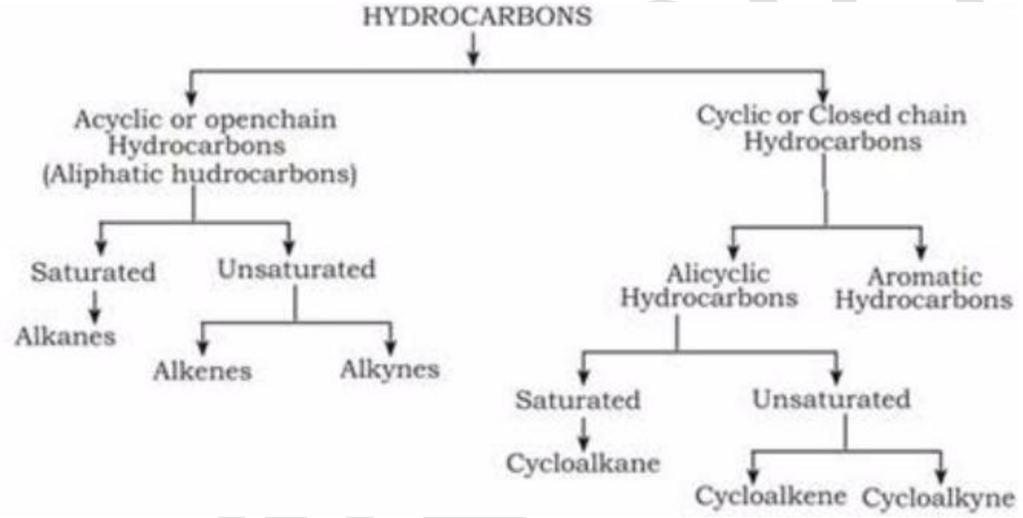
Chapter- 13: Hydrocarbon

1. Introduction: Hydrocarbons are composed of Carbon and hydrogen. The important fuels like Petrol, kerosene, coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

2. Sources: Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons.
The oil trapped inside the rocks is known as petroleum. PETRA – ROCK, OLEUM – OIL. The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane.

3. Classification of Hydrocarbons:



13.1 Alkanes (Paraffins)

1. General Characterstic:

- Also known as *paraffins* (*parum* means little, *affins* means affinity)
- General formula $CnH_{2n}+2$
- sp^3 hybridisation
- C–C bond length 1.15 4 A°
- Chemically unreactive
- Show chain, position and optical isomerism. Heptane has 9 isomers, Octane 18 & Decane 75.
- Nomenclature:

2. Preparation of Alkane:

1) By Wurtz Reaction: Follow mainly free radical mechanism, useful in preparing an alkane containing even number of carbon atoms. It's used to forms the higher alkanes.

$$\underset{\textbf{Bromoethane}}{CH_3-Br+2\,Na+Br-CH_3} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethane}}{CH_3-CH_3}+2\,NaBr$$

2) From Unsaturated Hydrocarbons (Hydrogenation):

$$CH_2 = CH_2 + H_2 \xrightarrow[573\,K]{Ni\ or\ Pt} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow[573\,K]{Ni\ or\ Pt} CH_3 - CH_3$$

3) By using Grignard's Reagent:

$$CH_3MgBr \quad + \quad C_2H_5OH \quad \rightarrow \quad CH_4 \quad + \quad Mg(OC_2H_5)Br$$

$$C_2H_5MgBr \quad + \quad H_2O \quad \rightarrow \quad C_2H_6 \quad + \quad Mg(OH)Br$$

4) From Carboxylic Acids: Carboxylic acids can produce alkanes in a number of ways as shown below

i) Heating with soda lime (Mixture of NaOH + CaO) or Decarboxylation of Carboxylic Acids: In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

ii) By Reduction of carboxylic acid:

$$RCOOH \ + \ 6\,HI \xrightarrow{red\ P/423\,K} RCH_3 + 3\,I_2 + 2H_2O$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The alkanes with even number of carbon atoms can easily be prepared by this method.

$$2CH_3COONa + 2H_2O \rightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2NaOH$$

