CHAPTER 5 INTRODUCTION TO HYDROCARBONS

Organic compounds which are made up of hydrogen and carbon atoms are known as hydrocarbons.

TYPES OF HYDROCARBONS

Aliphatic Hydrocarbons

Those hydrocarbons which contain a straight or branched chain are called aliphatic hydrocarbons. Carbon atoms maybe bonded through single, double or triple covalent bond. They are also called open chain hydrocarbons. The word 'Aliphatic' comes from 'fat' because these hydrocarbons were first extracted from fats and oils.

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

Saturated Hydrocarbons:

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

They are further classified into alkanes and cyclo alkanes.

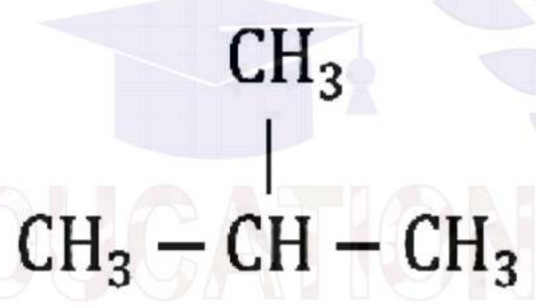
The general formula of alkanes is C_nH_{2n+2}

The general formula of cyclo alkanes is C_nH_{2n}

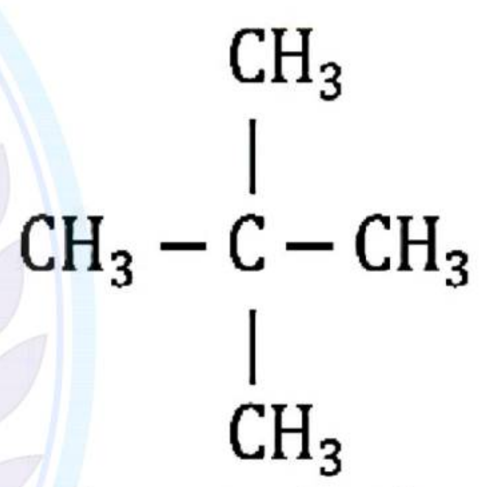
For example:

$$H_3C-CH_2-CH_2-CH_3$$

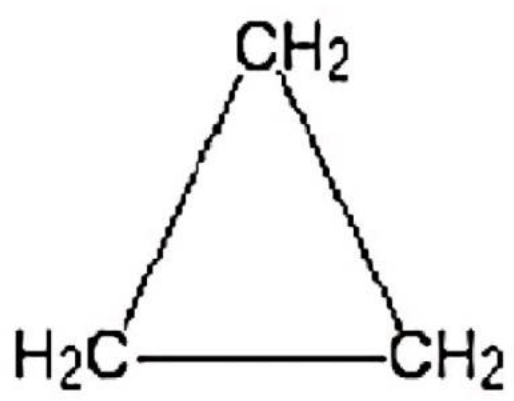
(n – butane)



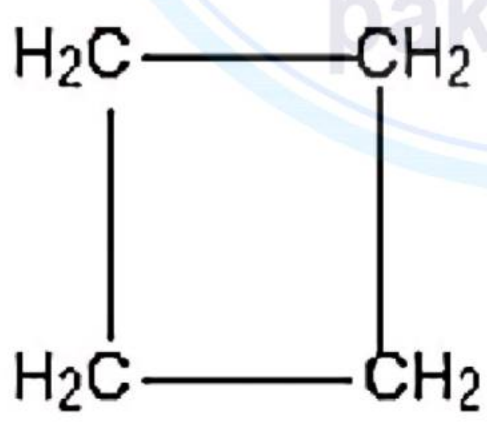
(iso butane)



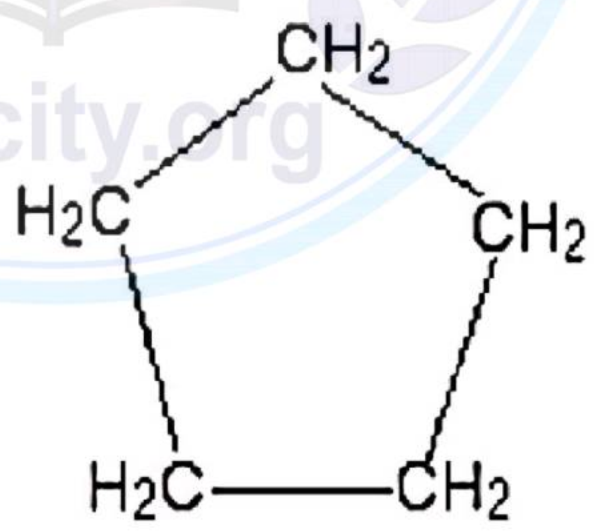
(neo pentane)



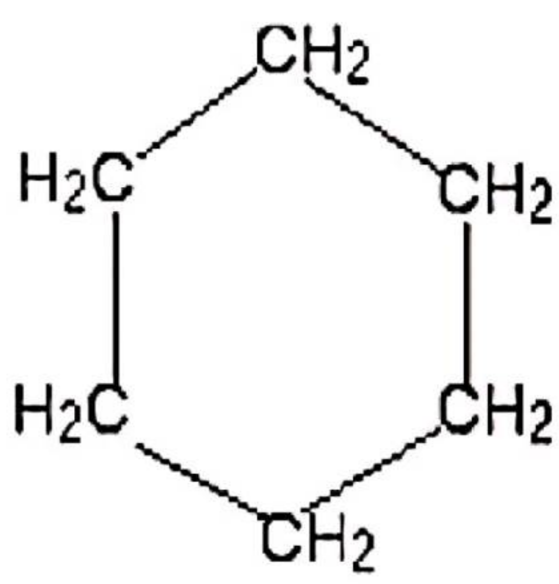
(cyclopropane)



(cyclobutane)



(cyclopentane)



(cyclohexane)

Saturated 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 alkanes and alkynes. The general formula for their homologous series is $\mathbf{C_nH_{2n}}$ and $\mathbf{C_nH_{2n-2}}$ respectively.

For example:

$CH_2 = CH - CH_3$ **(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

C_3H_6 → Unsaturated Hydrocarbon

C_7H_{12} → Unsaturated Hydrocarbon

C_8H_{18} → Saturated Hydrocarbon

C_5H_{10} → Unsaturated Hydrocarbon

C_5H_8 → Unsaturated Hydrocarbon

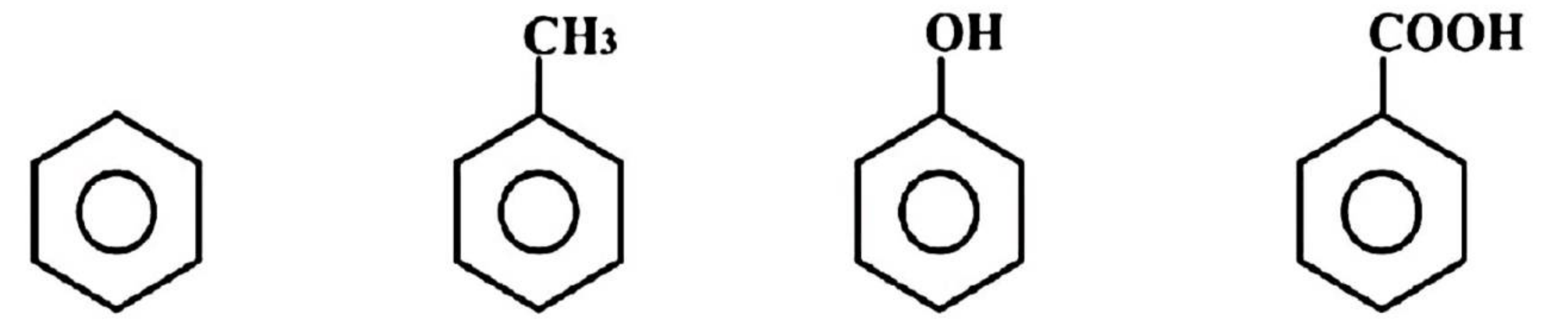
Aromatic Hydrocarbons

The term aromatic originates from Greek word "aroma" which means fragrance, 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.

"Aromatic hydrocarbons are those which are characterized by a cyclic arrangement of atoms that are connected by alternating double bonds, they generally follow the Huckle's rule (4n+2 π electrons.)"

Huckle's Rule: It 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.

Few examples of aromatic compounds are as follows:



(Benzene) (Toluene) (Phenol) (Benzoic acid)

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 more than branched chain alkanes.

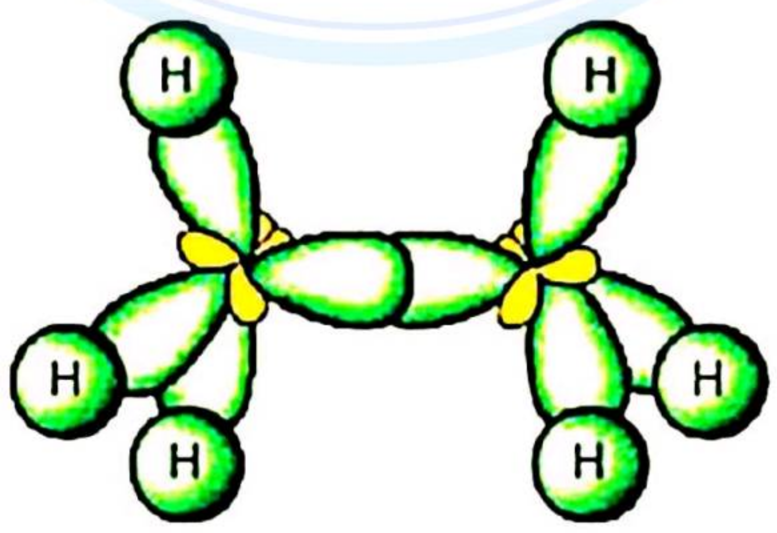
(iv) Alkanes which consist of C_1 to C_4 are gases C_5 to C_{17} are liquids and above C_{17} are waxy solids.

Structure of Alkanes

STRUCTURE OF ETHANE (C_2H_4)

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°.



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.

SUBSTITUTION REACTIONS:

Saturated hydrocarbons always undergo substitution reactions. Sigma bond breaks down in free radical reactions. In this reaction, a hydrogen is substituted by any other atom or group of atoms which is called substituent. Substituents may be a free radical, electrophile or nucleophile.

TYPES OF SUBSTITUTION REACTIONS:

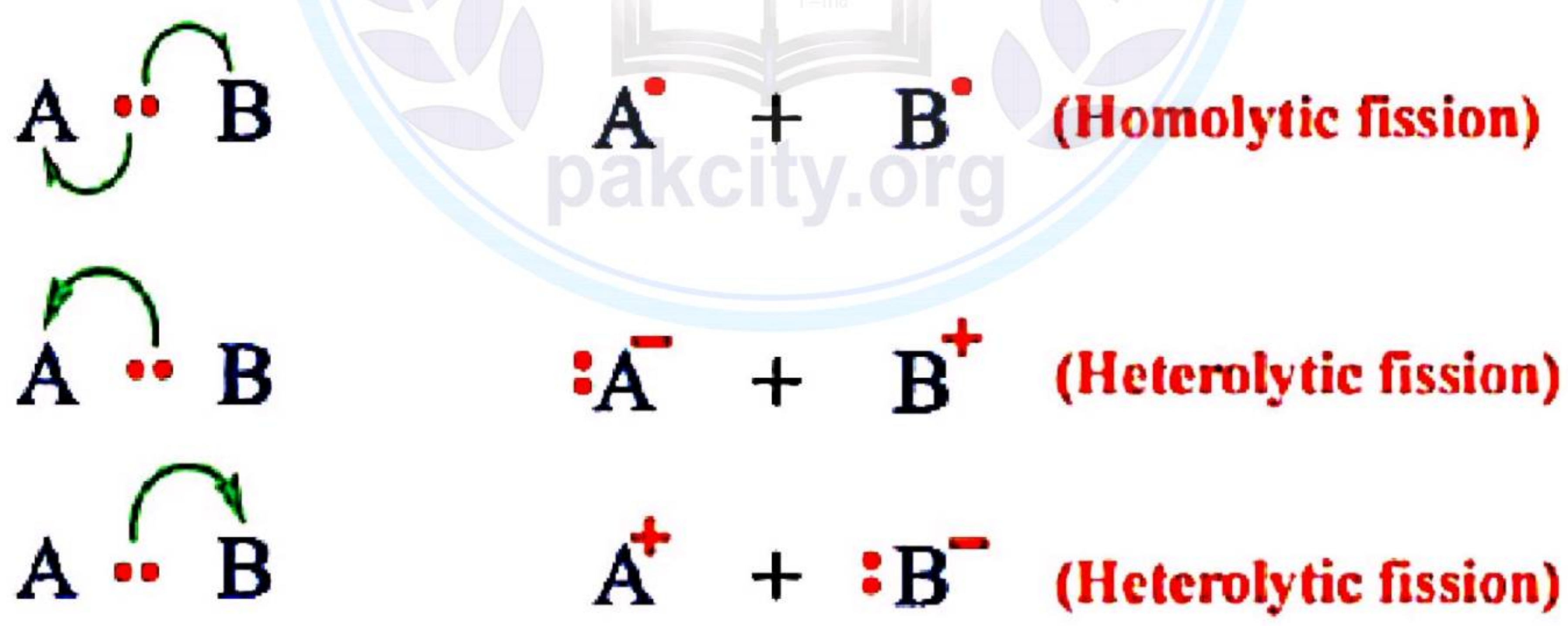
There are three types of substitution reactions.

(i) Free Radical substitution reactions → Characteristic reactions of alkanes

(ii) Electrophilic substitution reactions → Characteristic reactions of Benzene

(iii) Nucleophilic substitution reactions → Characteristic reactions of Alkyl halides

"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.



FREE RADICAL SUBSTITUTION REACTIONS:

Free radical substitution reactions are typically carried out by homolytic fission. The reaction between methane and chlorine in UV light takes place through free radical reaction.

The mechanism of free radical consists of three steps.

Step-1: Chain Initiation

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

$$Cl : Cl \xrightarrow{\text{U.V. light}} Cl\cdot + Cl\cdot$$

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.

