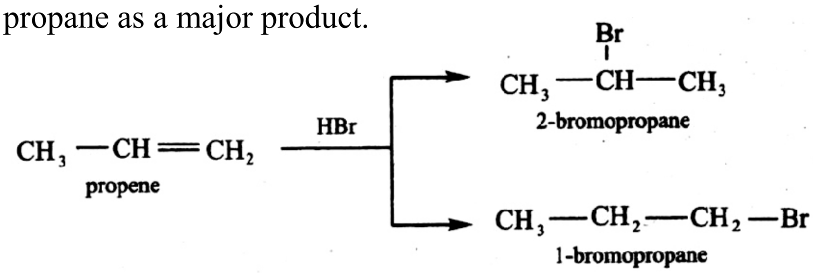
The addition of a halogen acid (HX) on an alkene to give an alkyl halide is known as hydrohalogenation of alkene.

$$CH_2=CH_2 + H-Br \longrightarrow CH_3-CH_2-Br$$

(ethene) (ethyl bromide)

The addition of halogen acid on an unsymmetrical 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.



$$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH(Br)-CH_3 \text{ (2-bromopropane)} + CH_3-CH_2-CH_2-Br \text{ (1-bromopropane)}$$

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

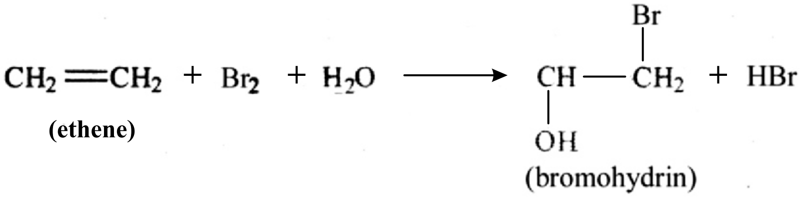
5.4.4.4 Hydration

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.

$$\underset{\text{(ethene)}}{H_2C=CH_2} + H_2O \xrightarrow[100°C]{H_2SO_4} \underset{\text{(ethyl alcohol)}}{CH_3-CH_2-OH}$$

5.4.4.5 Halohydration (confirmatory test for alkene)

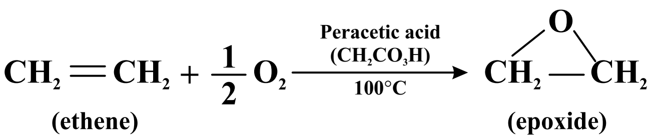
Halohydration is a reaction in which a halogen reacts with alkene in presence of water and forms halohydrin.



$$\underset{\text{(ethene)}}{CH_2=CH_2} + Br_2 + H_2O \longrightarrow \underset{\text{(bromohydrin)}}{CH(OH)-CH_2(Br)} + HBr$$

5.4.4.6 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.



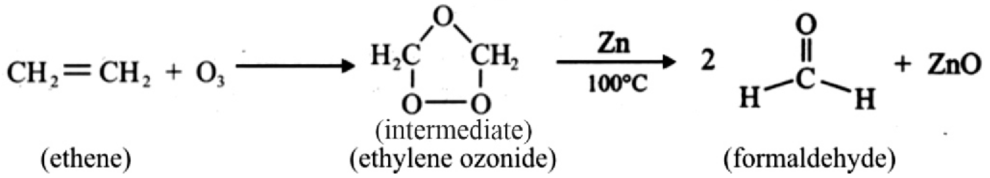
$$\underset{\text{(ethene)}}{CH_2=CH_2} + \frac{1}{2}O_2 \xrightarrow[100°C]{\text{Peracetic acid } (CH_3CO_3H)} \underset{\text{(epoxide)}}{CH_2-CH_2}$$

DO YOU KNOW?

Epoxides are used as versatile building blocks in the synthesis of pharmaceuticals, agrochemicals, and various fine chemicals, and they also serve as important intermediates in the production of polymers and surfactants.

5.4.4.7 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.

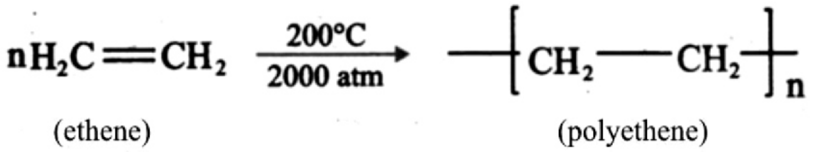


Self Assessment

What major product obtained when
- (i) Propene reacts with hydrogen iodide
- (ii) Ethene reacts with chlorine water
- (iii) Ethylene reacts with ozone

5.4.4.8 Polymerization

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



5.5 ALKYNES

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

5.5.1 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 Å

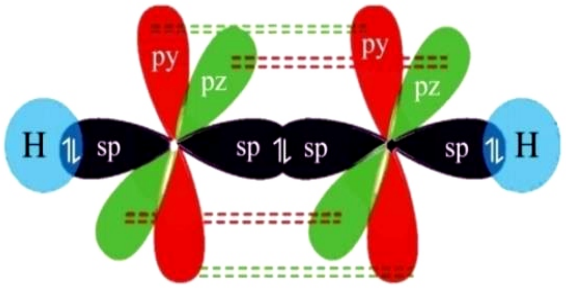


Fig. 5.3: Orbital structure of ethyne showing all sigma & pi bonds

5.5.2 Physical Properties

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

5.5.3 Preparation of Alkynes by elimination reaction

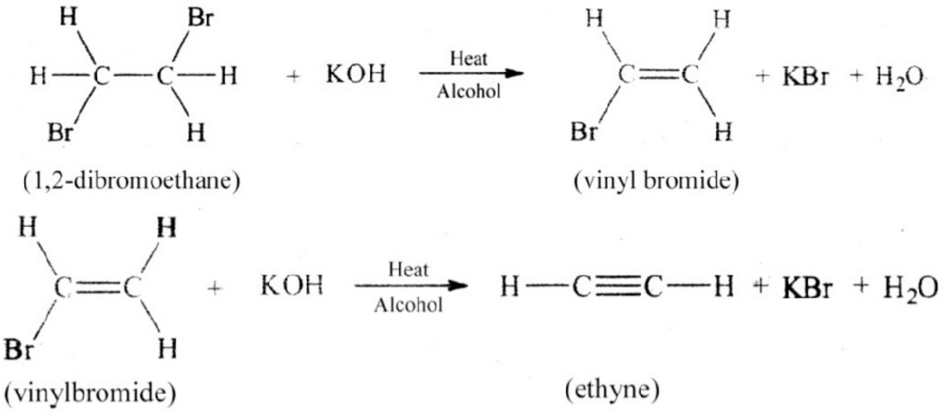
Alkynes are generally synthesized through elimination reactions, which involve the removal of atoms or groups from two adjacent carbon atoms.