Mechanism:

$$\underset{\text{Sodium salt of carboxylic acid}}{RCOONa} \xrightarrow{\text{electrolysis}} \underset{\text{Anion}}{RCOO^-} + \underset{\text{Cation}}{Na^+}$$

At Anode :

$$RCOO^- \longrightarrow RCOO^{\bullet} + e^-$$

$$RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\text{Sodium ethanote}}{2\,CH_3COONa} \longrightarrow \underset{\text{Ethane (at anode)}}{CH_3 - CH_3}$$

At Cathode:

$$H_2O + e^- \rightarrow H^{\bullet} + OH^-$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2$$

Que: *Why methane cannot be prepared by this method?*

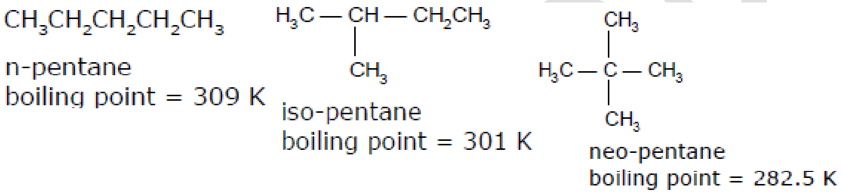
3. Physical Properties:

1) Nature:

- Non-Polar due to covalent nature of C—C bond and C—H bond.
- C—C bond enrgy = 83 kj/mole and C—H bond energy = 99 kj/mole.
- C1—C4 = gases, C5—C17 = colorless odourless liquid and > C17 = Solid.

2) Solubility: Due to non polar in nature so dissolve in non polar solvent.

3) Boiling point: Alkanes have low boiling point due to non polar in nature. The boiling points of alkanes also increase with the increase in the molecular mass. In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. For example, isopentane and neopantane have a lower boiling point than pentane.

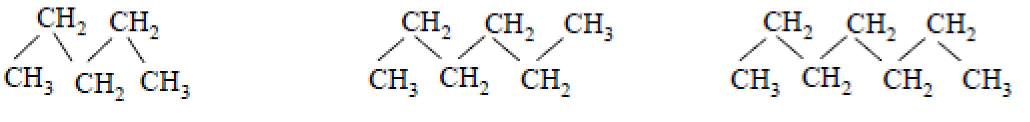


n-pentane
boiling point = 309 K

iso-pentane
boiling point = 301 K

neo-pentane
boiling point = 282.5 K

4) Melting Point: The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice. The alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms. For example



n-**Pentane** (Carbon atoms = 5, m.p.142 K)

n-**Hexane** (Carbon atoms =6, m.p. = 179 K)

n-**Heptane** (carbon atoms = 7, m.p. = 183 K)

In the above structures, the alkanes containing even number of carbon atoms are more symmetrical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, so they have higher melting points.

4. Chemical Properties of Alkanes:

1) Substitution Reaction or Halogenation Reactions:

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow{UV} CH_2Cl_2 \xrightarrow{UV} CHCl_3 \xrightarrow{UV} CCl_4$$

The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

The rate of replacement of Hydrogen of alkanes is 3° > 2° > 1°

Iodination is a very slow and reversible reaction. So it is carried out by heating alkane in the presence of some oxidizing agent like iodic acid (HIO_3) or nitric acid (HNO_3) which oxidizes HI formed during the reaction.

$$CH_4 + I_2 \rightarrow CH_3I + HI$$
$$5HI + HIO_3 \rightarrow 3H_2O + 3I_2$$
$$2HI + 2HNO_3 \rightarrow 2H_2O + I_2 + 2NO_2$$

Mechanism:

(i) **Chain Initiation Step:** It involves the formation of free radicals like as

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

(ii) **Chain Propagation Step:** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$$
$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

During propagation reaction many others steps are possible which formed highly halogenated products like as

$$CH_3Cl + Cl^{\bullet} \rightarrow CH_2Cl_2 + HCl$$
$$CH2Cl_2 + Cl^{\bullet} \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl^{\bullet} \rightarrow CCl_4 + HCl$$

(iii) **Chain Termination Step:** In this step, free radicals combine with one another and the further reaction stops.