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

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

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

Overall Reaction:

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

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

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

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

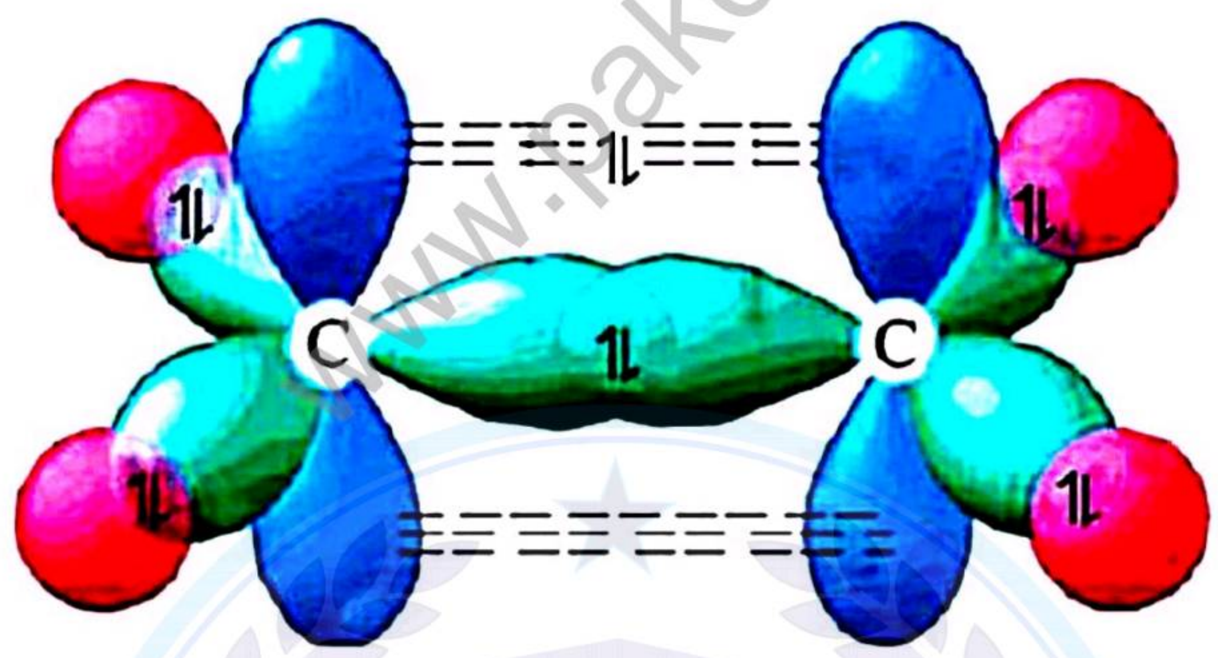
ALKENES

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

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

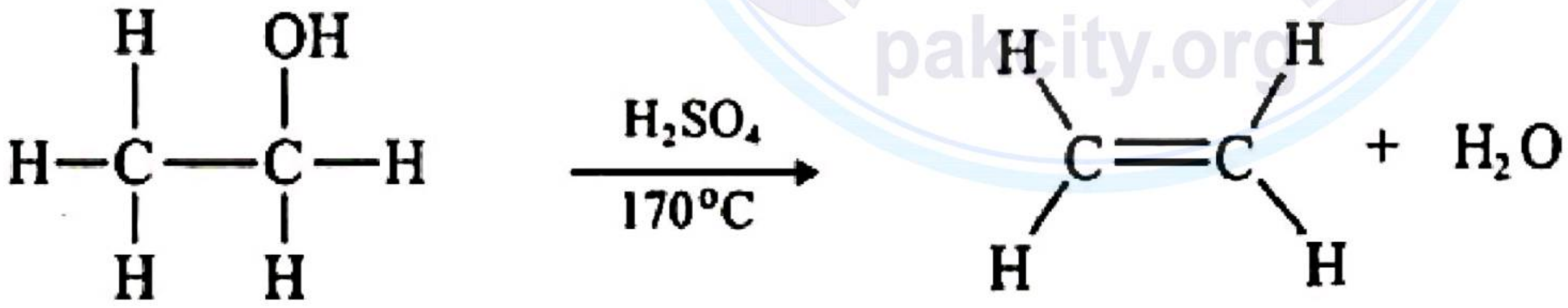
The structure of ethene is characterized by two sp^2 hybrid carbon atoms that are arranged in a trigonal planar geometry. The double bond between the carbon atoms is composed of a sigma bond, which arises from the overlap of two sp^2 hybrid orbitals from each carbon atom and a pi bond which forms due 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.



Preparation of Alkenes

1. Dehydration of Alcohol:

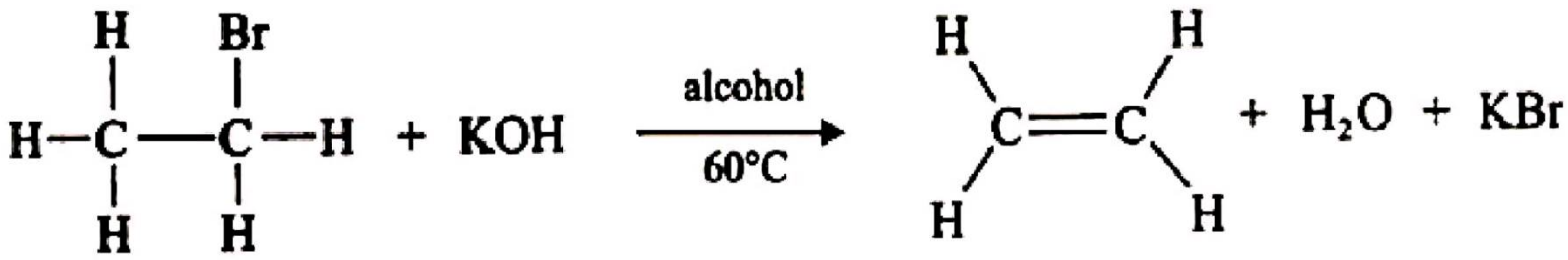
When an alcohol is heated in the presence of a dehydrating agent such as concentrated sulphuric acid, it undergoes elimination of water molecule and gives an alkene.



(alcohol) (ethene)

2. Dehydrohalogenation of 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)

Reactivity of Alkenes

Alkenes are more reactive than alkanes due to the presence of π bond. π bonds are weaker than σ bonds that's why they can easily be broken by providing a very little amount of energy. Alkenes undergo addition reactions due to the cleavage of pi bonds. They follow electrophilic addition reaction mechanism.

Reactions of Alkenes

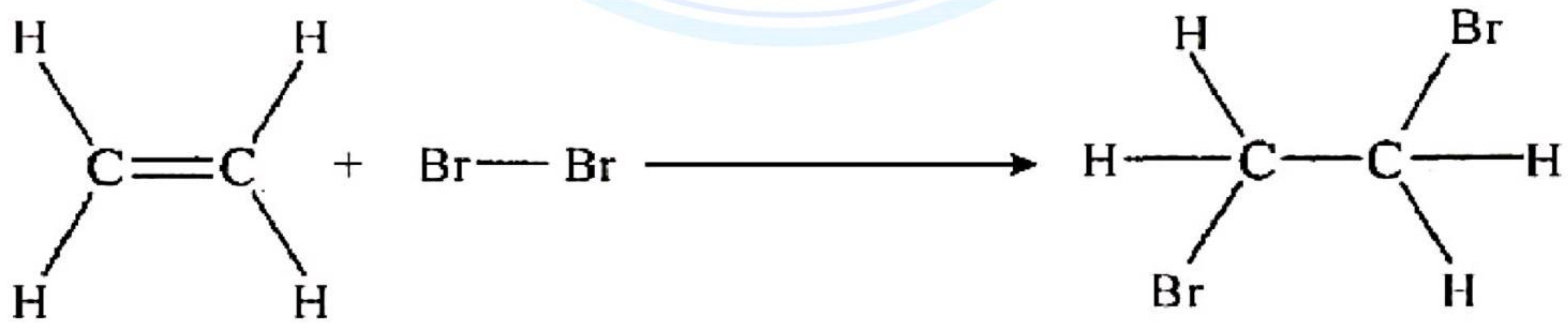
1. Hydrogenation:

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.

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

2. Halogenation:

In this reaction, a halogen (X_2) such as Cl_2 or Br_2 is added to produce 1,2-dihaloalkane or vicinal dihalide.



(ethene) (1,2-dibromo ethene)

3. Hydrohalogenation:

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

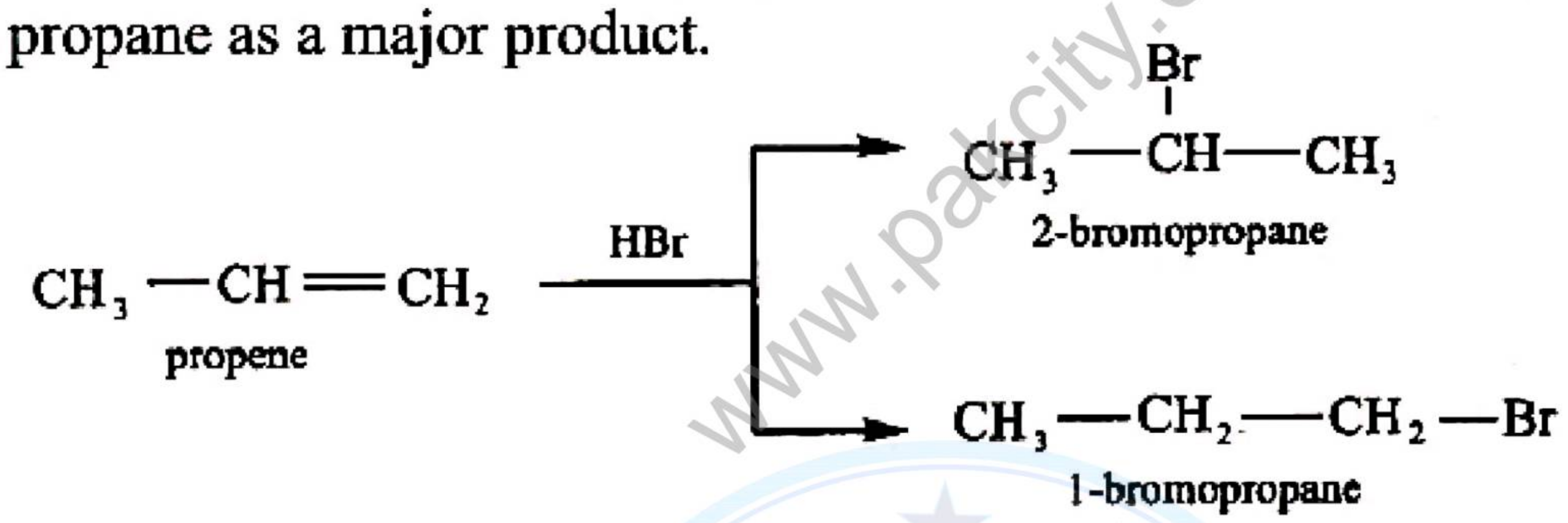
$$\underset{\text{(ethene)}}{CH_2=CH_2} + H-Br \longrightarrow \underset{\text{(ethyl bromide)}}{CH_3-CH_2-Br}$$

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

Markovnikov's Rule:

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.



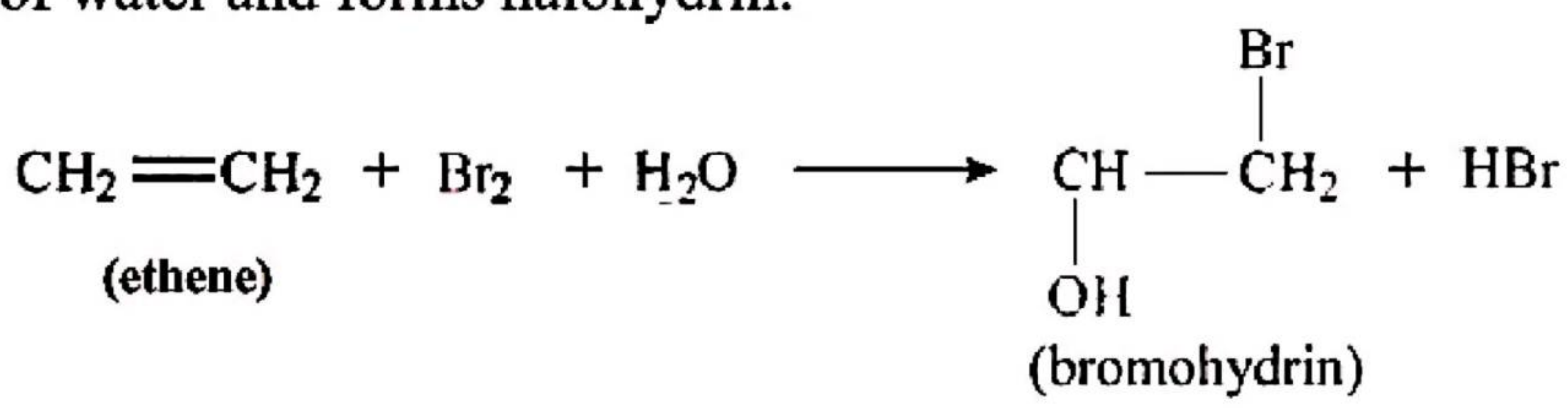
4. Hydration:

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.

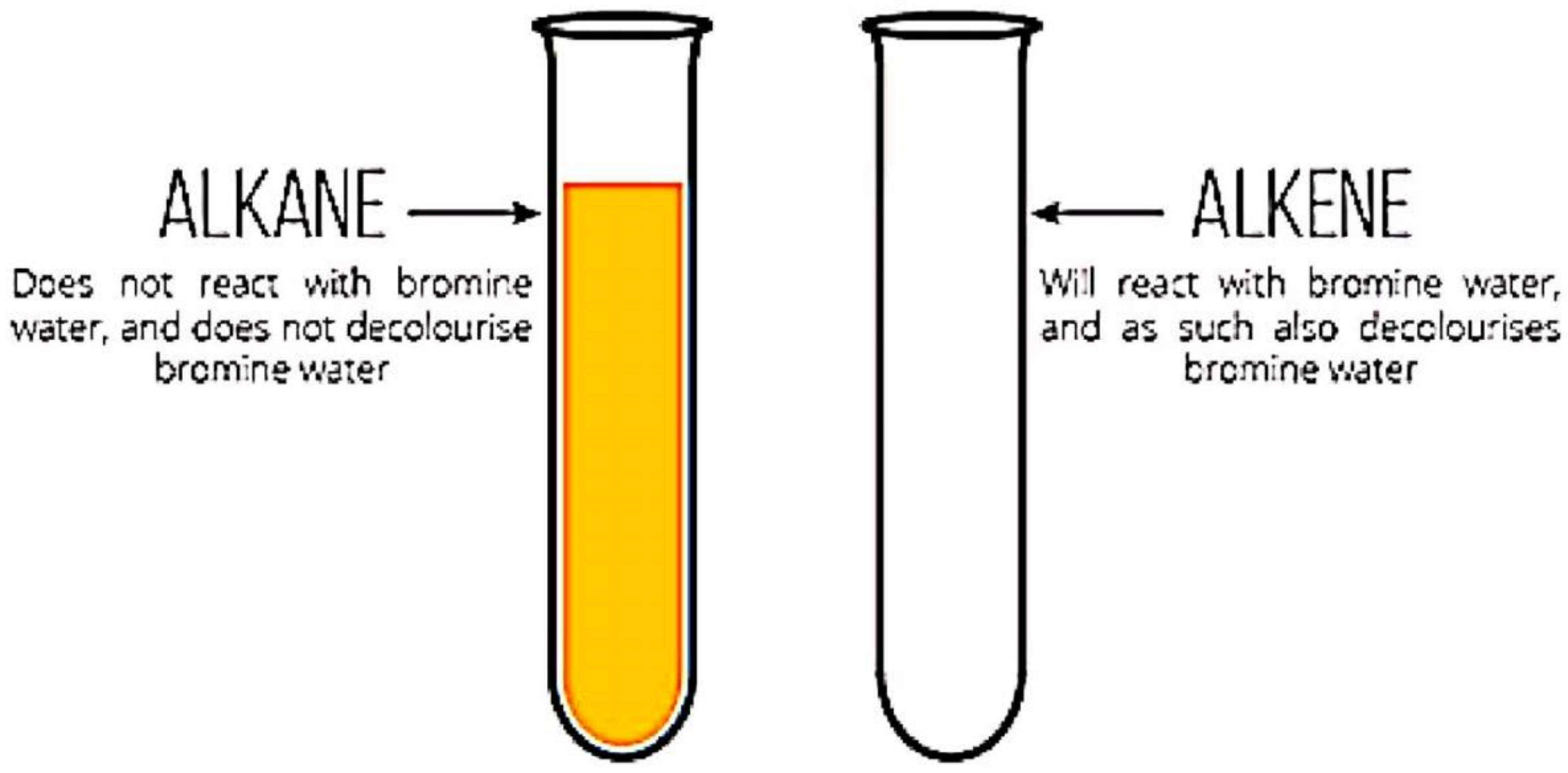
$$\underset{\text{(ethene)}}{H_2C=CH_2} + H_2O \xrightarrow[100^\circ C]{H_2SO_4} \underset{\text{(ethyl alcohol)}}{CH_3-CH_2-OH}$$

5. Halohydration: (Confirmatory Test for Alkene or Unsaturation Test)

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



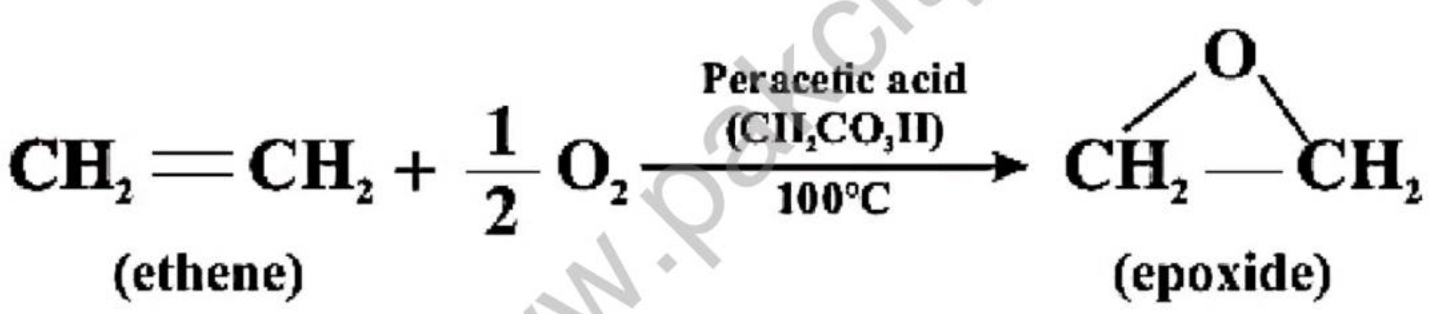
Brown color of bromine water decolorizes in this reaction. When alkane in treated with bromine water then brown color of bromine water does not discharge which confirms the absence of π bond in it.