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.

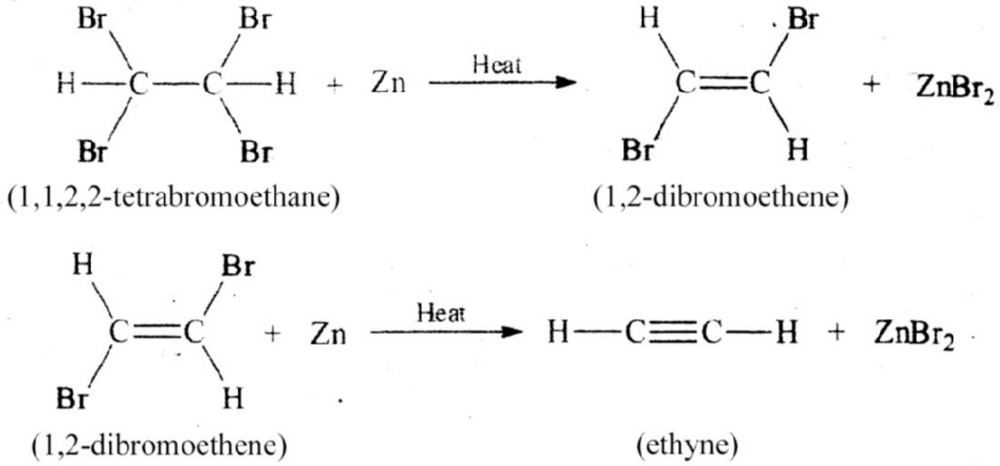
DO YOU KNOW?

When two halogen atoms are attached to two adjacent carbon atoms, it is called vicinal dihalide but if two halogen atoms are attached on the same carbon atom the molecule is said to be geminal dihalide.



Dehalogenation of Tetrahalides

A tetrahalide on heating with zinc dust forms ethyne.



5.5.4 Acidity of Terminal Alkynes

Hydrocarbons containing a triple bond on the terminal carbon, (ethyne, 1-propyne, 1-butyne etc) are characterized as weak acids.

The sp hybridization of carbon in terminal alkyne, such as ethyne, results in their slight acidity. The 50% s character of **sp** hybrid orbital of carbon makes it slightly electronegative. It cause the hydrogen atom attached to it to be slightly electro positive. This polarity weakens the C-H bond making it easier for a base to abstract the hydrogen atom from terminal carbon.

Table 5.1 s-character and pka values of ethane, ethene and ethyne

Hydrocarbon	Type of Hybridization	% s-character	pka value
Ethane	sp^3	25	-
Ethene	sp^2	33	44
Ethyne	sp	50	25

The acidic nature of terminal alkynes leads to their reaction with metal containing compounds including ammonical silver nitrate and ammonical cuperous chloride.

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_3} AgC \equiv CAg + 2H_2O$$

(silver acetylide)
(white ppt)

$$HC \equiv CH + Cu_2Cl_2 \xrightarrow{NH_3} CuC \equiv CCu + 2H_2O$$

(copper acetylide)
(red ppt)

Since silver acetylide and copper acetylide appear in the form of precipitates, these reactions are often used to identify terminal alkynes in the laboratory. It is also used to distinguish ethyne from ethene.

Self Assessment

How can you distinguish between an ethene and an ethyne by simple chemical test?

5.5.5 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.

The carbon-carbon triple bond in alkyne comprises of one sigma and two pi bonds, with the electron density between the carbon atoms being exceptionally high causing the atoms to be drawn closer together. As a result the electrons in the pi bonds are less exposed compared with the alkene. Consequently, alkynes exhibit lower reactivity than alkenes.

5.5.5.1 Hydrogenation

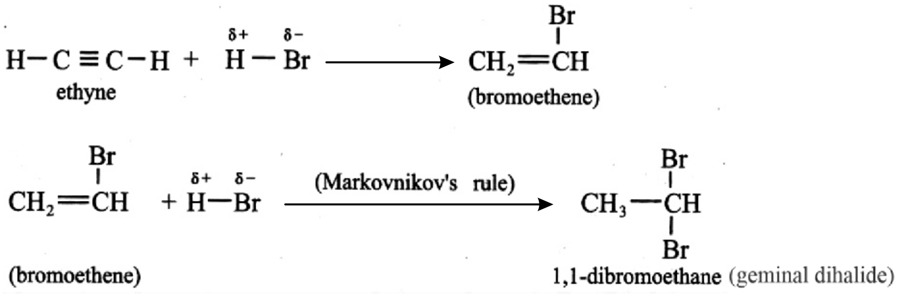
Alkyne reacts with hydrogen in the presence of metal catalysts such as nickel (Ni), platinum (Pt) and palladium (Pd) to give an alkene which then further reacts with another molecule of hydrogen to produce an alkane.

$$\underset{\text{(ethyne)}}{HC \equiv CH} + H_2 \xrightarrow[\text{Ni,Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethene)}}{H_2C = CH_2}$$

$$\underset{\text{(ethene)}}{H_2C = CH_2} + H_2 \xrightarrow[\text{Ni,Pt or Pd}]{250\text{-}300^\circ C} \underset{\text{(ethane)}}{CH_3 - CH_3}$$

5.5.5.2 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.