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$
$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$
$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

2) Combustion (Oxidation): Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 890KJ\ mol^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then incomplete combustion takes place forming carbon black instead of carbon dioxide.

$$CH_4\ (g) + O_2 \rightarrow C\ (s) + 2H_2O\ (l)$$

3) Controlled Oxidation: If alkanes heated with in a control supply of oxygen it gives different product at high temp and pressure with a presence of suitable catalyst like as

i) When a mixture of methane and oxygen is passed through Cu tubes at 523K and 100 atm, methanol is produced.

$$2CH_4 + O_2 \rightarrow 2CH_3OH$$

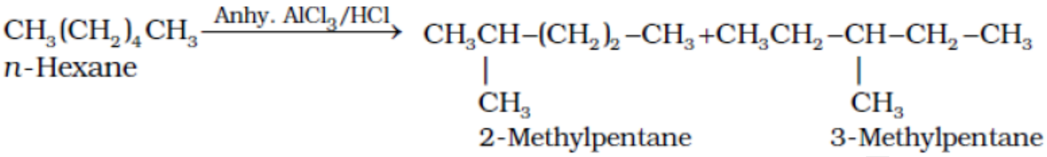
ii) When a mixture of methane and oxygen is passed through heated molybdenum oxide, methanal is produced.

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$$

iii) When a mixture of methane and oxygen is passed through heated manganese acetate, Ethanoic acid is produced.

$$2CH_3—CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

4) Isomerisation:



$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\text{Anhy. } AlCl_3/HCl} \underset{\text{2-Methylpentane}}{CH_3\underset{\substack{|\\CH_3}}{C}H-(CH_2)_2-CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{\substack{|\\CH_3}}{C}H-CH_2-CH_3}$$

5) Aromatization (Reforming):

$$C_6H_{14} \xrightarrow[773K \ \& \ 20 \ atm]{V_2O_5/Cr_2O_3/Mo_2O_3} C_6H_6$$

6) Reaction with steam: Methan reacts with steam in the presence of Ni catalyst at 1273k temp to form CO and H_2. This reaction is used for the industrial preparation of hydrogen from natural gas.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

7) Pyrolysis (Cracking or Thermal decomposition): when higher alkanes are heated at high temp (about 700-800k) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes.

$$CH_3-CH_2-CH_3 \xrightarrow{873\,K} CH_3CH=CH_2 + H_2 \quad \text{or} \quad CH_2=CH_2 + CH_4$$

5. Conformations (Conformational Isomerism): The different molecular arrangements arising as a result of rotation around carbon carbon single bonds are called conformational isomers or rotational isomers and the phenomenon is called conformational isomerism.

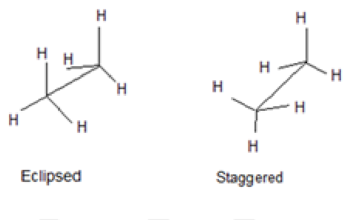
In ethane there are two extreme conformations or arrangement are possible which are known as eclipsed conformation and staggered conformation.

Eclipsed Conformation: H atoms on two adjacent carbon atoms are closest to each other i.e. dihedral angle (angle of rotation) is zero degree.

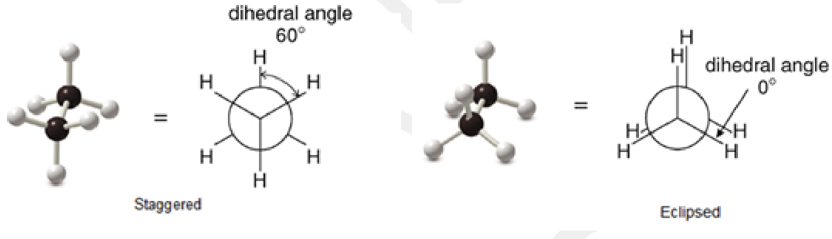
Staggered Conformation: H atoms on two adjacent carbon atoms are farthest to each i.e. dihedral angle is 60°.