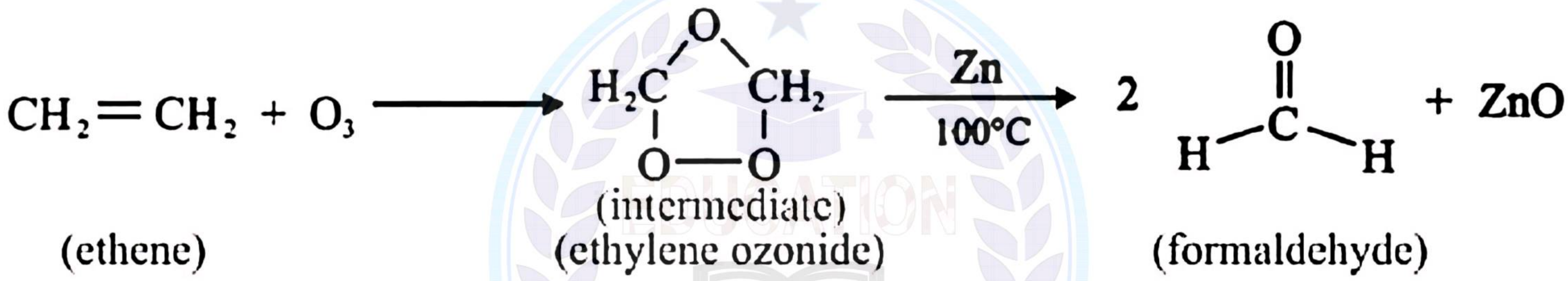
ADDITION OF BROMINE WATER TO ALKANES & ALKENES

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.



7. Ozonolysis:



8. Polymerization:

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

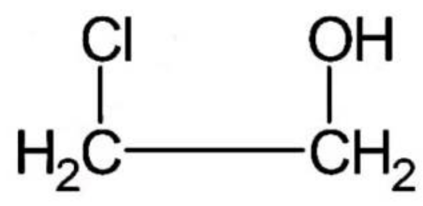
$$nH_2C{=}CH_2 \xrightarrow[2000\ \text{atm}]{200^\circ C} \left[CH_2 - CH_2 \right]_n$$

(ethene) (polyethene)

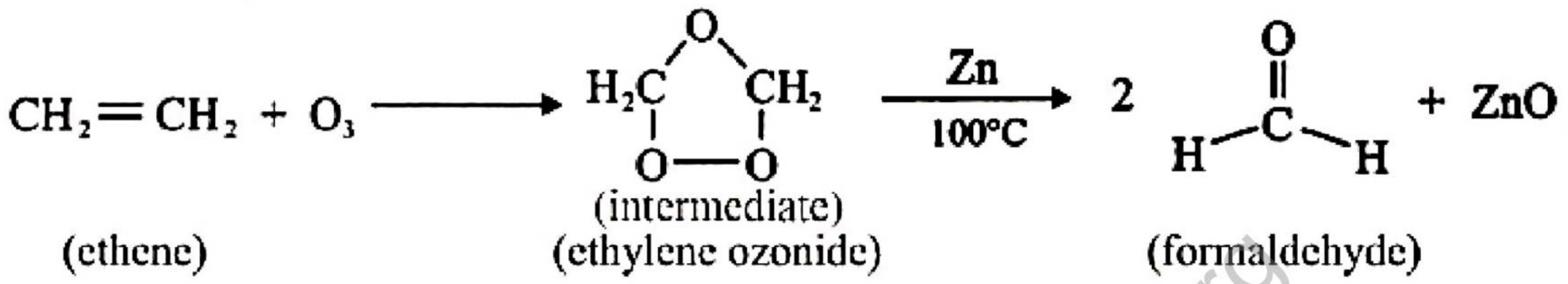
Self Assessment

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

i) $C_3H_6 + HI \rightarrow C_3H_7I$ (Propyl iodide / iodo propane)

ii) $C_2H_4 + Cl_2 + H_2O \rightarrow$ 

(Chloro Hydrin)

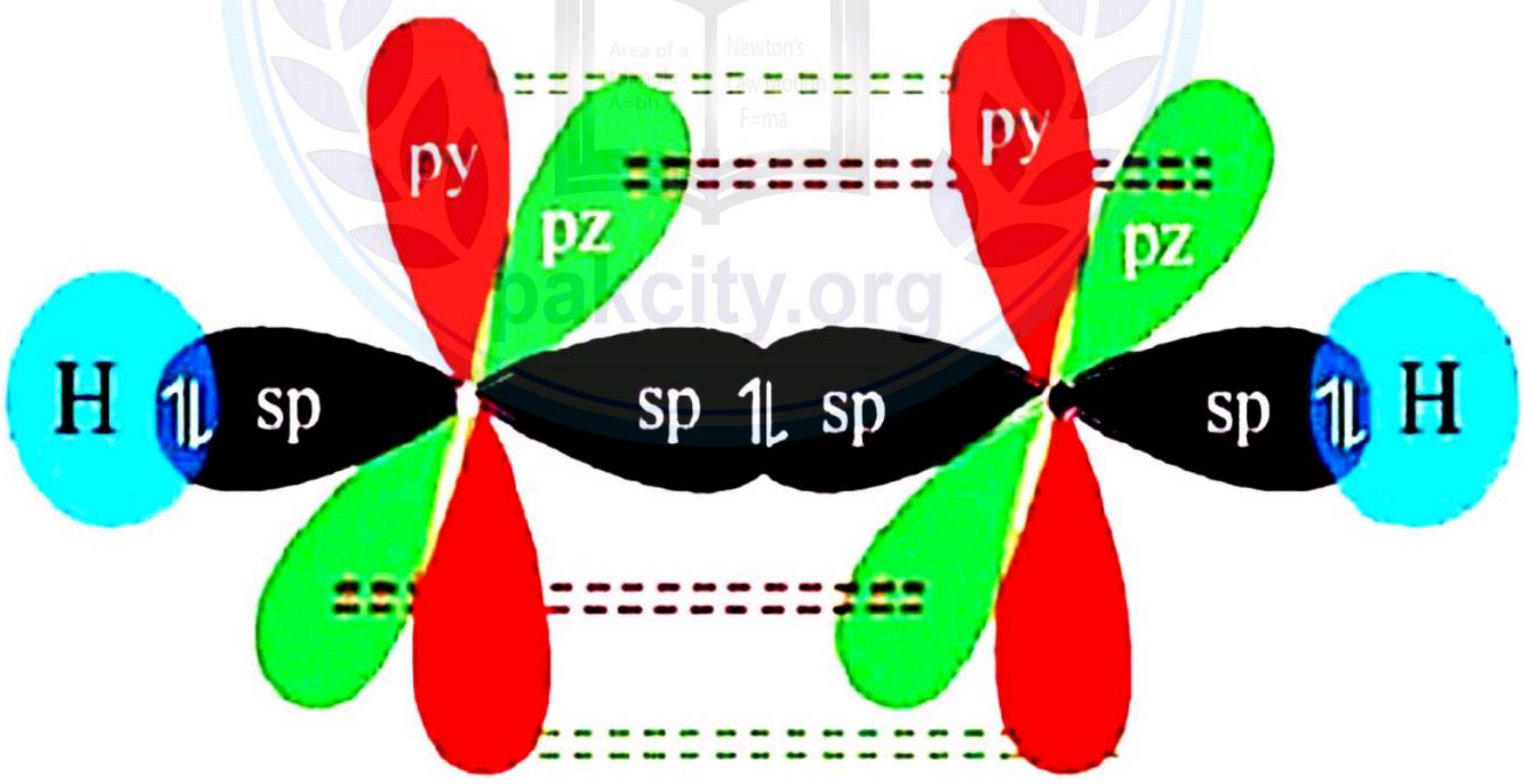
iii) 

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°.

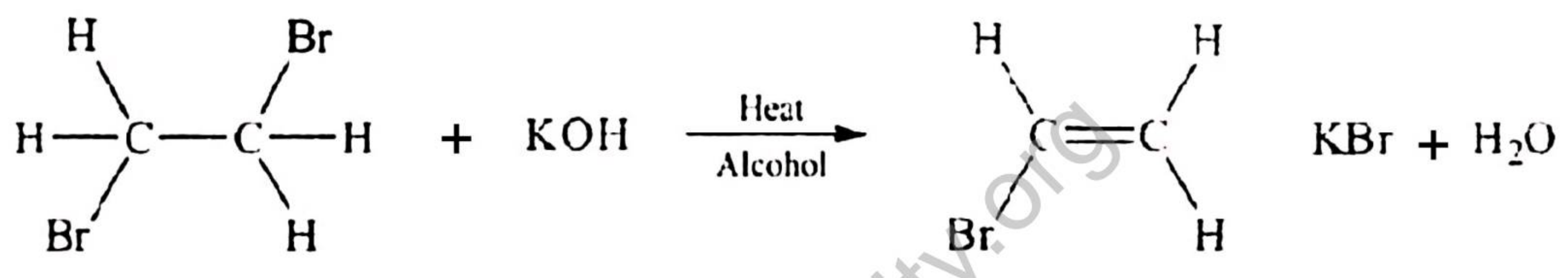


PHYSICAL PROPERTIES OF ALKYNE:

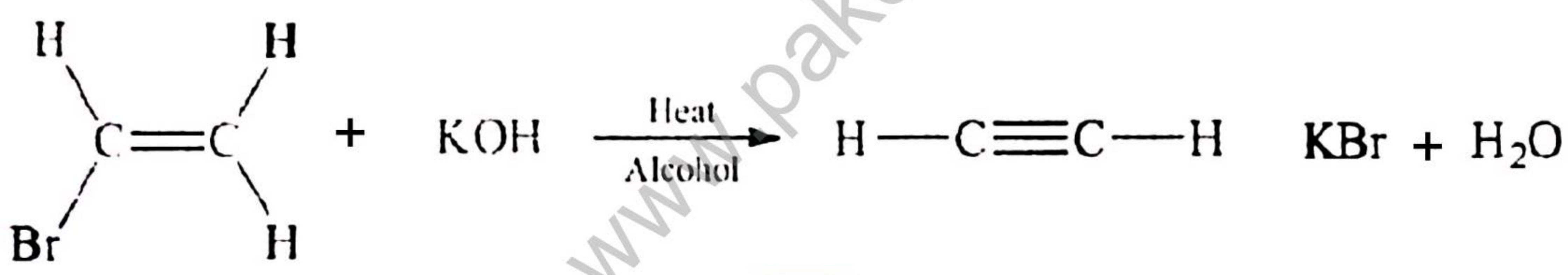
- Alkynes are colourless and odourless except for acetylene gas which has garlic like odour.
- Alkynes are insoluble in water but soluble in the organic solvents like acetone, ether, Ethyl acetate etc.
- Melting and boiling points increase with increasing molecular mass of alkynes.
- First three members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

PREPARATION OF ALKYNE:

1. Dehydrohalogenation of Vicinal dihalides:



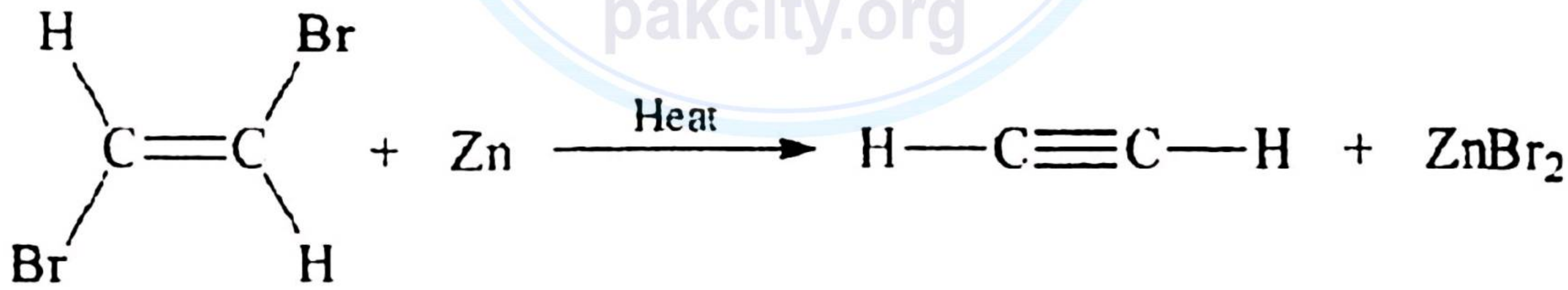
(1,2-dibromoethane) (vinyl bromide)



(vinylbromide) (ethyne)

2. Dehalogenation of tetrahalides:

(1,1,2,2-tetrabromoethane) (1,2-dibromoethene)



(1,2-dibromoethene) (ethyne)

CHEMICAL PROPERTIES OF ALKYNE:

Acidity of Terminal Alkynes

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

In terminal alkynes, the hydrogen is bonded to sp hybridized carbon atom which is more strongly bonded to other carbon atom with a sigma and 2 pi bonds. Due to this the sigma bond between terminal hydrogen and carbon becomes weaker and it is easily lost.

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_3} \underset{\text{(silver acetylide) (white ppt)}}{AgC \equiv CAg} + 2H_2O$$

$$HC \equiv CH + Cu_2Cl_2 \xrightarrow{NH_3} \underset{\text{(copper acetylide) (red ppt)}}{CuC \equiv CCu} + 2H_2O$$

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?