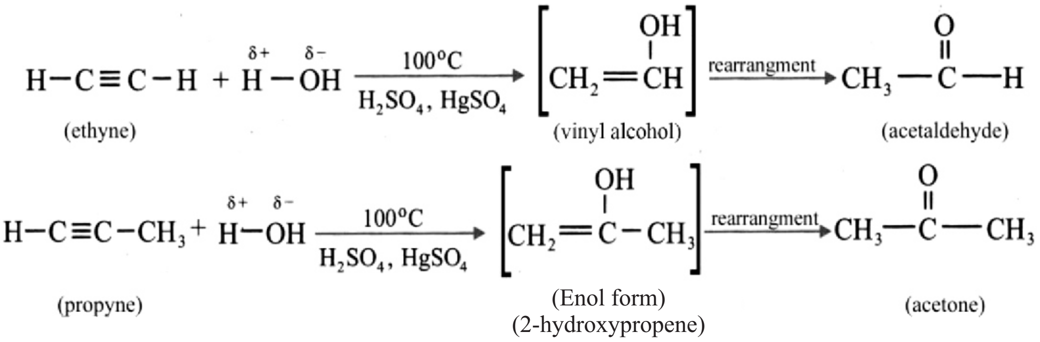
$$\underset{\text{ethyne}}{H-C\equiv C-H} + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow \underset{\text{(bromoethene)}}{CH_2{=}\overset{\overset{\large Br}{|}}{CH}}$$

$$\underset{\text{(bromoethene)}}{CH_2{=}\overset{\overset{\large Br}{|}}{CH}} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} CH_3-\underset{\underset{\large Br}{|}}{\overset{\overset{\large Br}{|}}{CH}}$$

1,1-dibromoethane (geminal dihalide)

5.5.5.3 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.



$$H-C\equiv C-H + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_2SO_4,\ HgSO_4]{100^\circ C} \left[CH_2=\overset{\overset{\displaystyle OH}{|}}{C}H\right] \xrightarrow{\text{rearrangment}} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H$$

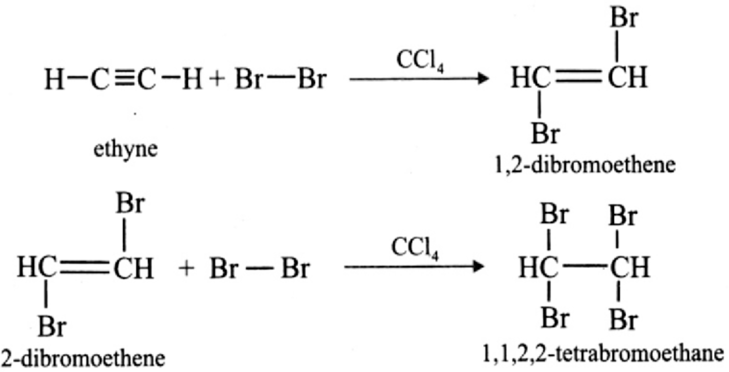
(ethyne) (vinyl alcohol) (acetaldehyde)

$$H-C\equiv C-CH_3 + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_2SO_4,\ HgSO_4]{100^\circ C} \left[CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3\right] \xrightarrow{\text{rearrangment}} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

(propyne) (Enol form) (2-hydroxypropene) (acetone)

5.5.5.4 Bromination

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



$$H-C\equiv C-H + Br-Br \xrightarrow{CCl_4} \underset{\underset{\displaystyle Br}{|}}{HC}=\overset{\overset{\displaystyle Br}{|}}{CH}$$

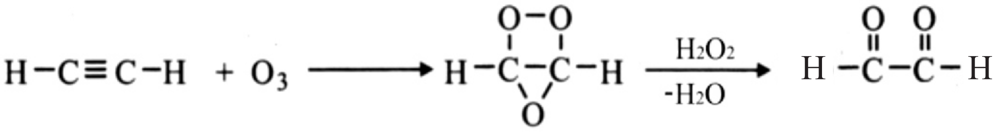
ethyne 1,2-dibromoethene

$$\underset{\underset{\displaystyle Br}{|}}{HC}=\overset{\overset{\displaystyle Br}{|}}{CH} + Br-Br \xrightarrow{CCl_4} \underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{HC}}-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle Br}{|}}{CH}}$$

1,2-dibromoethene 1,1,2,2-tetrabromoethane

5.5.5.5 Ozonolysis

Ozonolysis is a reaction in which the pi bonds between carbon-carbon atoms are broken down by the addition of ozone (O_3). The ozonolysis of an alkyne initially gives an ozonide, which subsequently undergoes oxidation with hydrogen peroxide. This oxidation results in the formation of glyoxal.



(ethyne) (ozonide) (glyoxal)

Table 5.2 **Comparison of the reactivity of alkanes, alkenes and alkyens**

Alkanes	Alkenes	Alkynes
Alkanes are chemically less reactive since the sigma bond between carbon-carbon requires high energy to break.	Alkenes are more reactive because the electron density of pi electrons spreads above and below the axis which offers an electrophile to attack on the substrate molecule.	Alkynes display higher reactivity than alkanes but lower reactivity than alkenes because pi electrons are not entirely exposed owing to the short length of triple bond.
They do not oxidized by $KMnO_4$.	They oxidize by $KMnO_4$.	They oxidize by $KMnO_4$.

5.6 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

5.6.1 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.

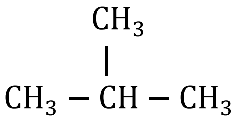
Chain isomers

"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.

$H_3C - CH_2 - CH_2 - CH_5$

(n – butane)



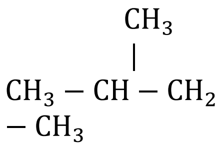
$$\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_3 \end{array}$$

(isobutene)

Similarly C_5H_{12} has the following three possible chain isomers.

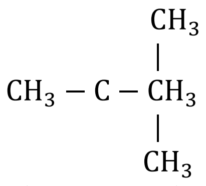
$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

(n - pentane)



$CH_3 - \underset{}{\overset{\overset{\displaystyle CH_3}{|}}{CH}} - CH_2 - CH_3$

(isopentane)



$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_3$

(neopentane)

Position isomerism

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

For example C_4H_8 has two position isomers.

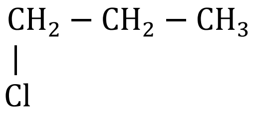
$CH_3 - CH = CH - CH_3$

(2 – butene)

$CH_3 - CH_2 - CH = CH_2$

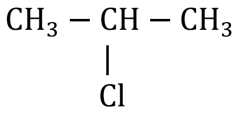
(1 – butane)

Similarly the two possible position isomers of C_3H_7Cl are given as.



$\underset{\underset{\displaystyle Cl}{|}}{CH_2} - CH_2 - CH_3$

(1 – chloropropane)



$CH_3 - \underset{\underset{\displaystyle Cl}{|}}{CH} - CH_3$

(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.

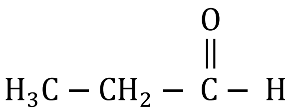
$CH_3 - CH_2 - OH$

(ethyl alcohol)

$CH_3 - O - CH_3$

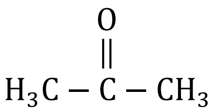
(Diethyl ether)

Another example of molecule exhibiting functional group isomerism is C_3H_6O.



$H_3C - CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - H$

(propanal)



$H_3C - \overset{\overset{\displaystyle O}{||}}{C} - CH_3$

(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 $C_4H_{10}O$ are.