Above both conformations can be represent two types-

a) Sawhorse Representation b) Newman's representation



Sawhorse Representation of Ethane



Newman's Representation of Ethane

13.2 Alkenens (olefins)

Introduction:

- These are Open chain, unsaturated hydrocarbons containing at least one double bond between two carbon atoms.
- General molecular formula C_nH_{2n}.
- At least one >c=c< group i.e. sp2 hybridisation, is present throughout the chain.
- When we treated Alkene with chlorine, oily products are obtained so Alkenes are also known as Olefins (Greek olefiant meaning oil forming).
- C=C bond length is 134 pm or 1.34 A^0
- Orbital Structure of Ethene:

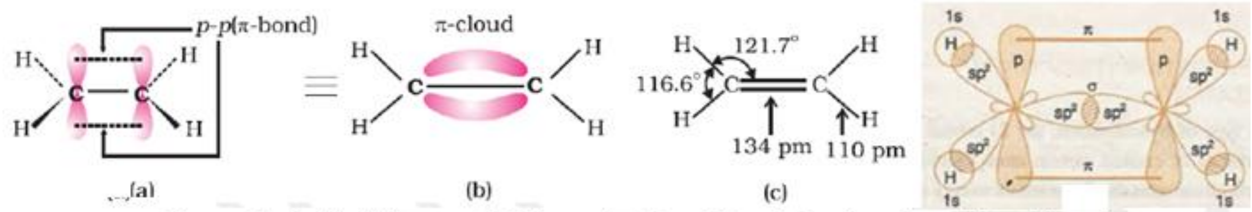
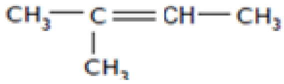


Figure -1: Orbital diagram of Ethene showing pi bond, bond angle and bond length

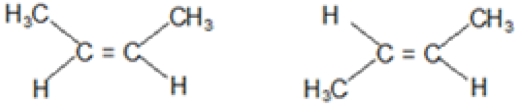
- **Isomerism:** Its show chain, positional and geometrical isomerism like as

Chain Isomerism: $CH_2=CH-CH_2-CH_2-CH_3$ (Pent-1-ene) &  (2-methylbut-2-ene)

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$$

Position Isomerism: $CH_2=CH-CH_2-CH_3$ (But-1-ene) & $CH_3-CH=CH-CH_3$ (But-2-ene)

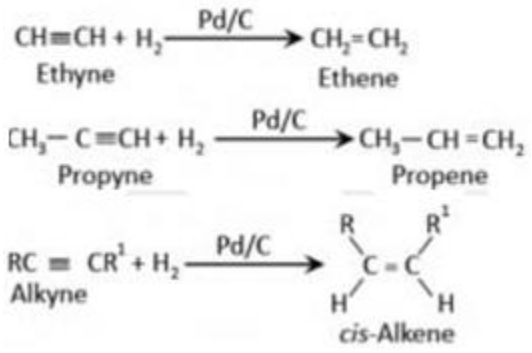
Geometric Isomers:



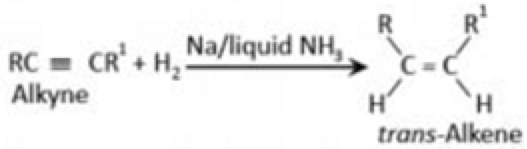
CH₃'s on same side called cis- CH₃'s on opposite sides called trans-

1. Preparation of Alkenes:

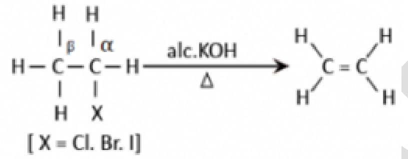
1) From Alkynes: On partial reduction of Alkynes with partially deactivated palladised charcoal known as Lindlar's catalyst give alkenes.

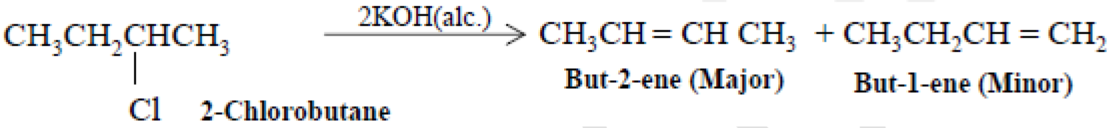


If alkynes reduction carried out in presence of sodium in liquid ammonia it gives trans –alkenes.