Ethene and ethyne can be distinguished by acidic character test. Ethyne is acidic nature so it will form precipitates which ethene is not acidic so it cannot form precipitates.

$$HC \equiv CH + 2AgNO_3 \xrightarrow{NH_3} \underset{\text{(silver acetylide) (white ppt)}}{AgC \equiv CAg} + 2H_2O$$

$C_2H_4 + AgNO_3 \rightarrow$ No white precipitates

Addition reaction of alkynes

1. Hydrogenation:

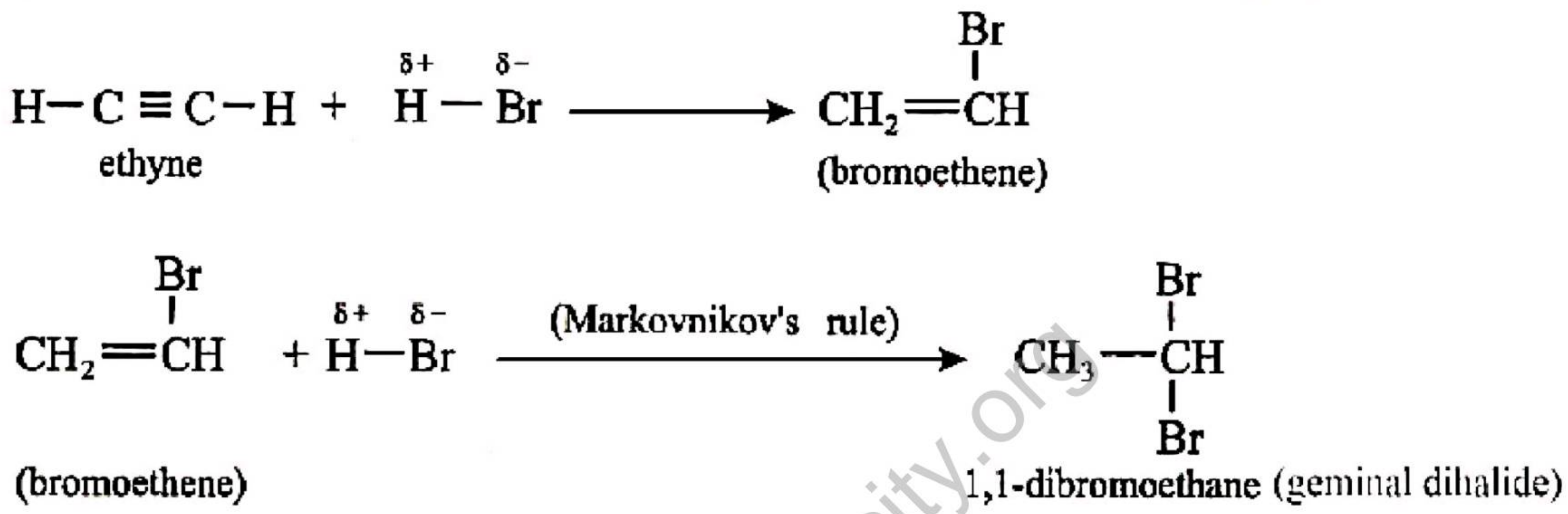
$$HC \equiv CH + H_2 \xrightarrow[\text{Ni, Pt or Pd}]{250\text{-}300^\circ C} H_2C = CH_2$$

(ethyne) (ethene)

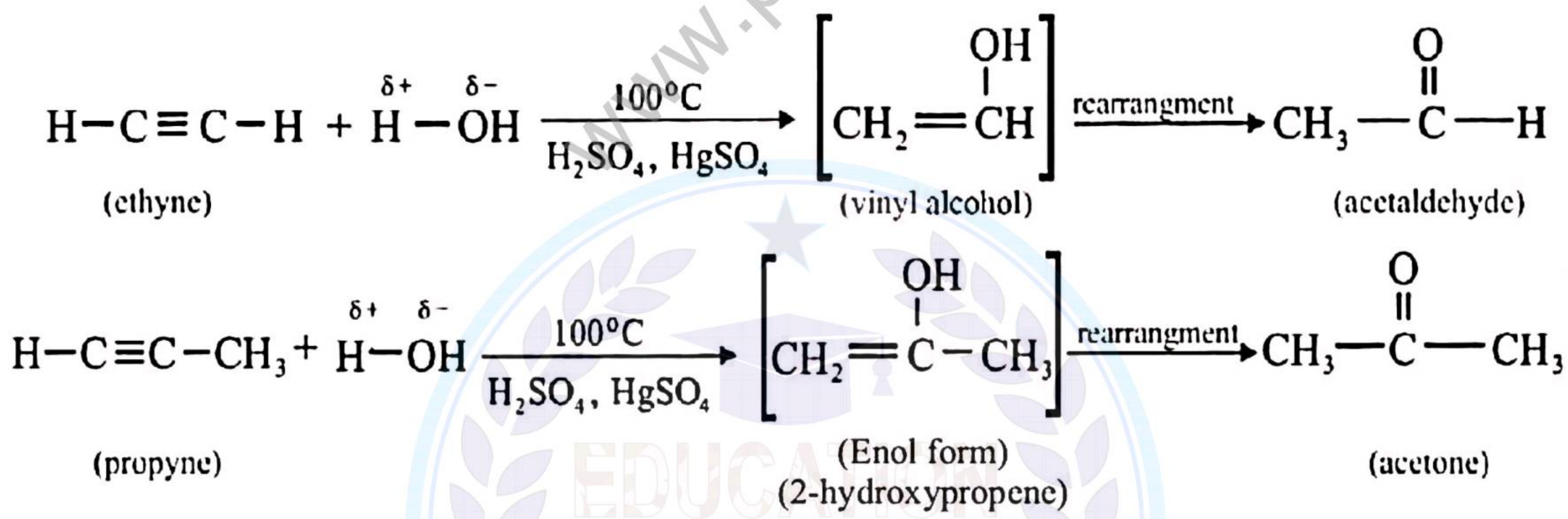
$$H_2C = CH_2 + H_2 \xrightarrow[\text{Ni, Pt or Pd}]{250\text{-}300^\circ C} CH_3 - CH_3$$

(ethene) (ethane)

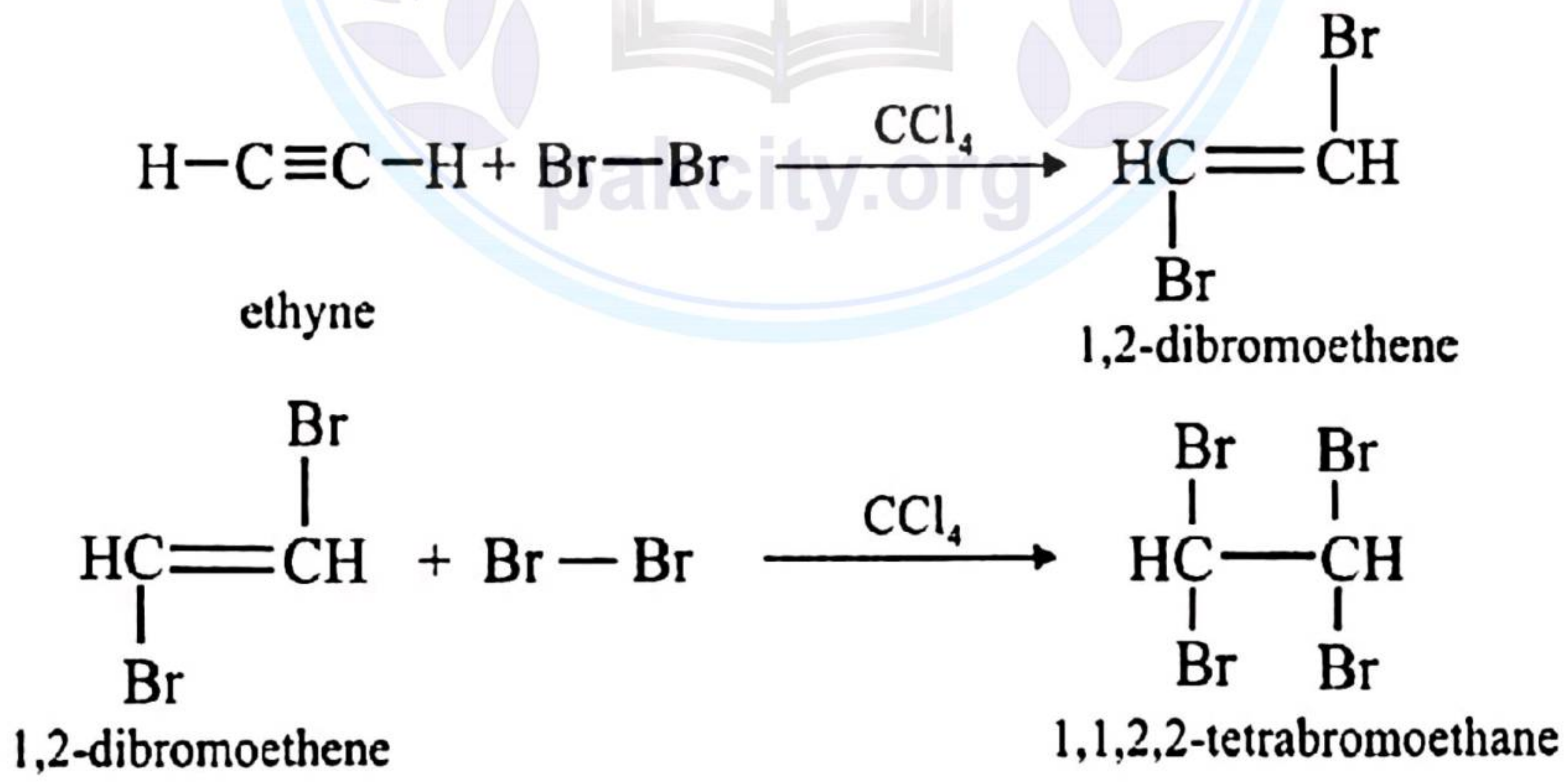
2. Halogenation:



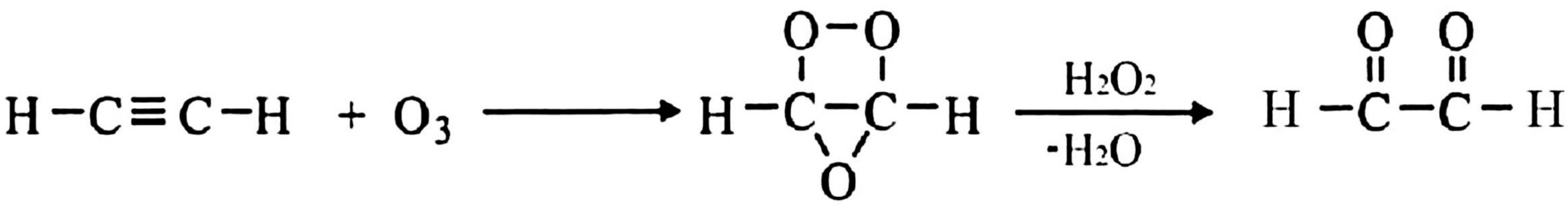
3. Hydration:



4. Halogenation:



5. Ozonolysis:



(ethyne) (ozonide) (glyoxal)

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 $KMnO_4$.

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.

1. Chain Isomerism

2. Position Isomerism

3. Functional Group Isomerism

4. Metamerism

1. Chain Isomerism:

"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)

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3 - CH - CH_2 \\ - CH_3 \end{array}$$

(isopentane)

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

(neopentane)

2. 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.

$$\begin{array}{l} CH_2 - CH_2 - CH_3 \\ | \\ Cl \end{array}$$

(1 – chloropropane)

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

(2 – chloropropane)

3. Functional Group Isomerism:

"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)

4. 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.

Position isomers of C_4H_{10} and C_5H_{12} is not possible as they don't contain any functional group.

Position isomers of C_4H_8 are:

$CH_3 - CH = CH - CH_3$
(2 – butene)

$CH_3 - CH_2 - CH = CH_2$
(1 – butane)

Position isomers of C_5H_{10} are:

$H_2C=CH-CH_2-CH_2-CH_3$

pent-1-ene

$H_3C-CH=CH-CH_2-CH_3$

pent-2-ene

Position isomers of C_4H_6 are:

$HC\equiv C-CH_2-CH_3$ but-1-yne

$H_3C-C\equiv C-CH_3$ but-2-yne

Position isomers of C_5H_8 are:

$HC\equiv C-CH_2-CH_2-CH_3$ pent-1-yne

$H_3C-C\equiv C-CH_2-CH_3$ pent-2-yne

Functional group isomers of C_2H_6O

CH_3-CH_2-OH
(ethyl alcohol)
(ethanol)

CH_3-O-CH_3
(Diethyl ether)
(methoxy methane)

Functional group isomers of C_3H_6O

$H_3C-CH_2-\overset{\overset{\large O}{||}}{C}-H$
(propanal)

$H_3C-\overset{\overset{\large O}{||}}{C}-CH_3$
(2 – propanone)

Functional group isomers of $C_2H_4O_2$

CH_3COOH (Ethanoic Acid) and $HCOOCH_3$ (methyl methanoate)

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.

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

Optical Activity

When plane polarized light is passed through a solution containing chiral carbon then the plane polarized light is rotated either in clockwise or in anticlockwise direction. This rotation of plane polarized light is called optical activity. The device which is used to measure optical activity is called **polarimeter.**

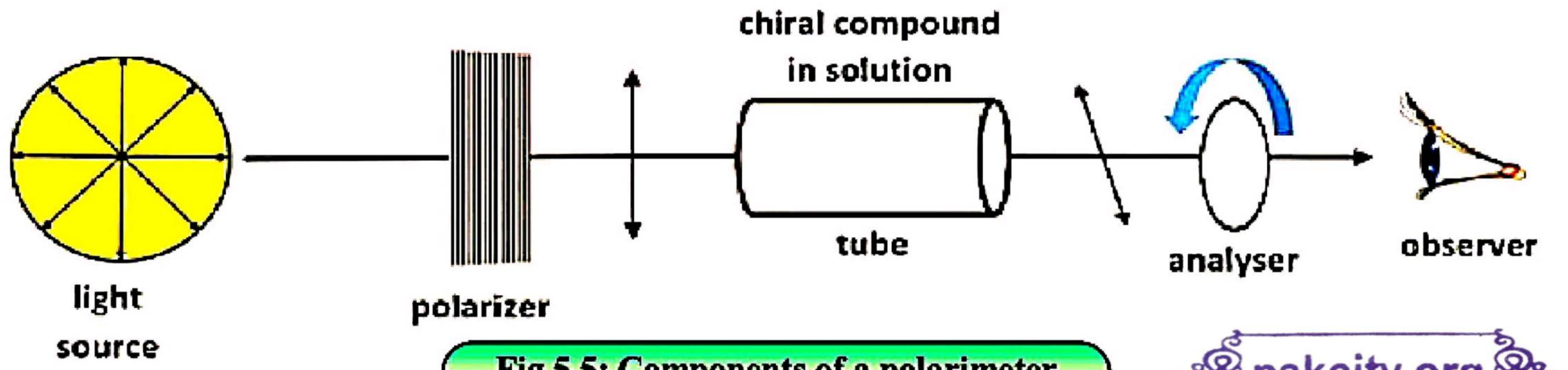


Fig 5.5: Components of a polarimeter

Optical Isomers

"Two compounds having the same molecular formula and same molecular structure but different from each other by the optical rotation of plane polarized light are called optical isomers or enantiomers."

The compounds that rotate 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 called levorotatory or L-isomer. These two optical isomers are mirror images to each other.

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.

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).