$CH_3 - O - C_3H_7$
(methyl propyl ether)

$C_2H_5 - O - C_2H_5$
(Diethyl ether)

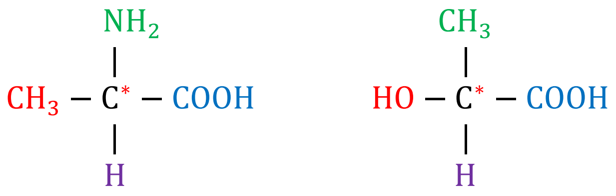
Self Assessment

- Draw the possible position isomers of C_4H_{10}, C_5H_{12}, C_4H_8, C_5H_{10}, C_4H_6, C_5H_8 with their IUPAC names.
- Draw the possible functional group isomers of C_2H_6O, C_3H_6O, $C_2H_4O_2$ with their IUPAC names.

5.6.2 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.



$$CH_3 - \overset{\overset{NH_2}{|}}{\underset{\underset{H}{|}}{C^*}} - COOH \qquad HO - \overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C^*}} - COOH$$

Fig 5.4: Structure of (a) amino acid and (b) lactic acid showing chiral carbon

5.6.3 Optical Activity

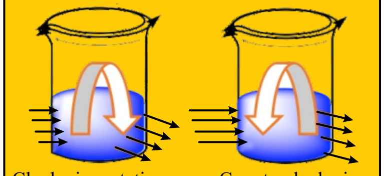
Light is composed of waves that vibrate in multiple planes, however when this light passes through a polarizer, the waves are restricted to a single plane of vibration and this is now called as plane of polarized light.

When a plane of polarized light is passed

DO YOU KNOW?

A racemic mixture is formed if both D and L isomers of a compound are present in equal amounts within a solution. The solution exhibits no rotation of polarized light.

A pair of enantiomer



Clockwise rotation (d) or (+) enantiomer dextrorotatory

Counterclockwise rotation (l) or (–) enantiomer levorotatory 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 5.5.

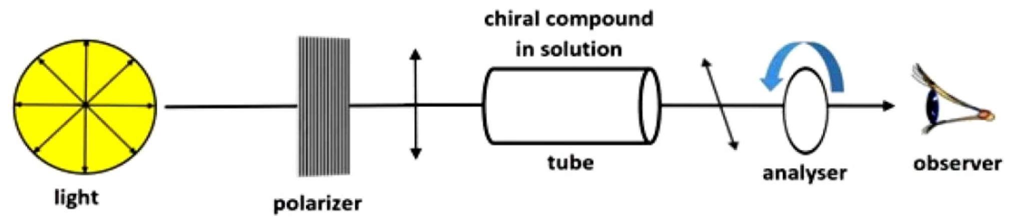


Fig 5.5: Components of a polarimeter

5.6.4 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 called optical isomers or 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 (Fig:5.6).

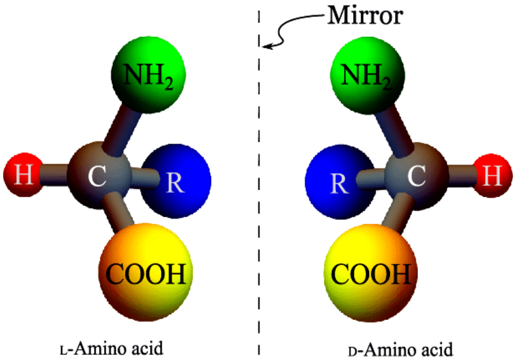


Fig 5.6: Enantiomers of amino acids

5.6.5 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 a type of stereo isomers and are found in the compounds having two different groups on double bonded carbon atoms. Both compounds have restricted movement of atoms of groups around double bond.

“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 (Fig:5.7).

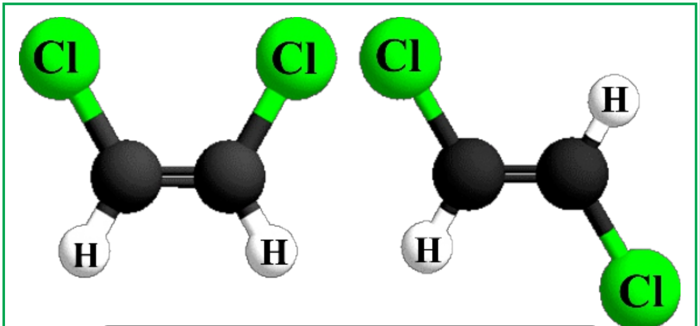


Fig 5.7: Cis and trans isomers of 1,2-dichloro ethene

5.7 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. Its molecular formula is C_6H_6. 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.

5.7.1 Physical Properties

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

5.7.2 Molecular orbital structure of benzene

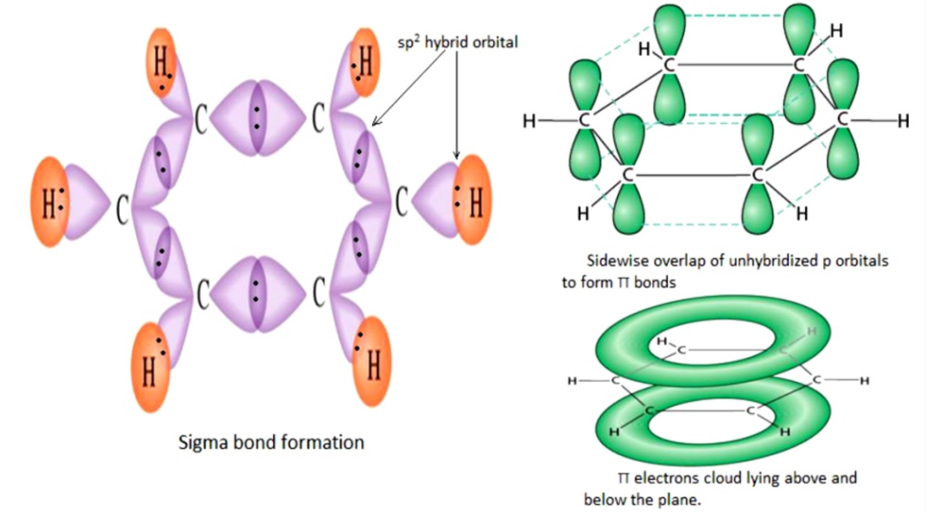
Benzene consists of six carbon atoms in a ring, each carbon is sp^2 hybridized and has three sp^2 hybrid orbitals.