2) From Alkyl halides (dehydrohalogenation): When alkyl halides, reacted with alcoholic solution of potassium hydroxide, it eliminate one molecule of halogen acid (HX) to form alkenes. This is also example of beta elimination reaction because hydrogen atom is removed from beta carbon.



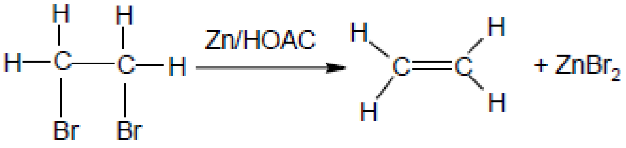


$$\underset{\substack{|\\ Cl}}{CH_3CH_2CHCH_3} \xrightarrow{2KOH(alc.)} \underset{\text{But-2-ene (Major)}}{CH_3CH = CH\ CH_3} + \underset{\text{But-1-ene (Minor)}}{CH_3CH_2CH = CH_2}$$

2-Chlorobutane

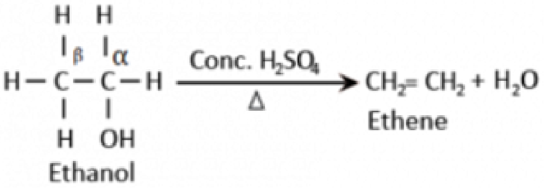
Saytzeff's Rule: In above reaction, the major product is formed according to the Saytzeff's Rule. According to it during dehydration or dehydrohalogenation reaction, if possibilities to form two alkenes, then the major product should be which one that should be more substituted. In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the –C=C– group. In other words during dehydration and dehydrohalogenation the preferential order for removal of an H is 3° > 2° > 1°

3) From vicinal dihalide (dehalogenation): With treatment of Zn metal, vicinal dihalide form alkenes. When two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides.



4) From Alcohols: Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as Al_2O_3 or concentrated H_2SO_4.

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule. This is also example of beta elimination reaction because hydrogen atom is removed from beta carbon.



2. Physical Properties of Alkenes:

1) Physical State: Unbranched alkenes containing up to 4 carbon atoms are gases and containing 5 to 16 carbon atoms are liquids while those with more than 16 carbon atoms are solids.

2) Boiling Points: The boiling points of alkenes increase with molecular mass. The increase in boiling point can be attributed to the van der Waals forces which increase with number of carbon atoms of the Alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers. Cis isomers have higher b.p. rather than trans due to its more polar nature increases the dipole – dipole interaction b/w them.

3) Melting Point: In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the cis and trans isomers have different melting points like melting point of trans-But-2-ene = 167 K and cis-But-2-ene = 134 K.

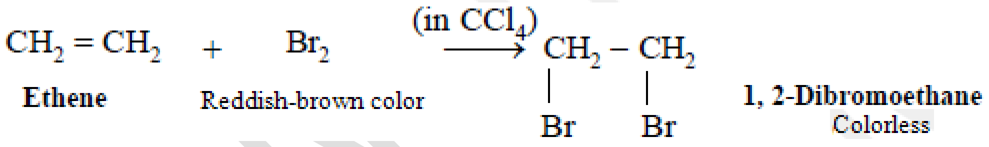
3. Chemical Properties of Alkenes:

1) Addition Reaction: Alkenes show electrophilic addition reaction.

(a) Addition of Hydrogen (Reduction of Alkenes): Due to it form alkanes.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{Ni\ (Pt\ or\ Pd)} \underset{\textbf{Ethane}}{CH_3 - CH_3}$$

(b) Addition of Halogens: Due to addition of halogens with alkenes, it form 1, 2- dihaloalkanes (vicinal dihalide). As a result of this addition reaction, the reddish-brown color of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

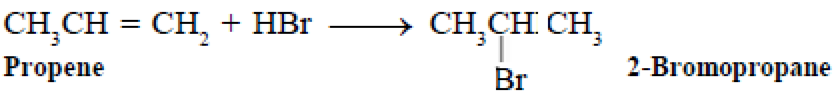


$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + \underset{\text{Reddish-brown color}}{Br_2} \xrightarrow{(in\ CCl_4)} \underset{Br\qquad Br}{CH_2 - CH_2} \quad \textbf{1, 2-Dibromoethane}\ \text{Colorless}$$

(c) Addition of Halogen acids or Hydrogen halide (HX): When halogen acids are added to alkenes, first hydrogen atom adds to one carbon atom then halogen atom adds to the carbon atom of the double bond. It is also example of electrophilic addition reaction. The order of reactivity of hydrogen halides is HI > HBr > HCl.