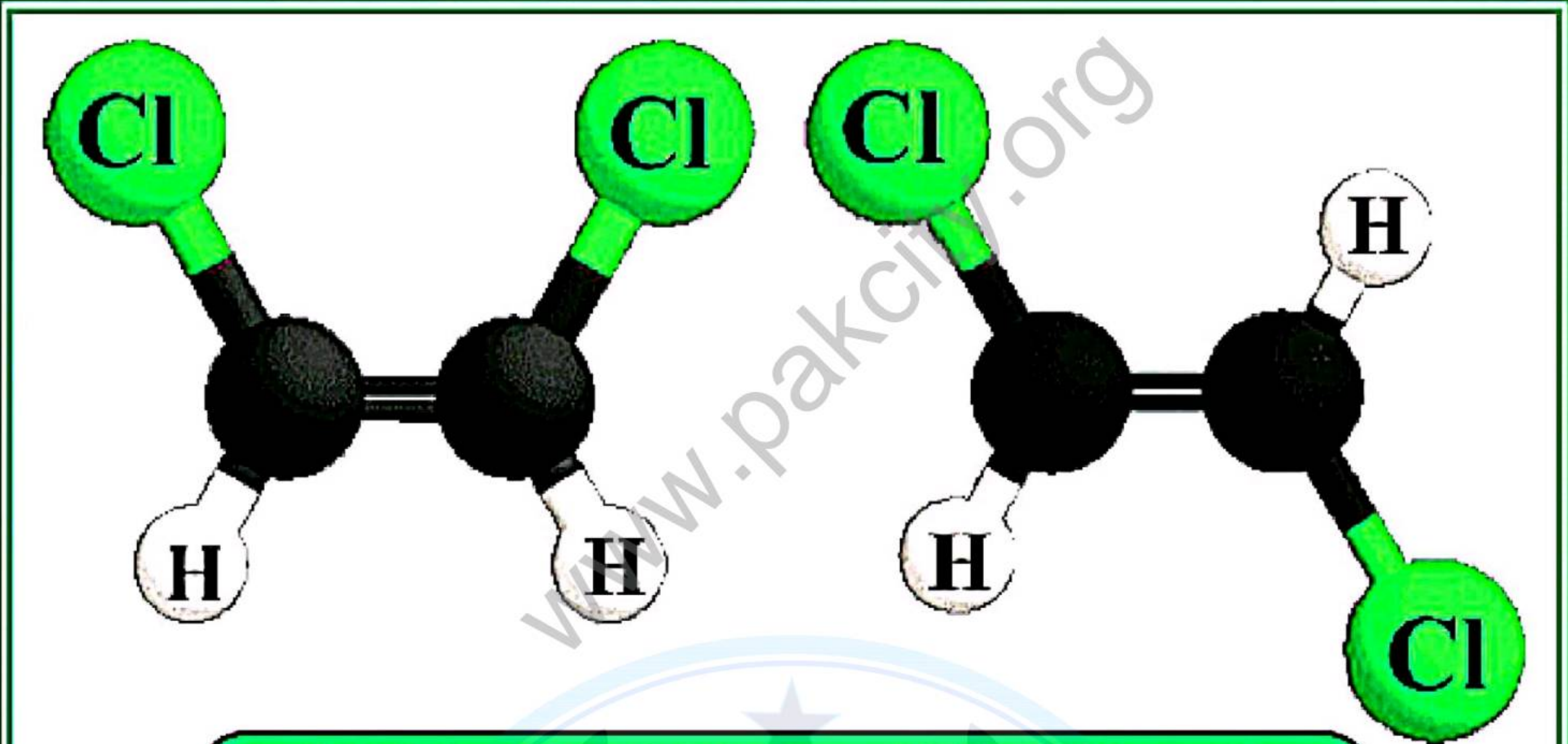


Fig 5.7: Cis and trans isomers of 1,2-dichloro ethene

BENZENE AND ITS DERIVATIVES

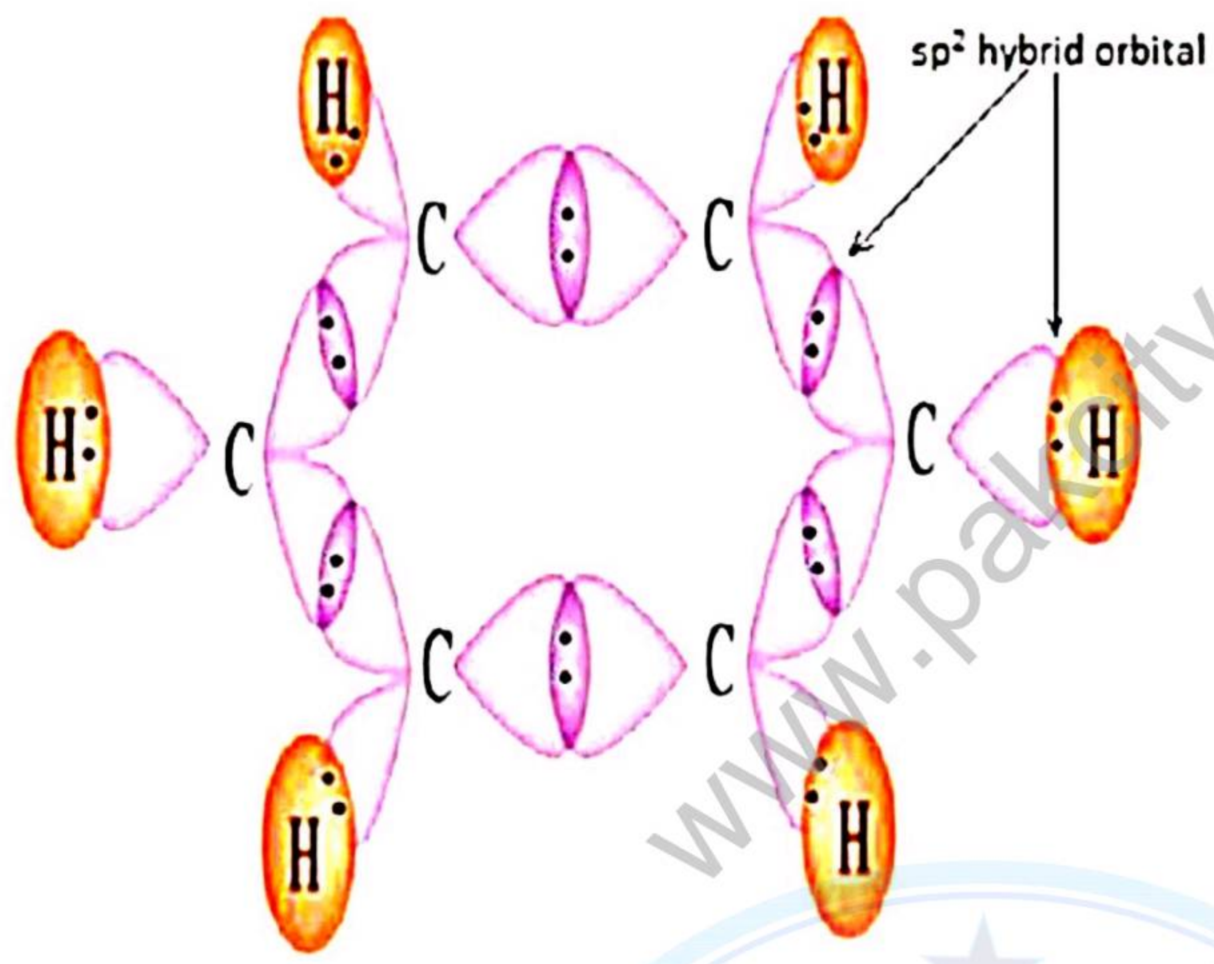
- Benzene is the simplest aromatic compound
- It's a colorless, carcinogenic and highly inflammable liquid.
- It burns with black soot due to high percentage of carbon.
- Its molecular formula is C_6H_6
- It was first isolated by Michael Faraday in 1825.
- It is insoluble in water but soluble in organic solvents.

Molecular orbital structure of benzene

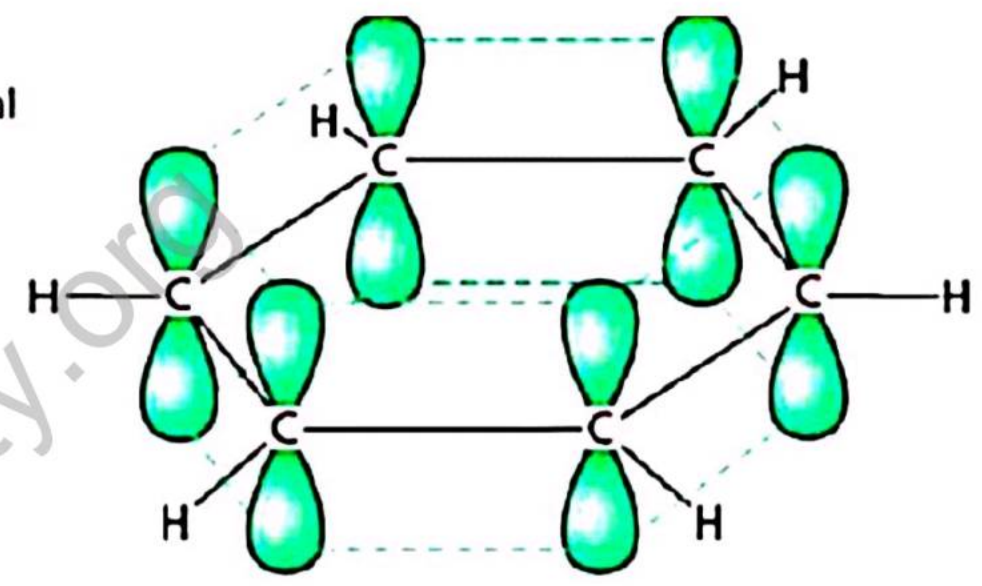
Benzene consists of six carbon atoms in ring, each carbon is sp^2 hybridized and has three sp^2 hybrid orbitals.

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. Carbon atoms have a trigonal planar shape with 120° bond angle. In benzene, the C – C bond length and C = C bond length is approximately 1.39 Å.

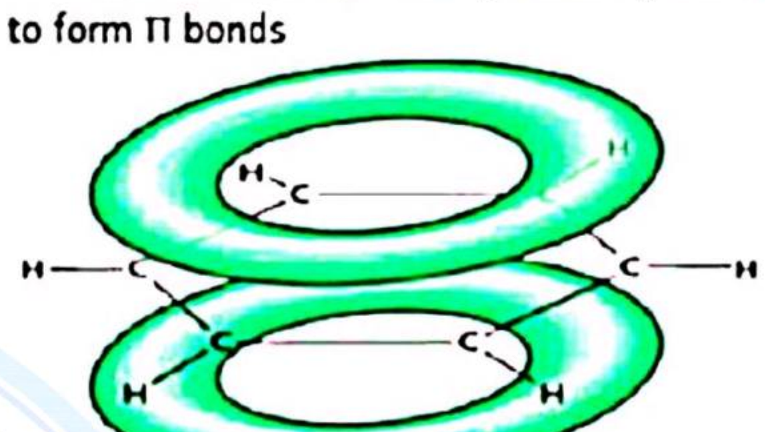
The six carbon atoms in benzene possess six unhybridized p-orbitals that are oriented perpendicular to the sigma bonds. The side wise overlapping of p orbitals gives six delocalized pi molecular orbitals where half of them is located above the plane while other half below the plane of sigma bonds. The six electrons present in pi molecular orbitals are delocalized over all six carbon atoms in molecule.



Sigma bond formation



Sidewise overlap of unhybridized p orbitals to form π bonds

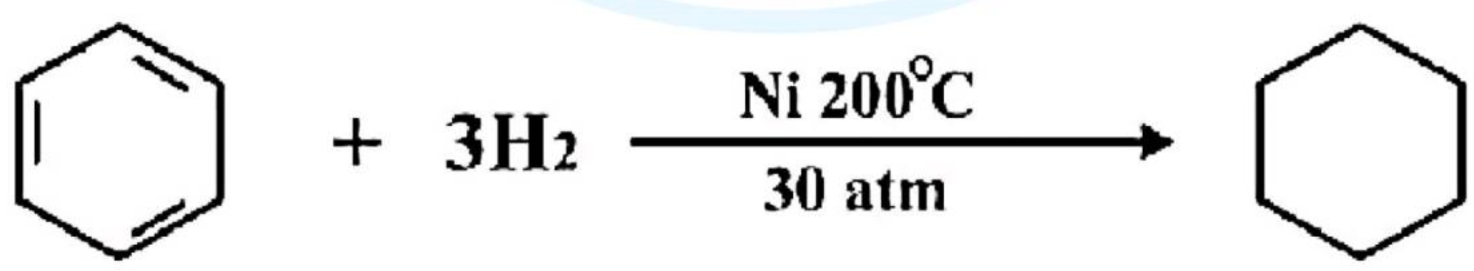


π electrons cloud lying above and below the plane.

Addition reactions of benzene

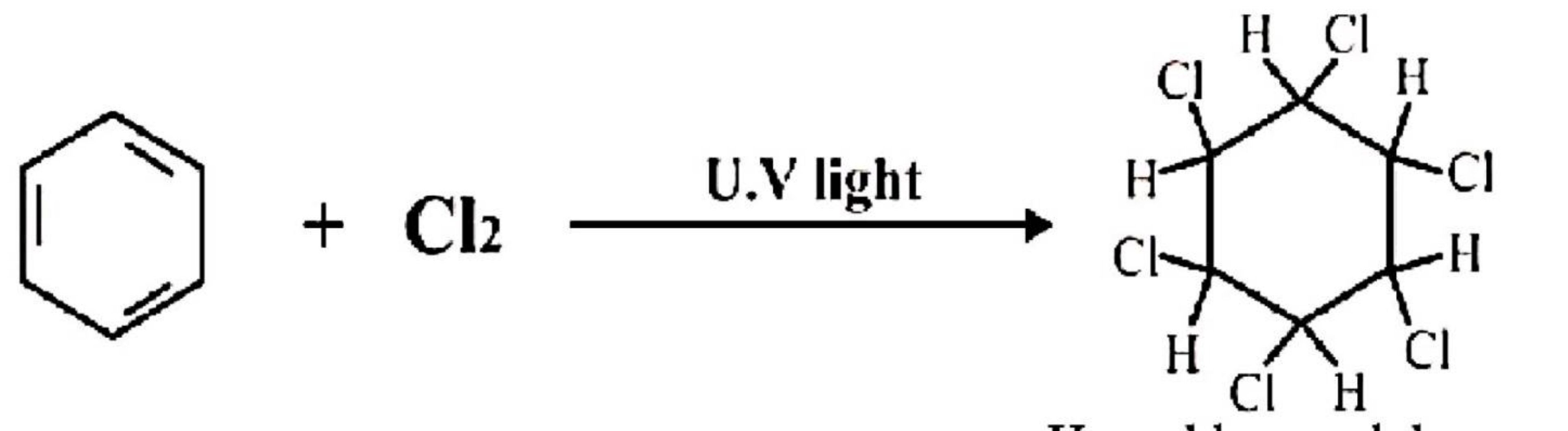
Benzene, being an aromatic compound, is highly resistant to addition reactions due to its stability. However, under specific conditions, it can undergo addition reactions. So far only the addition of hydrogen and chlorine to benzene has been observed.

1. Addition of Hydrogen:



(Benzene) (Cyclohexane)

2. Addition of Halogen:



Electrophilic substitution reactions of benzene

Electrophilic substitution reactions are a type of organic reaction in which an electrophile reacts with benzene and replace its hydrogen. The general mechanism of electrophilic substitution reaction of benzene consists of following steps:

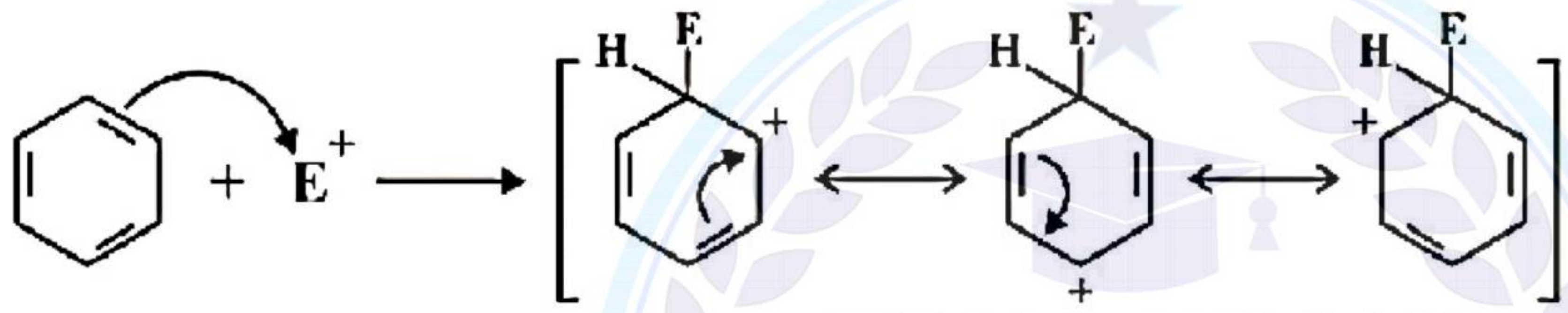
Step-1: Generation of an electrophile

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

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

Step-2: Formation of Arenium ion

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

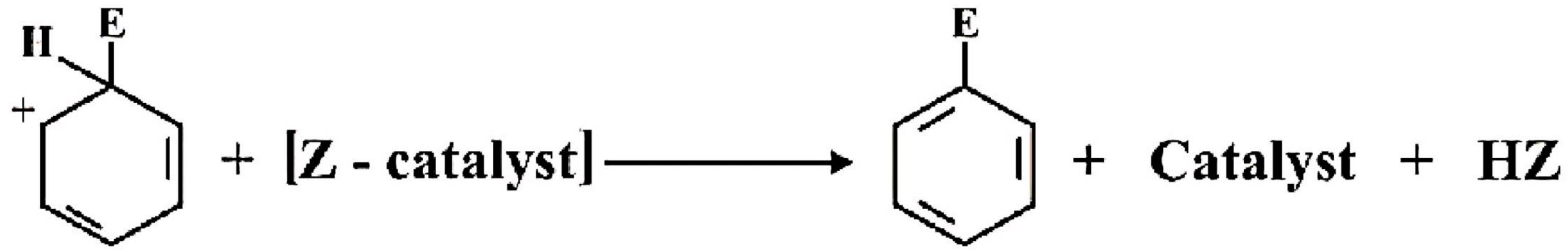


(Sigma complex)

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.



TYPES OF ELECTROPHILIC SUBSTITUTION REACTIONS:

There are 5 types of electrophilic substitution reactions.