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°. In benzene, the carbon-carbon (C-C) bond length as well as carbon-carbon double bond (C=C) length is approximately 1.39 Å.

DO YOU KNOW?

Delocalized pi electrons are not confined to a specific bond but instead spread out over a larger region of a molecule. Delocalized pi electrons are commonly found in molecules with alternate single and double bonds like benzene.

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 (Fig:5.8).



Sigma bond formation

Sidewise overlap of unhybridized p orbitals to form π bonds

π electrons cloud lying above and below the plane.

Fig 5.8: Molecular orbital structure of benzene showing sigma & pi bonds

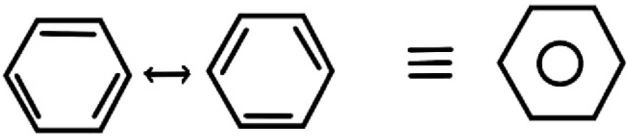
The molecular orbital structure of benzene provides the following information.

(i) Benzene is a planar hexagonal molecule.

(ii) Pi electrons of benzene are delocalized and responsible for the extra stability of molecule.

(iii) Actual structure of benzene is a hybrid of two resonating structures described by Kekule.

Kekule Structures



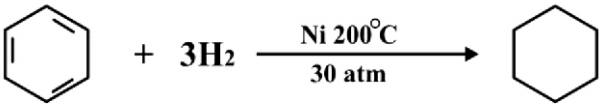
Two equivalent resonating structures of benzene   Resonance hybrid

5.7.3 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.

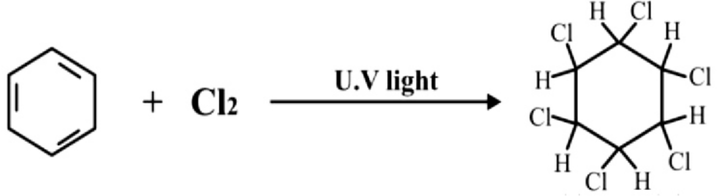


(Benzene)   (Cyclohexane)

Benzene, despite having six delocalized pi electrons in its six p orbitals, is less susceptible to addition reaction compared to alkenes and alkynes. The reason for this is that pi electrons in alkenes and alkynes are more localized between the two carbon atoms, making them more easily accessible for an electrophilic attack. In contrast, the pi electrons in benzene are highly delocalized, which makes it difficult for incoming electrophile to attack and add on the benzene ring. So far only the addition of hydrogen and chlorine to benzene has been observed.

Addition of Halogen

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



Hexachlorocyclohexane

Self Assessment

Benzene is highly unsaturated but it shows stability towards addition reaction. why?

5.7.4 Electrophilic substitution reactions of benzene

5.7.4.1 General Introduction

Electrophilic substitution reactions are a type of organic reaction in which an electrophile reacts with an electron-rich compound and replaces an electrophile in the compound. The six pi electrons of p orbital of benzene are spread out over all six carbon atoms, this makes benzene less reactive towards addition reactions and more reactive towards Electrophilic substitution reactions.

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

DO YOU KNOW?

Electrophile is an electron deficient species that seeks to gain an electron. Some common examples of electrophiles are chloro cation (Cl^+), alkyl cation (R^+), acyl cation (COR^+), nitronium ion (NO_2^+) and sulphonium ion (SO_3H^+).

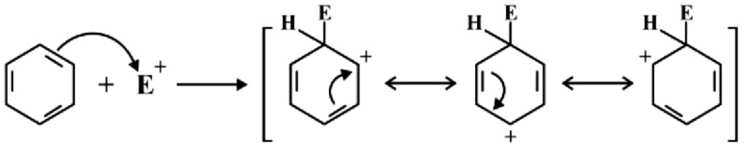
Step-1: Generation of an electrophile

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

$$E - Z + \text{Catalyst} \longrightarrow E^+ + [Z - \text{catalyst}]$$

Step-2: Formation of Arenium ion

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

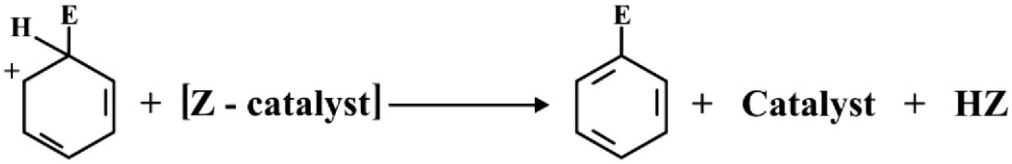


(Sigma complex)

In this attack, one carbon of benzene becomes sp^3 hybridized and hence the aromaticity of benzene has lost.

Step-3: Abstraction of proton

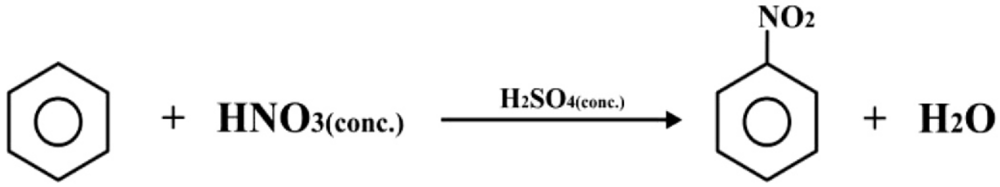
The unstable non aromatic arenium ion then loses a proton and changes into the product.



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

5.7.4.2 Nitration

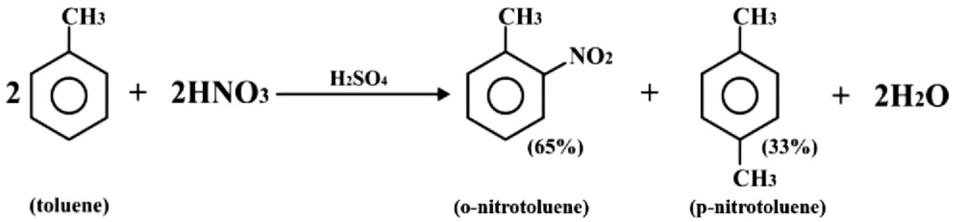
The reaction of benzene with conc. nitric acid to produce nitrobenzene is known as nitration. This reaction is carried out at 50°C in the presence of conc. sulphuric acid.