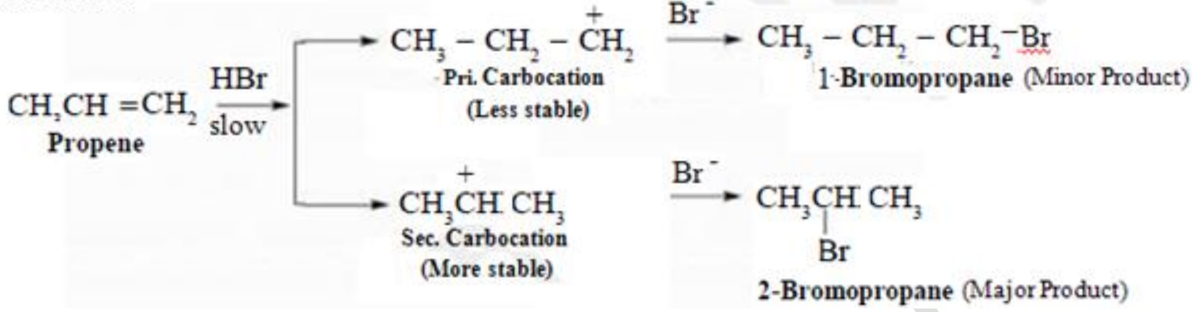
$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3 - CH_2 - Br}$$

Markovnikov's rule for addition of HBr to unsymmetrical alkenes: In case of unsymmetrical alkenes the addition of HBr takes place according to the Markownikoff's rule. According to that in the addition of halogen acids (HX) to unsymmetrical alkenes, the halogen (negative part) of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.



$$\underset{\textbf{Propene}}{CH_3CH = CH_2} + HBr \longrightarrow CH_3\underset{Br}{\underset{|}{CH}}CH_3 \quad \textbf{2-Bromopropane}$$

Mechanism:



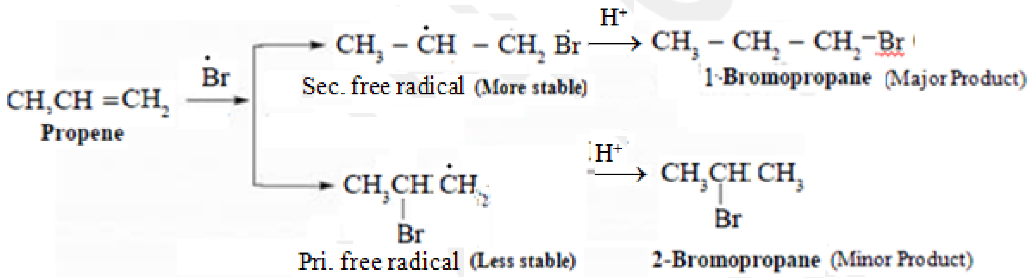
Anti Markovnikov's addition or **peroxide effect or Kharash Effect:** If the addition of HBr (This effect is not happen with HCl and HI) is carried out in the presence of peroxides such as ROOR or benzoyl peroxide $(C_6H_5CO)_2O$, then the reaction takes place contrary to Markovnikov's rule. This is also known as Anti Markovnikov's addition or peroxide effect.

$$\underset{\textbf{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{benzoyl peroxide}} \underset{\textbf{1 – Bromopropane}}{CH_3CH_2-CH_2-Br}$$

Mechanism:

$$\underset{\text{peroxide}}{ROOR} \xrightarrow{\text{Homolysis}} R\dot{O}$$

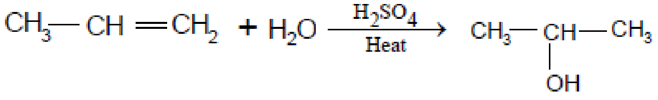
$$RO + HBr \xrightarrow{\text{Homolysis}} ROH + \dot{Br}$$