(i) Nitration

(ii) Sulphonation

(iii) Halogenation

(iv) Friedel – Craft's Alkylation

(v) Friedel – Craft's Acylation

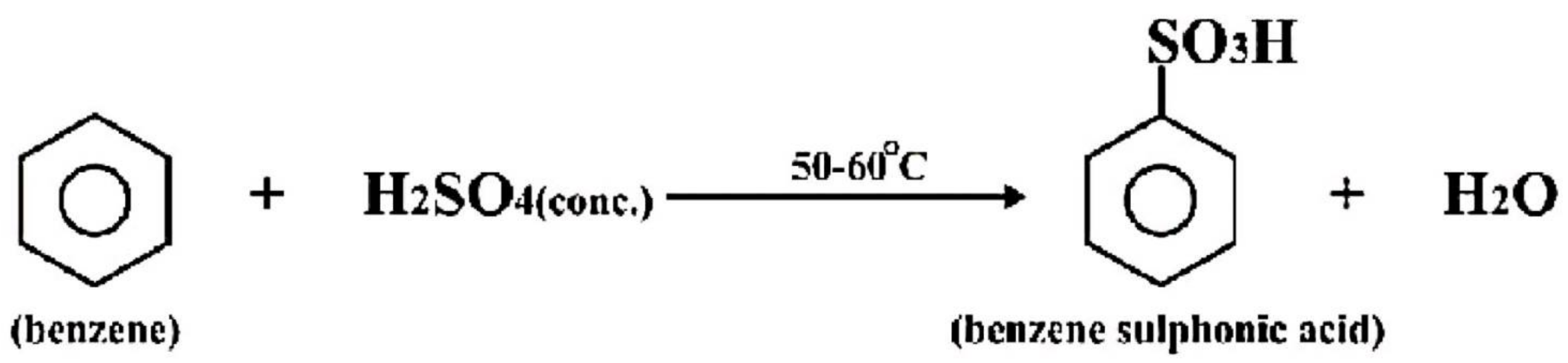
1. Nitration:

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.

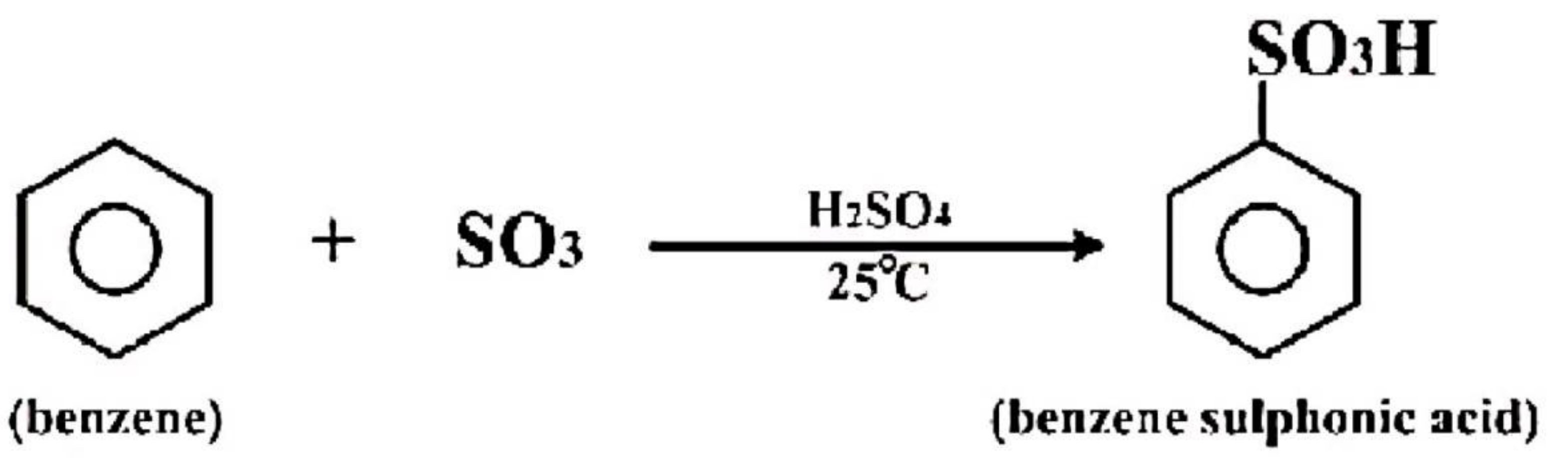
In this reaction, one hydrogen of benzene is replaced by a nitronium ion (NO_2^+).

2. Sulphonation:

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

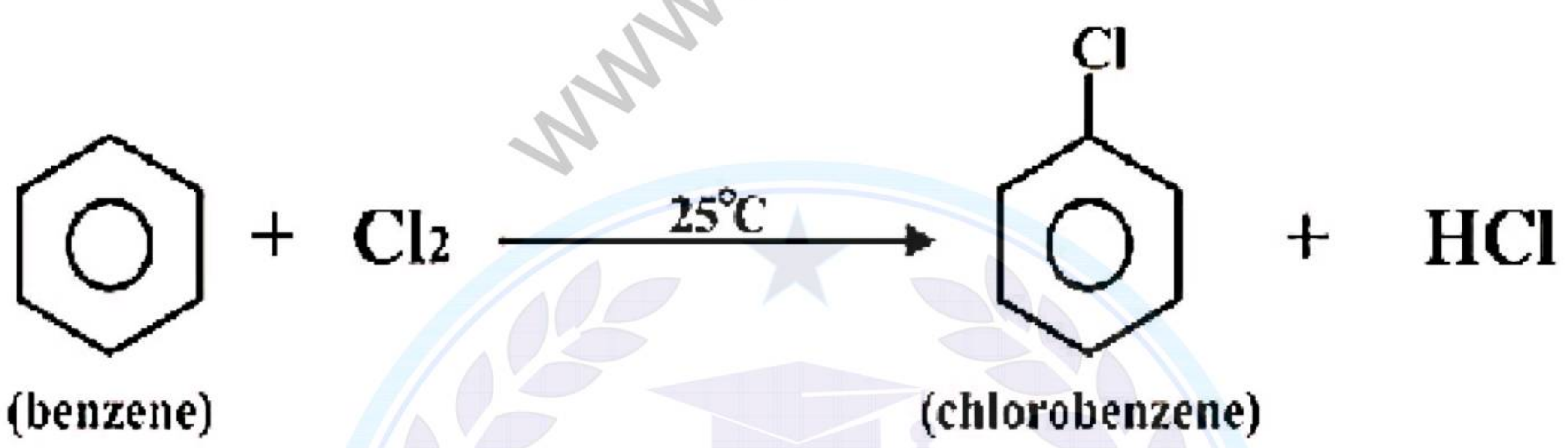


This reaction may also be carried out at room temperature if fuming sulphuric acid is used.



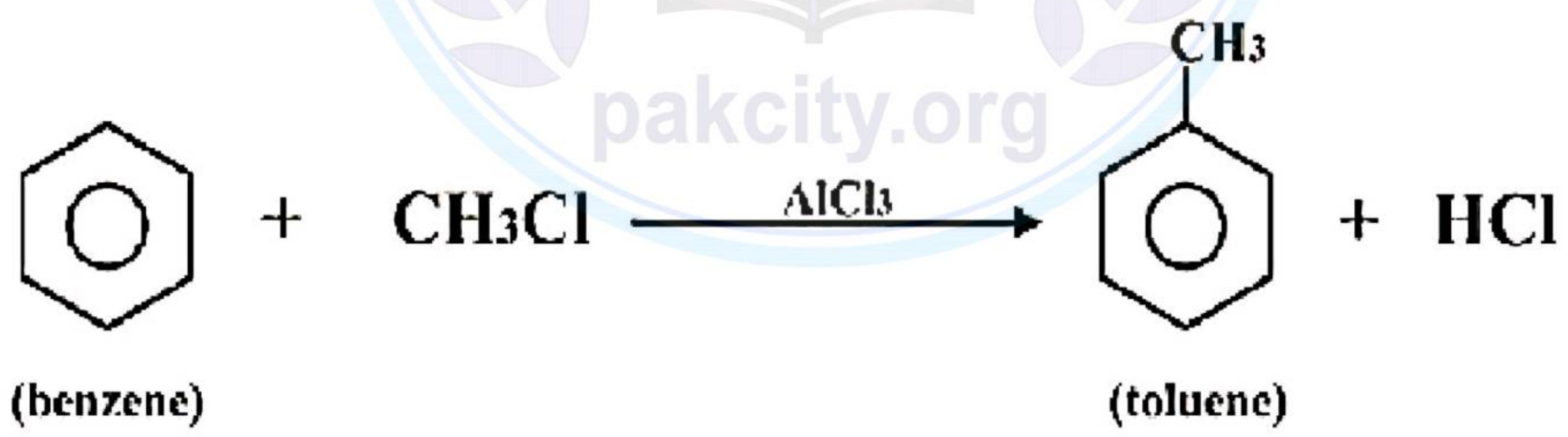
3. Halogenation:

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



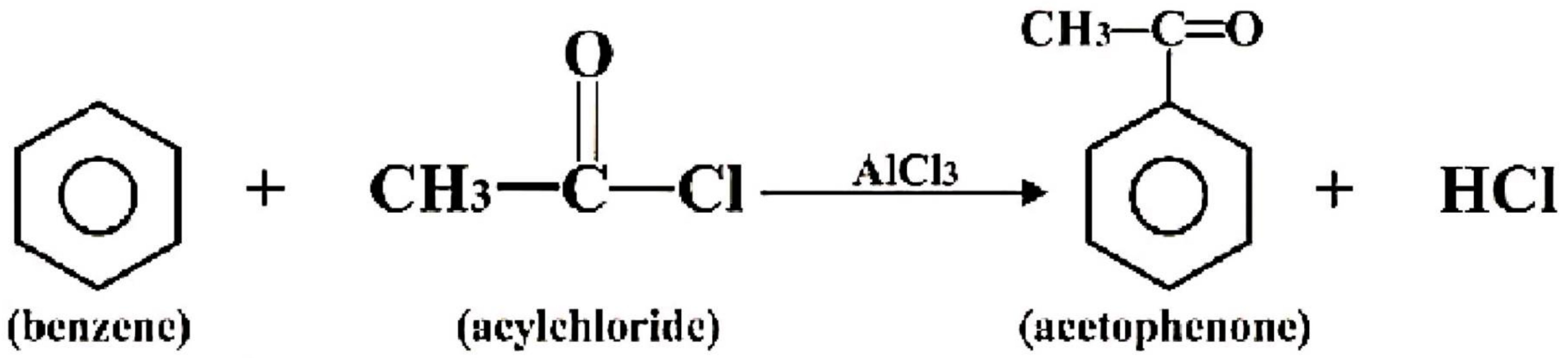
4. Friedel-Craft's Alkylation:

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



5. Friedel-Craft's Acylation:

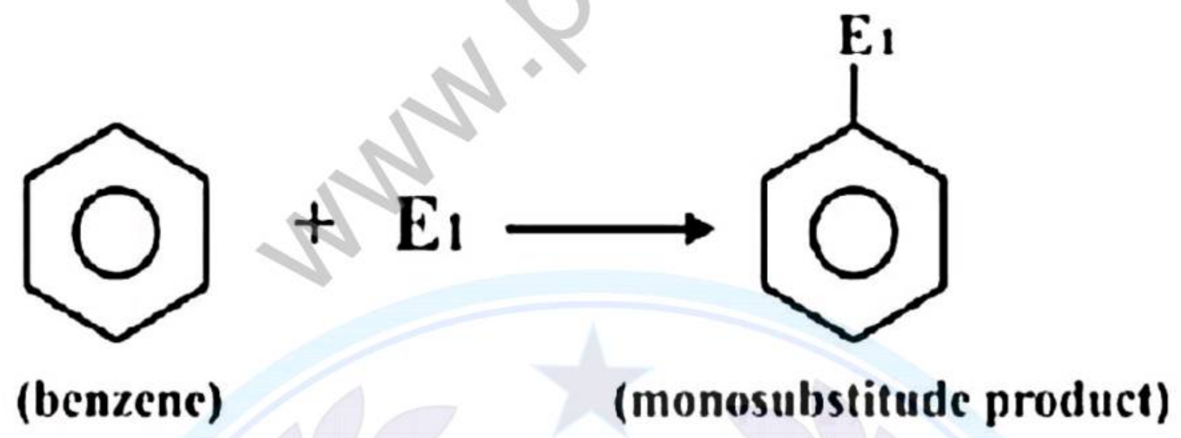
The reaction of benzene with an acylhalide (RCOCl) in the presence of lewis acid ($AlCl_3$) is known as Friedal Craft acylation.

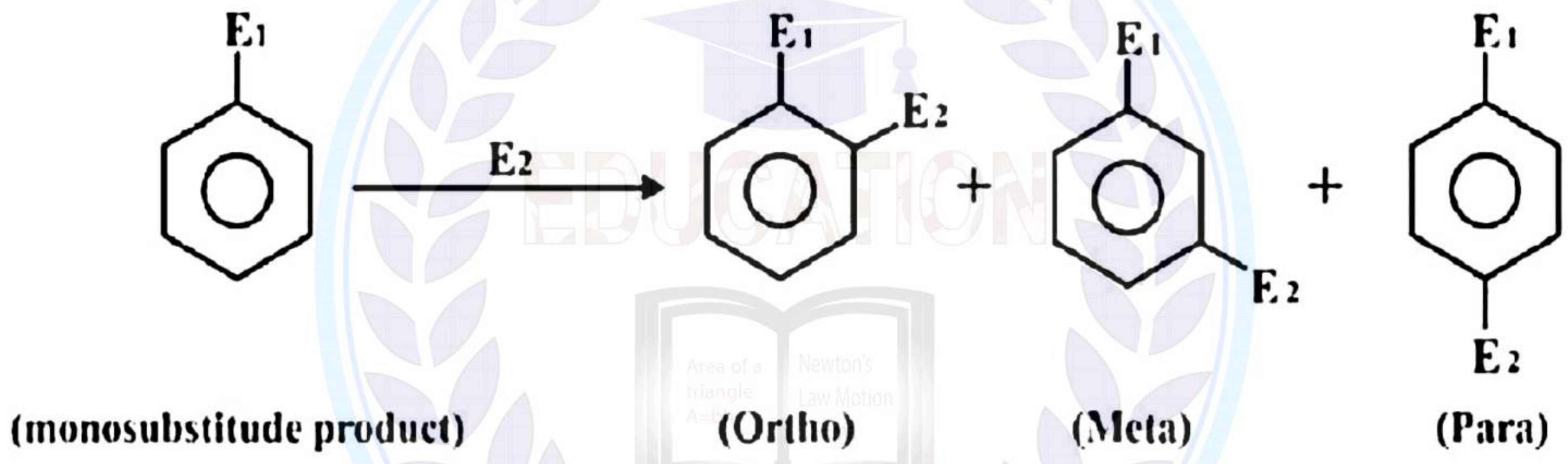


Substituent Effect

When an electrophile reacts with benzene, a monosubstituted product is obtained. The second electrophile is substituted according to the substituent effect of first electrophile,

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

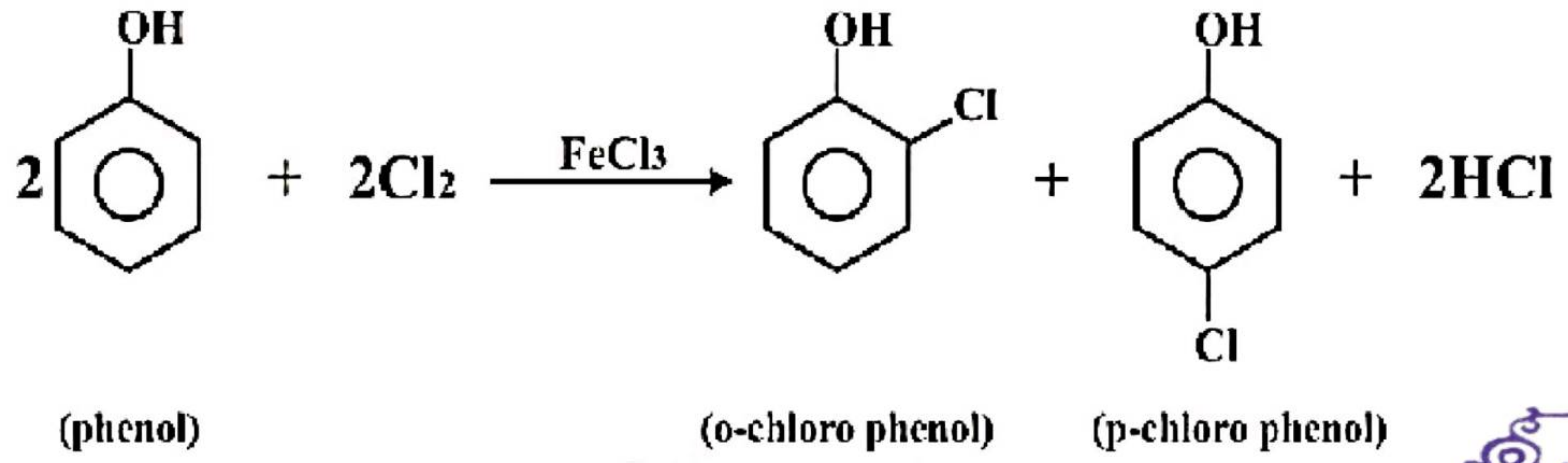




(i) Ortho, para directing groups

"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.