(benzene) (nitrobenzene)

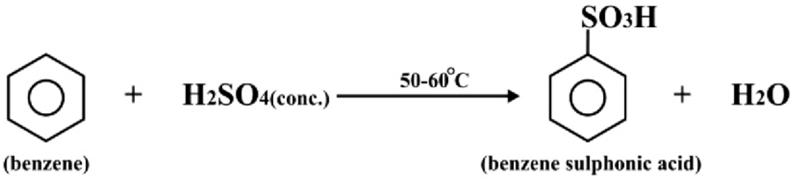
In this reaction, one hydrogen of benzene is replaced by a nitronium ion (NO_2^+).

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

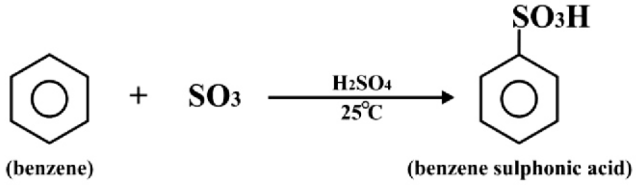


5.7.4.3 Sulphonation

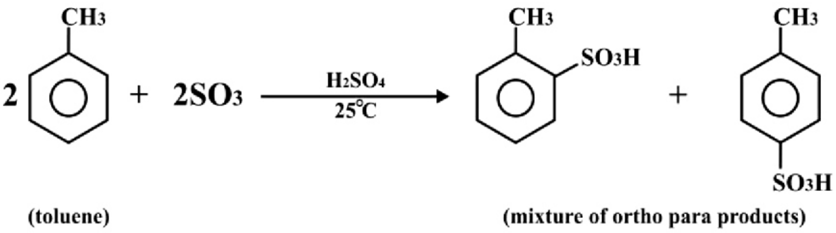
Benzene reacts with conc. sulphuric acid at 50 to 60°C to give benzene sulphonic acid.



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

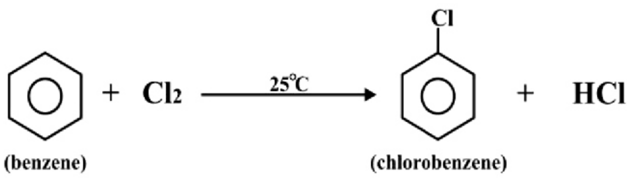


Sulphonation of toluene gives a mixture of ortho, para methyl benzene sulphonate.

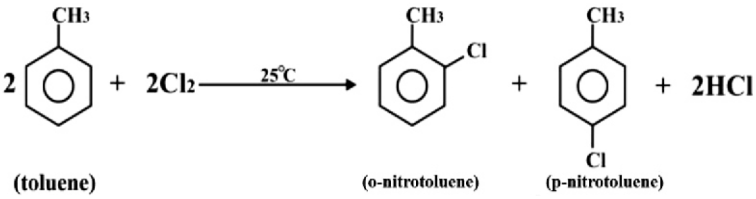


5.7.4.4 Halogenation

Benzene reacts with halogens (Cl_2, Br_2) at room temperature in the presence of a Lewis acid ($FeCl_3$) to give a halobenzene.

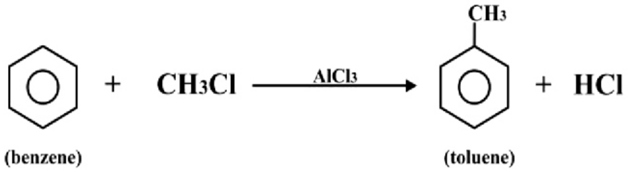


If toluene is allowed to undergo halogenations, it give a mixture of ortho, para chlorotoluene.

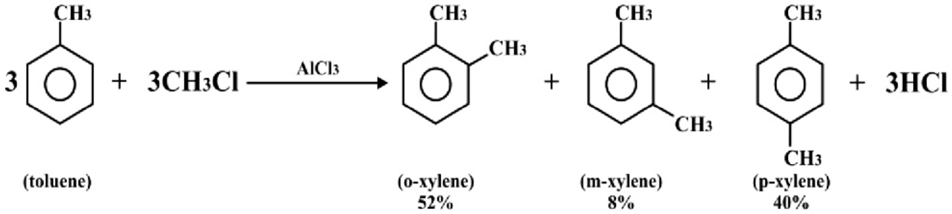


5.7.4.5 Friedal Craft Alkylation

Benzene undergoes reaction with an alkyl halide in the presence of a Lewis acid ($AlCl_3$) to produce an alkyl benzene.

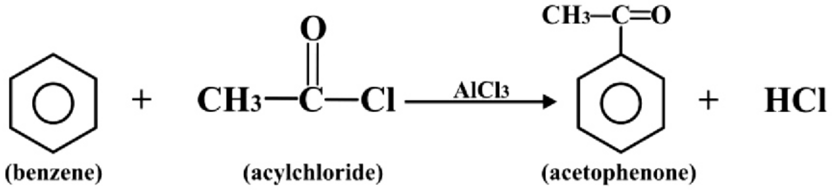


The reaction of toluene with an alkyl halide gives a mixture of ortho, para and meta products.

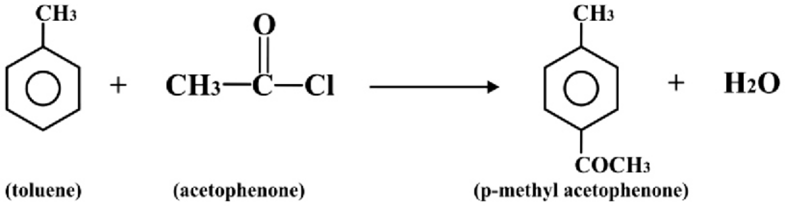


5.7.4.6 Friedal Craft Acylation

The reaction of benzene with an acylhalide (RCOCl) in the presence of lewis acid ($AlCl_3$) is known as Friedal Craft acylation.



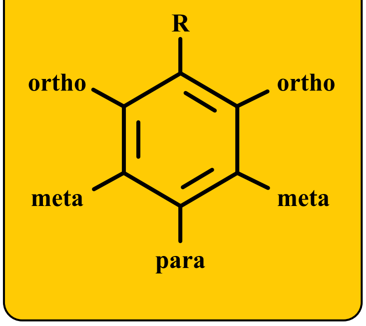
The attacking electrophile in this reaction is acyl cation (RCO^+) which is produced by the reaction of acyl chloride with Lewis acid ($AlCl_3$). Acylation of toluene give only the para product.