This effect is not observed with HF, HCl and HI because in HF and H-Cl bond (430.5 kJ mole^{-1}) is stronger than H-Br bond (363.7 kJ mole^{-1}) so not cleaved by the free radical. In case of HI (296.8 kJ mole^{-1}) bond is weaker so iodine free radicals combine to form iodine molecules instead of adding with double bond.

d) Addition of water: Alkenes react with water to form alcohols with presence of few drop of concentrated sulphuric acid. This is electrophilic addition which is carried out as Markonikov rules.

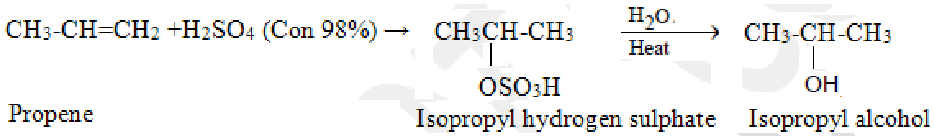
$$CH_2=CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3-CH_2-OH$$



$$CH_3-CH=CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

e) Addition of Sulphuric Acid: Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphate. This is electrophilic addition carried out as Markonikov rules. When water reacts with alkyl hydrogen sulphate it converts in to alcohol which can be distil off.

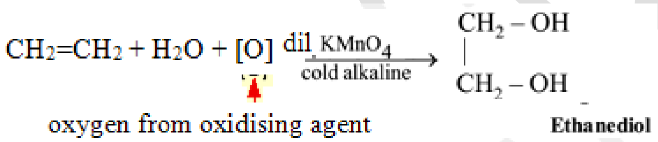
$$CH_2{=}CH_2 + H_2SO_4 \text{ (Con 98\%)} \rightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_3H} \xrightarrow[\text{Heat}]{H_2O} \underset{\text{Ethyl Alcohol}}{CH_3CH_2OH}$$



$$\underset{\text{Propene}}{CH_3\text{-}CH{=}CH_2} + H_2SO_4 \text{ (Con 98\%)} \rightarrow \underset{\text{Isopropyl hydrogen sulphate}}{CH_3\underset{|\atop OSO_3H}{C}H\text{-}CH_3} \xrightarrow[\text{Heat}]{H_2O} \underset{\text{Isopropyl alcohol}}{CH_3\text{-}\underset{|\atop OH}{C}H\text{-}CH_3}$$

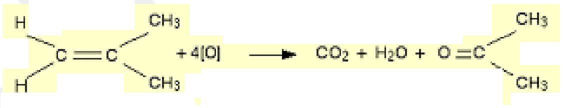
2) Oxidation:

a) With dilute KMnO4 or Hydroxylation or Bayer Test: It reacts with 1% solution of potassium permanganate (Bayer reagent) and form vicinal glycols (Ethane diol). During reaction, color of KMnO4 change from pink to colorless so this reaction also used as a test for unsaturation in hydrocarbon.



$$CH_2{=}CH_2 + H_2O + \underset{\text{oxygen from oxidising agent}}{[O]} \xrightarrow[\text{cold alkaline}]{\text{dil } KMnO_4} \underset{\text{Ethanediol}}{\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}}$$

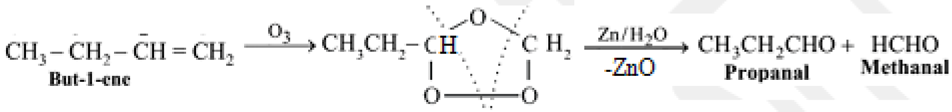
a) With strong oxidising agent (With acidic KMnO4 or potassium dichromate): It forms ketons or carboxylic acid like as