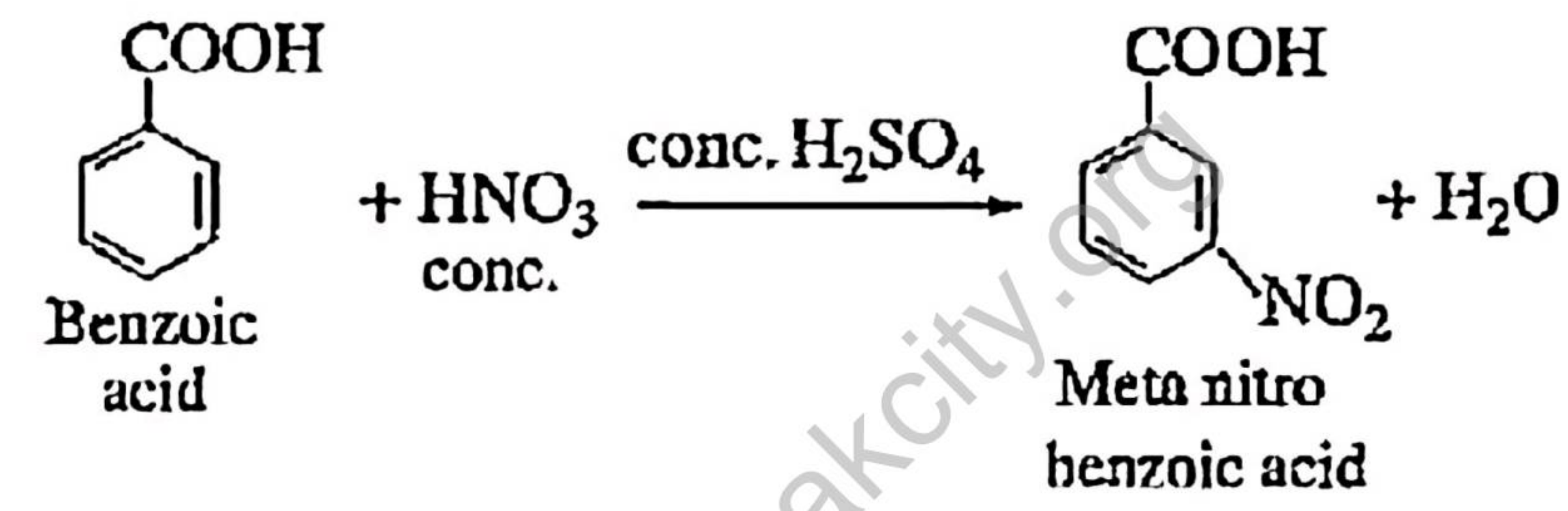
For example the $-OH$ group of phenol is ortho, para director



(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.



DIFFERENCE BETWEEN ORTHO-PARA DIRECTORS AND META DIRECTORS

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

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?

Aliphatic Hydrocarbons	Aromatic Hydrocarbons
1) It has less percentage of carbon.	*1) It has more percentage of carbon.*
2) It doesn't burn with black soot.	*2) It burns with black soot.*
3) It can be cyclic and acyclic.	*3) It is always cyclic.*

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

Already discussed above

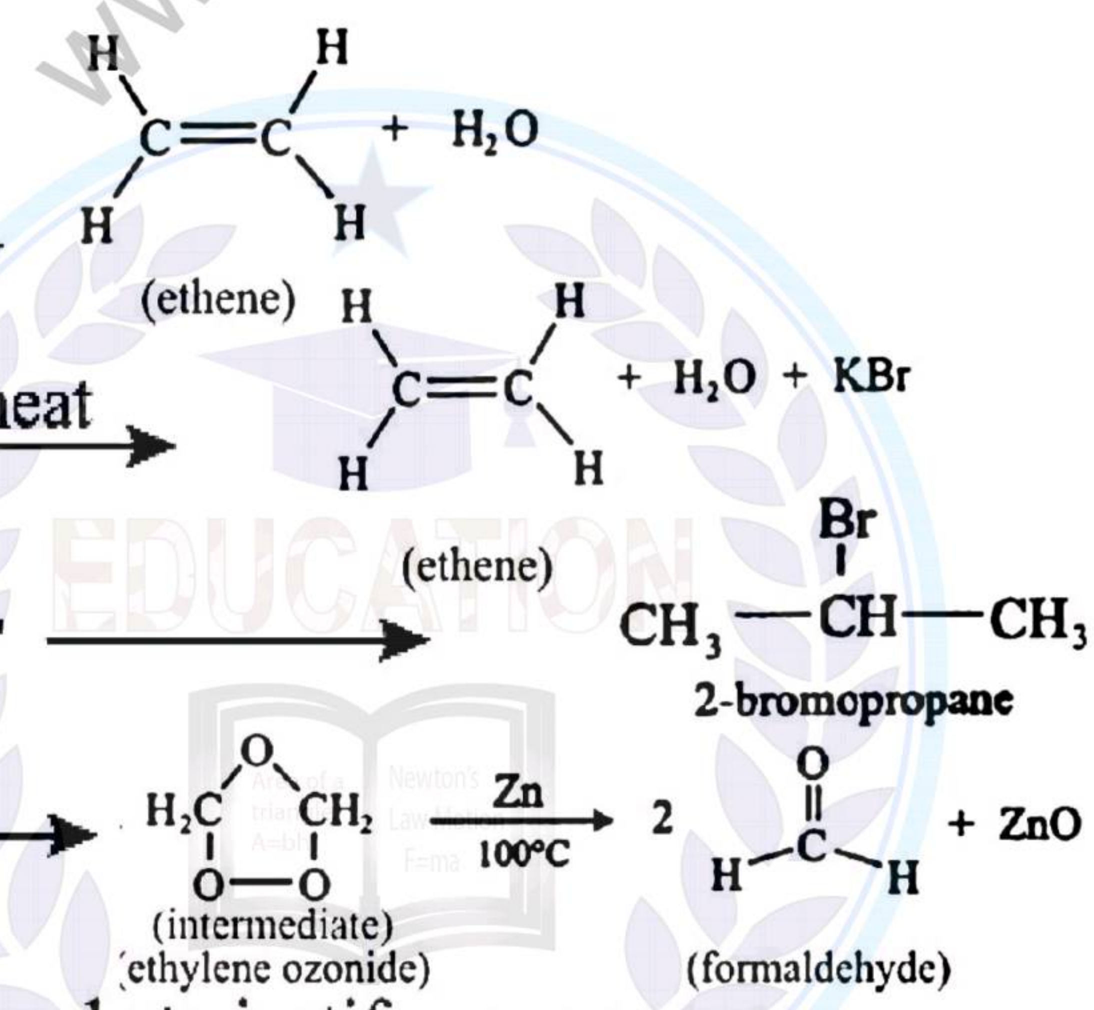
3. Complete the following reactions and name the major product formed in each reaction.

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

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

$CH_3 - CH = CH_2 + HBr \longrightarrow$

$CH_2 = CH_2 + O_3 \longrightarrow$

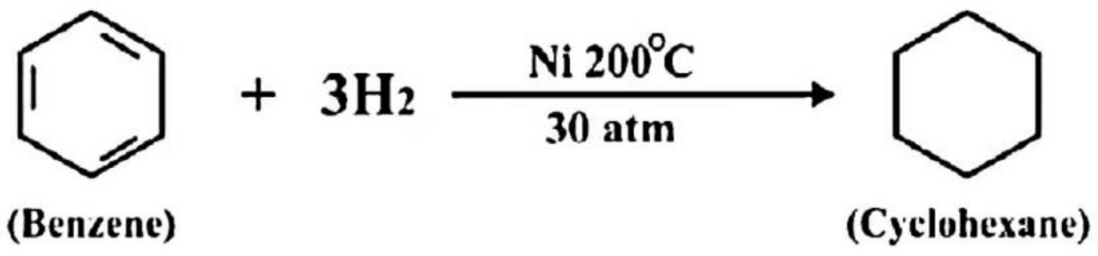


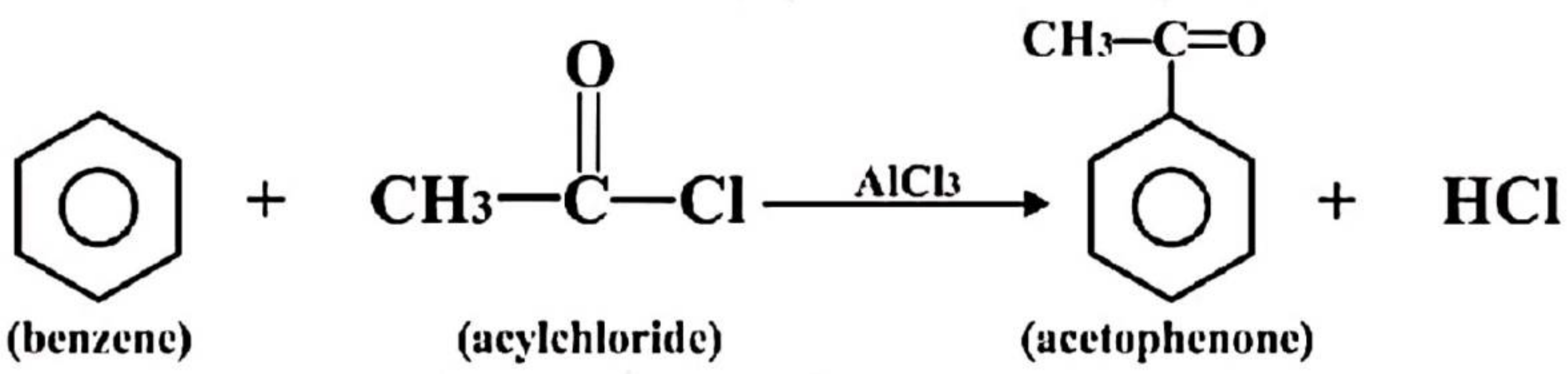
4. Define a chiral carbon? Give an example to justify your answer.

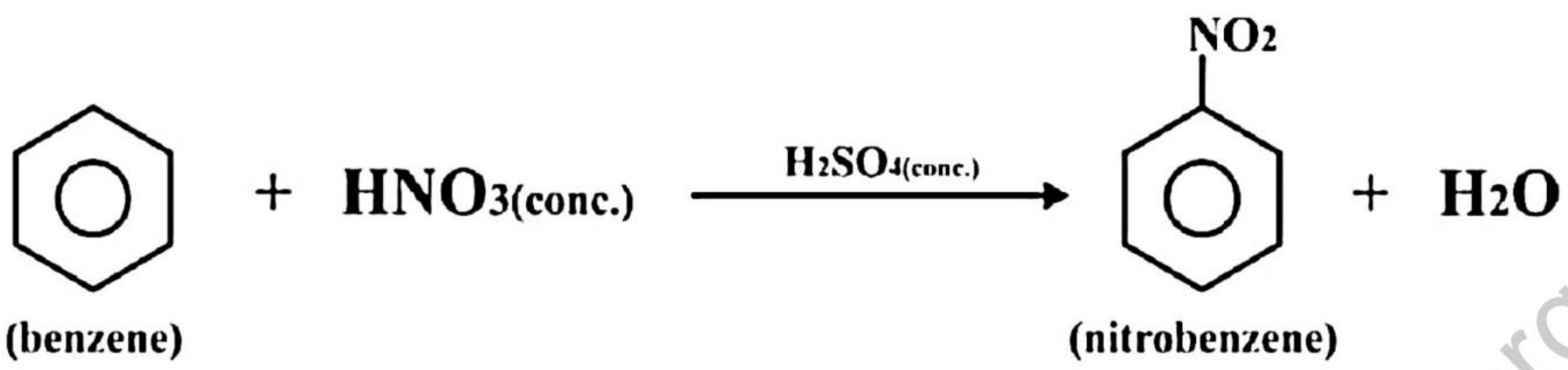
Already discussed above

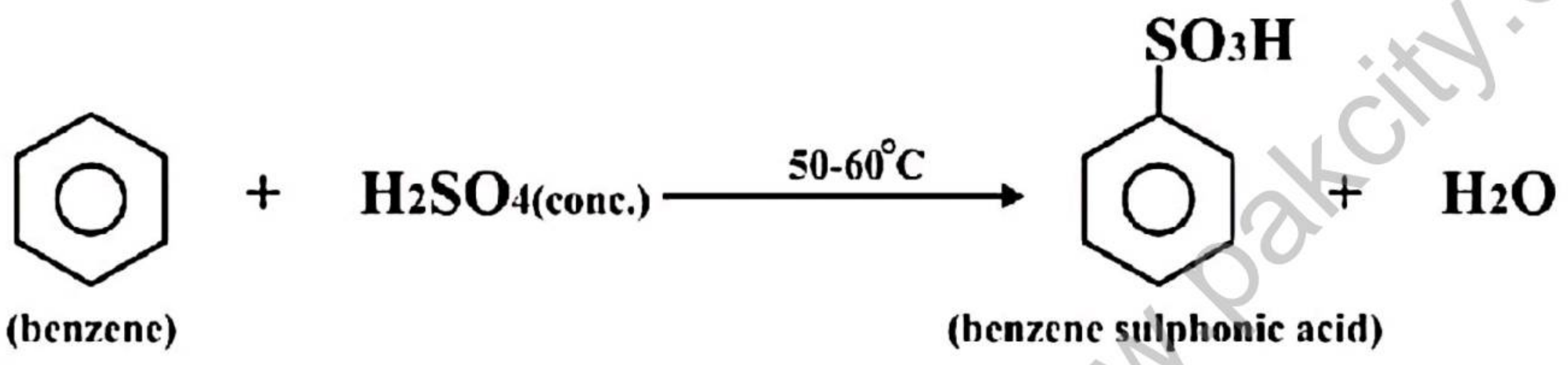
5. Write the equations with all required conditions for the reaction of benzene with the following:

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

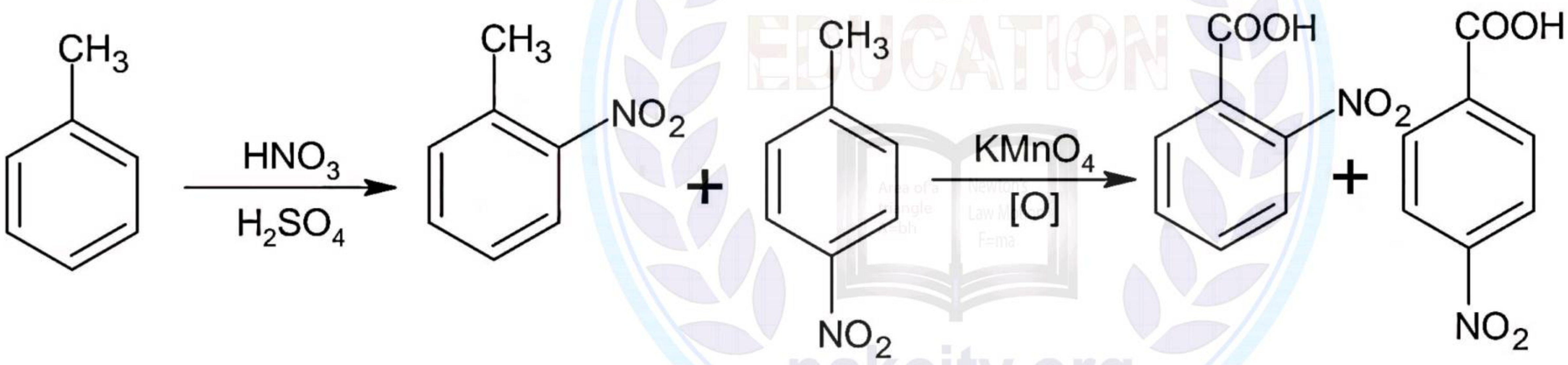
(i)