5.7.4.7 Substituent Effect

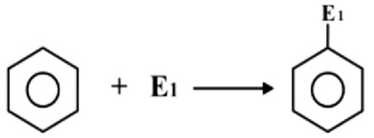
When an Electrophilic reagent reacts with benzene, a monosubstituted product is obtained because all the hydrogen atoms in benzene are equivalent and any one of them can be replaced by an external electrophile. However, if a second substituent is introduced into the benzene ring, it can be substituted at any one of the remaining hydrogen atoms and occupy one of three isomeric positions (ortho, para, meta) while it might be expected that the three isomers would be formed in approximately equal proportion, in reality, the percentage of each disubstituted product is quite different.

DO YOU KNOW?

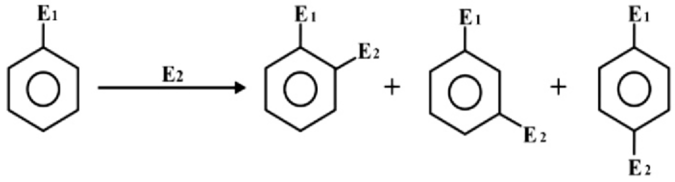


It is because the first substituent influences the position occupied by incoming Electrophilic reagent. **“The effect of the first substituent on the**

incoming electrophilic reagent is known as substitution effect or orientation of benzene”. Generally the substituent of mono substituted benzene provides a direction towards ortho-para or meta positions.



(benzene) (monosubstitude product)

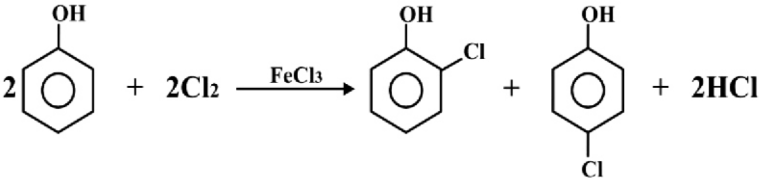


(monosubstitude product) (Ortho) (Meta) (Para)

(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 ortho, para director and when reacted with chlorine in presence of ferric chloride $(FeCl_3)$, it gives a mixture of ortho para chloro phenol.



(phenol) (o-chloro phenol) (p-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.

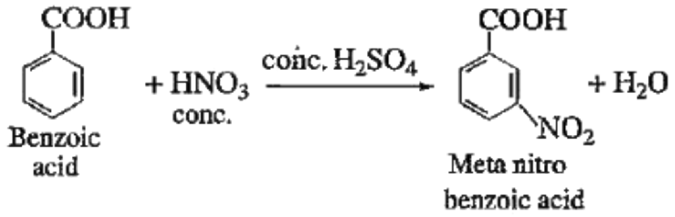


Table 5.3 **Comparative studies of ortho, para and meta directing group**

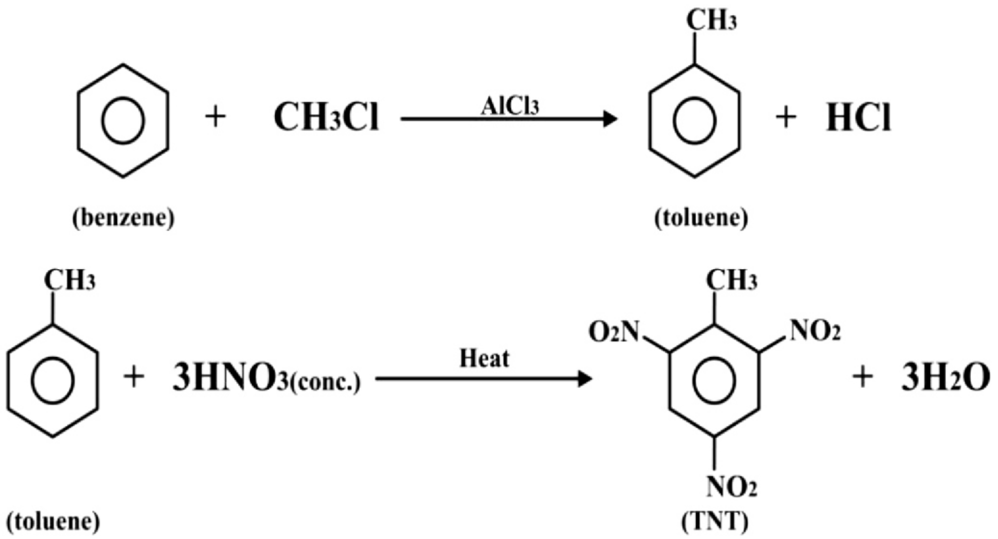
Ortho para directors	Meta director
They release electron to the aromatic ring and increasing the electron density on ortho para position.	They withdraw electron from benzene ring and decrease the electron density on ortho para position.
When they attached with the benzene rings they allow the incoming electrophilic reagent toward ortho and para positions.	When they attached with the benzene ring, they invite the incoming electrophilic reagent towards meta positions.
Example are $-R$, $-RCO$, $-OR$ $-Cl$, $-Br$, $-CH_3$, $-OH$ etc	Examples are $-COOR$, $-CHO$ $-COOH$,$-NO_2$,$-COCH_3$, $-SO_3H$ etc

5.7.4.8 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. When synthesizing a derivative of benzene, it is important to consider whether the electrophile already attached to the mono substituted benzene is meta directing or ortho para directing.

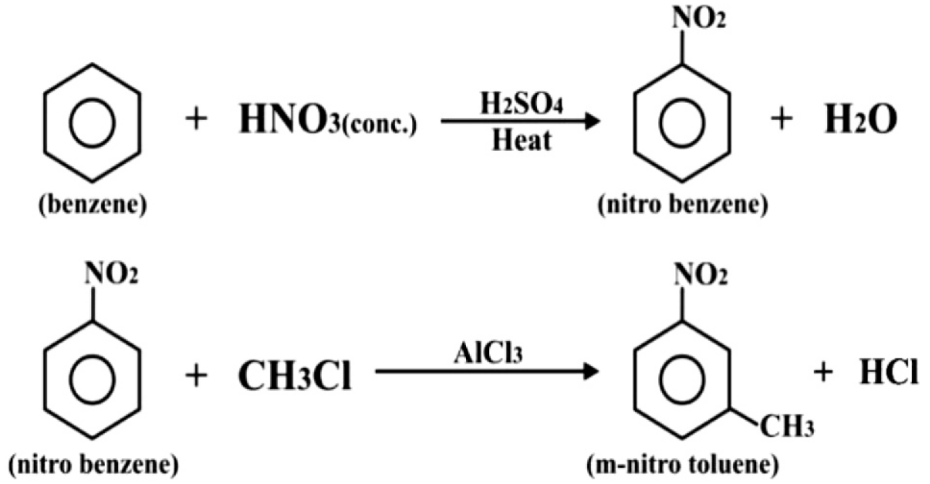
Preparation of trinitro toluene (TNT)

Trinitro toluene is an explosive organic material. During its preparation from benzene, the benzene is first converted into toluene and then toluene is treated with hot concentrated nitric acid. Since $-CH_3$ group of toluene is ortho para directing, it invites the NO_2^+ 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 $-CH_3$ group towards the meta position.