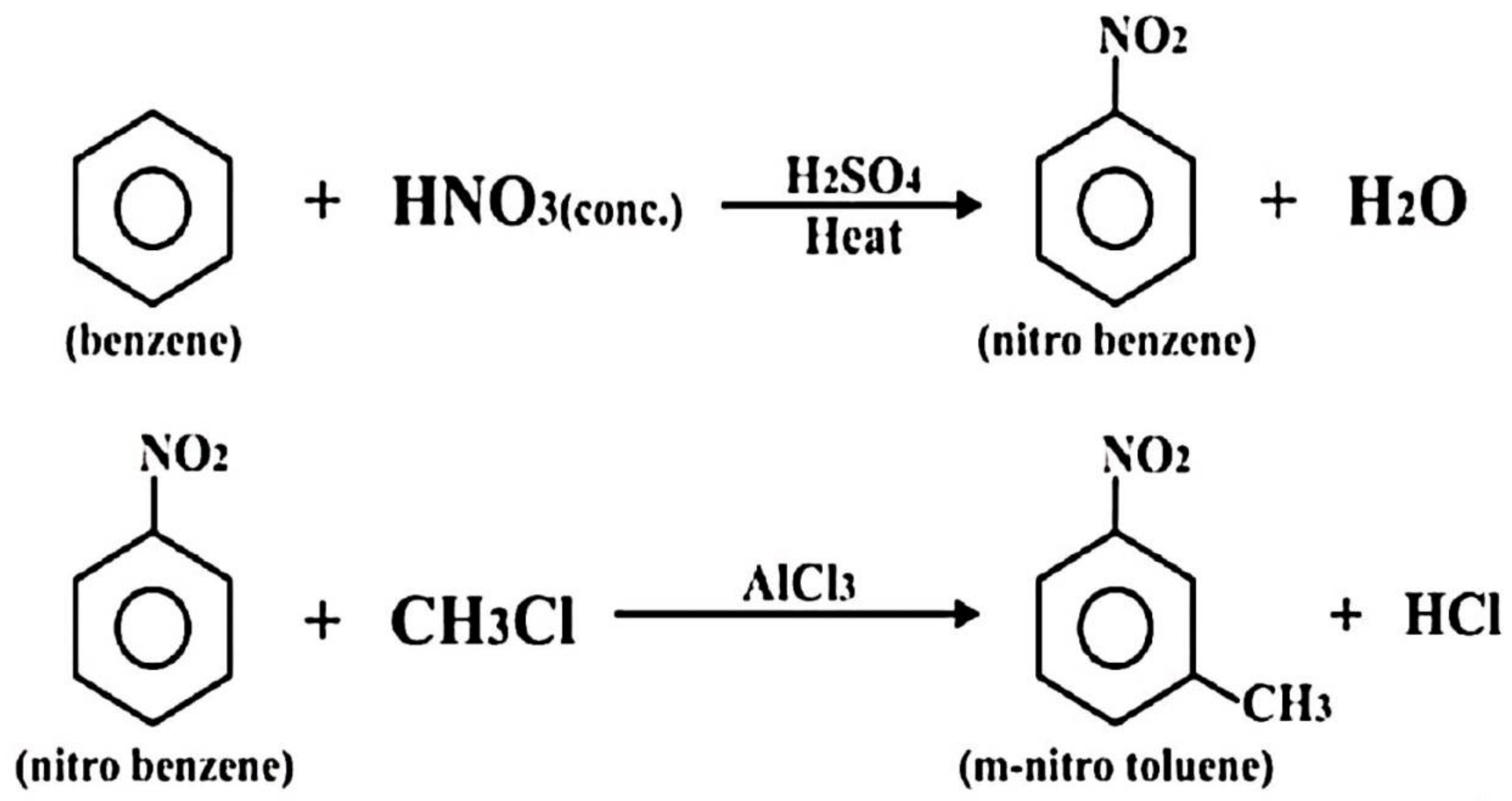
(ii)


(iii)


(iv)


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

(i)




(ii)

7. How can you prepare ethene from dehydration of ethanol and ethyne from dehydro halogenations of ethyl chloride?

Already discussed above

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

Ans. A Sigma bond is present between carbon atoms of alkanes. Sigma bond is stronger bond due to head-to-head overlapping. It's more difficult to break sigma bond that's why alkanes are less reactive towards chemical reactions.

Descriptive Questions

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

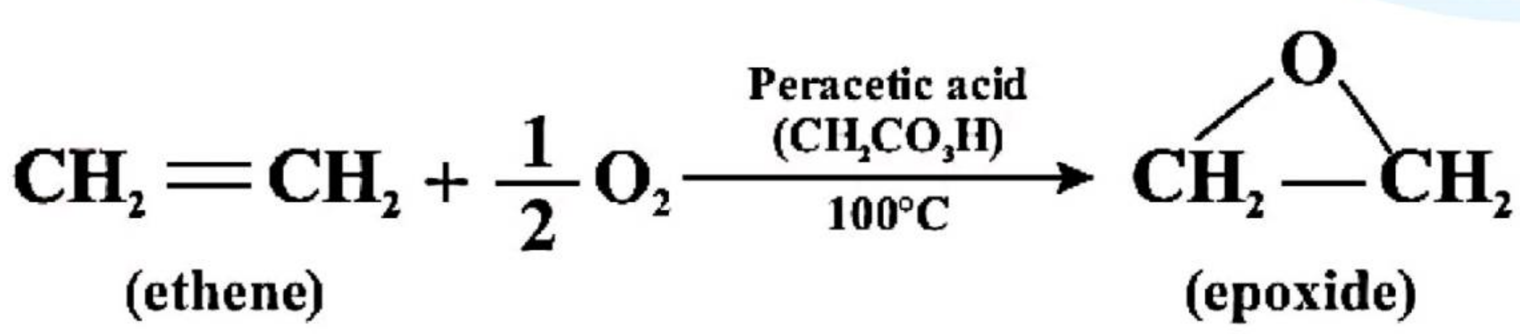
Already discussed above

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

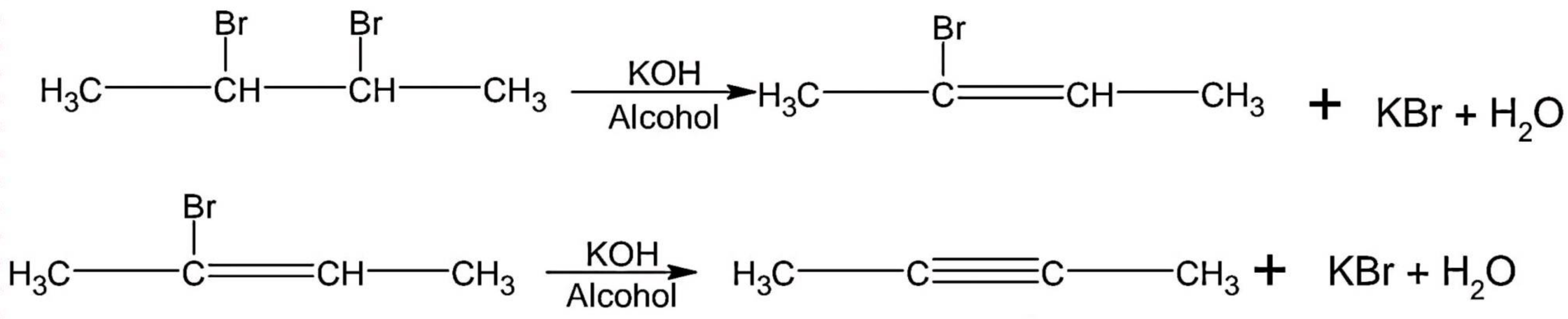
$$nH_2C{=}CH_2 \xrightarrow[2000\ atm]{200^\circ C} \left[CH_2 - CH_2 \right]_n$$

(ethene) (polyethene)

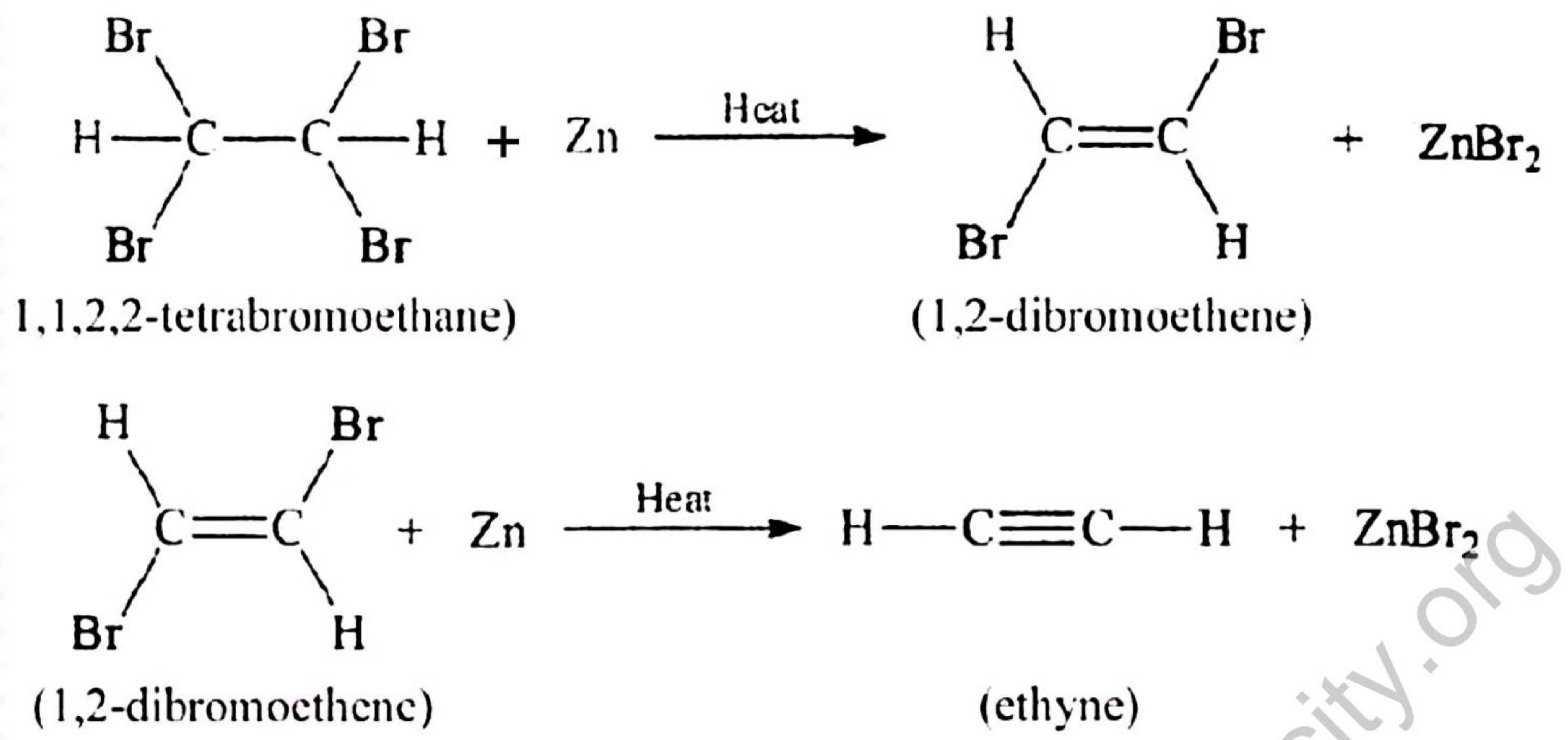
(ii) Ethene is burnt in air in the presence of per acetic acid.



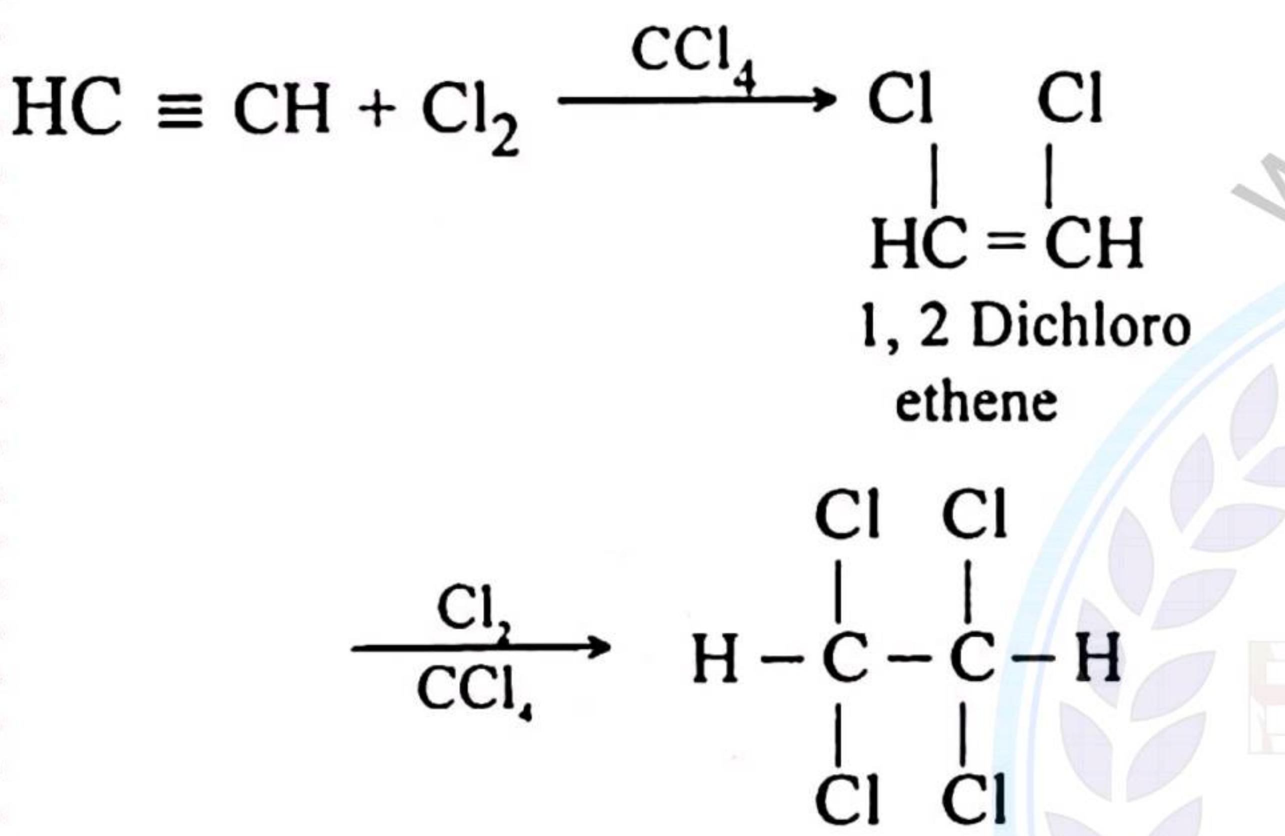
(iii) 1,2-di bromo butane is heated with alcoholic potassium hydroxide.



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



(v) Reaction of chlorine with acetylene



1, 1, 2, 2-Tetrachloroethane

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

Ans. Ethene is more reactive than ethane due to the presence of pi bond which is weaker than sigma bond. Ethene is less reactive than ethyne because ethyne contains two pi bonds.

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

Already discussed above

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

Already discussed above

6. Describe the molecular orbital structure of benzene.

Already discussed above

7. Give the mechanism of following Electrophilic substitution reaction of benzene.
(a) Nitration (b) Acylation (c) Chlorination

Already discussed above

8. What is meant by ortho, para and meta directing groups. Explain the influence of substituent of benzene to the incoming Electrophile.

Already discussed above

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

Already discussed above