SOCIETY, TECHNOLOGY AND SCIENCE

Biofuel as energy need of Pakistan

The rising energy demand in Pakistan has led to a growing interest in exploring domestic and low cost alternatives. Biofuel is a type of renewable energy derived from organic material known as biomass.
There are three main biofuels manufacturing in Pakistan.

(i) Bio diesel: It is produced by animal fats and vegetable oils by special chemical process.

(ii) Bio gas: It is produced from cow dung and other organic wastes.

(iii) Bio ethanol: It is produced by the fermentation of starch or sugar.

SUMMARY

- Organic compounds which are made up of hydrogen and carbon atoms are known as hydrocarbons.
- In saturated hydrocarbons all carbon atoms are attached with each other by single bond only.
- In unsaturated hydrocarbons one or more double or triple bonds are present in the carbon chain.
- Aromatic compounds are characterized by a cyclic arrangement of atoms that are connected by alternating double bonds.
- The boiling point of straight chain alkanes is higher than branched chain alkanes.
- Cyclopropane is the smallest and simplest cycloalkanes with a ring composed of three carbon atoms and six hydrogen atoms.
- The cleavage of chemical bond takes place in the organic molecule either by homolytic fission or heterolytic fission.

- Alkenes are mostly prepared by dehydration of alcohol and dehydrohalogenation of alkyl halides.
- The higher reactivity of alkene as compared to alkane is attributed to the presence of a pi bond between the carbon atoms.
- Markovnikov's rule 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.
- The addition of oxygen to the double bond of alkene is known as epoxidation.
- 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.
- Polymerization of alkene involves the joining of many alkene monomers together to produce a polymer chain.
- All those alkynes which contain terminal hydrogen possess an acidic character.
- Organic molecules having the same molecular formula but differing in the way their atoms are connected to each other are called as structural isomers.
- A chiral centre is formed in a molecule when a carbon atom is bonded to four different atoms or groups.
- Two compounds having the same molecular formula and same structure but differing from each other by the optical rotation of plane polarized light are called optical isomers.
- Benzene, despite having six pi electrons in its six p orbitals, is less susceptible to addition reactions compared to alkenes and alkynes.

EXERCISE

Multiple Choice Questions

(i) The final product obtained when hydrogen bromide (HBr) is added to an ethyne molecule:
(a) Bromo ethene
(b) 1, 1-dibromo ethane
(c) 1,2-bromo ethane
(d) 1,1,2,2 tetra bromoethane

(ii) The formula of a saturated hydrocarbon is C_3H_6, it should be:
(a) Propane
(b) Propene
(c) Propyne
(d) Cyclopropane

(iii) Ozonide on heating with zinc dust produce:
(a) Alcohol
(b) Aldehyde
(c) Alkene
(d) Ether

(iv) Which of the following pairs of compounds represent functional group isomerism?
(a) 1-butene and 2-butene
(b) Ethanol and dimethyl ether
(c) n-butane and iso butane
(d) Diethyl ketone and methyl propyl ketone

(v) The substituent that can act as a meta director is:
(a) -Cl
(b) $-CH_3$
(c) -OH
(d) -COOH

(vi) Welding gas among the following is:
(a) Ethylene
(b) Acetylene
(c) Ethane
(d) Methane

(vii) Benzene burns with smokey flame because of its:
(a) Inflammability
(b) High carbon % age
(c) High resonance energy
(d) Aromaticity

(viii) Select the suitable chemical to distinguish between Ethene and Ethyne:
(a) Alkaline $KMnO_4$
(b) Acidified $KMnO_4$
(c) Bromine water
(d) Ammonical $AgNO_3$

(ix) Meta directing group among the following is:

(a) – OH (b) – NH_2
(c) – CH_3 (d) – NO_2

(x) Acylation of benzene in the presence of $AlCl_3$ gives:

(a) Toluene (b) Acetophenone
(c) Phenol (d) Xylene

Short Questions

1. Give three differences between aliphatic and aromatic hydrocarbons?
2. Give the mechanism of free radical reaction between methane and chlorine in the presence of sunlight.
3. Complete the following reactions and name the major product formed in each reaction.

$$C_2H_5OH \xrightarrow{H_2SO_{4(conc.)}\ 170^\circ C}$$

$$C_2H_5Br + KOH \xrightarrow{\text{Alcohol, heat}}$$

$$CH_3 - CH = CH_2 + HBr \longrightarrow$$

$$CH_2 = CH_2 + O_3 \longrightarrow$$

4. Define a chiral carbon? Give an example to justify your answer.
5. Write the equations with all required conditions for the reaction of benzene with the following:

(i) H_2 (ii) CH_3COCl (iii) $HNO_{3(conc.)}$ (iv) $H_2SO_{4(conc.)}$

6. Bring about the following conversions.
   (i) Toluene to ortho-para nitro benzoic acid
   (ii) Benzene to m-nitro toluene

7. How can you prepare ethene from dehydration of ethanol and ethyne from dehydro halogenations of ethyl chloride?
8. Alkanes are generally referred as parafins due to their less reactivity, why are they stable towards chemical reactions?

Descriptive Questions

1. Draw the orbital structures of the following hydrocarbons.
   (i) Ethane (ii) Ethylene (iii) Acetylene
2. Write the equations of the following chemical processes.
   (i) Ethylene is heated at high temperature and pressure.
   (ii) Ethene is burnt in air in the presence of per acetic acid.
   (iii) 1,2-di bromo butane is heated with alcoholic potassium hydroxide.
   (iv) 1,1,2,2 tetra bromo ethane is heated with zinc powder.
   (v) Reaction of chlorine with acetylene
3. Ethene is more reactive than ethane but less reactive than ethyne, how can you explain this behavior?
4. What is meant by isomerism? Explain four different types of structural isomers and give one example of each.
5. Explain the following with suitable examples.
   (a) Optical isomers (b) Geometrical isomers
6. Describe the molecular orbital structure of benzene.
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.
9. Why ethyne terminal hydrogen is acidic in nature? Give two reactions of ethyne to show their acidic behavior.