Propane-2-one

$CH_3\text{-}CH{=}CH_2 + 2[O] \rightarrow 2CH_3COOH$ Ethanoic Acid

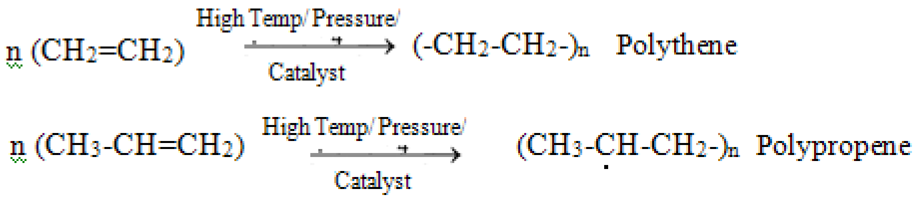
3) Ozonolysis (Oxidation with Ozone): Addition of alkenes with O_3, it forms ozonide which cleavage in to carbonyl compounds, in presence of Zn-H_2O. Ozonolysis is useful to detect the position of double bond in alkenes.



Butene ozonide

Note: Bromine water test and Baeyer's test are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.

4) Polymerisation: Polymerisation is a process of reacting monomer molecules joining together in a chemical reaction to form polymer chain. During the polymerisation of ethene, thousand of ethene molecules joining together to make polythene polymer.



$$n\,(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High Temp/ Pressure/}} (\text{-}CH_2\text{-}CH_2\text{-})_n \quad \text{Polythene}$$

$$n\,(CH_3\text{-}CH{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High Temp/ Pressure/}} (CH_3\text{-}CH\text{-}CH_2\text{-})_n \quad \text{Polypropene}$$

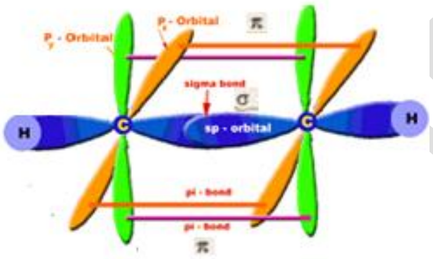
13.3 Alkynes

Introduction:

- Unsaturated hydrocarbon which have at least one triple bond (-c≡c-)
- General molecular formula C_nH_{2n-2}
- sp hybridization (linear geometry)
- Shows chain, positional and functional isomerism

1. Nomenclature and Isomerism: As previous chapter

2. Structure of Triple Bond: Sigma and pi bond formation can be show by orbital structure of simplest alkynes (Ethyne) like as



3. Preparation of Alkynes:

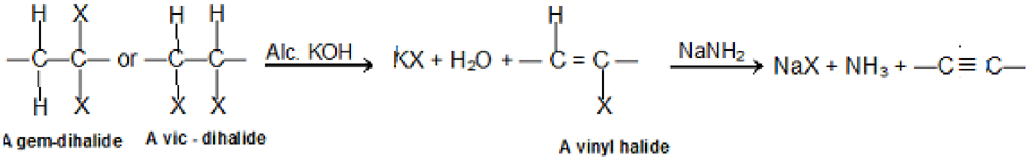
1) From Calcium Carbide (Industrial Method): On industrial scale, it prepared by the action of water on calcium carbide. Calcium carbide also prepared by heating quick lime with coke.

$$\underset{\text{Limestone or Calcium carbonate}}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2$$

$$\underset{\text{Lime}}{CaO} + \underset{\text{Coke}}{3C} \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

2) From vicinal or gem dihalides (dehalogenation):



4. Physical Properties: Physical properties of alkynes are similar to those of the corresponding alkenes.

5. Chemical Properties:

1) Acidic Character of Alkynes: Alkynes of the general structure R-C≡C-H are referred to as terminal alkynes. These types of alkynes are weakly acidic. Exposure to a strong base, such as sodium amide, produces an acid-base reaction.

$$HC\equiv CH + Na \quad \underset{\text{Monosodium ethynide}}{HC\equiv C^-Na^+} + \tfrac{1}{2}H_2$$

$$CH_3-C\equiv C-H + Na^+NH_2^- \rightarrow \underset{\text{Sodium propynide}}{CH_3-C\equiv C^-Na^+} + NH_3$$

The acidity of a terminal alkynes is due to the high level of ‘s’ character in the sp hybrid orbital, which bonds with the s orbital of the hydrogen atom to form a single covalent bond. The high level of s character in a sp-hybridized carbon causes the overlap region of the σ bond to shift much closer to the carbon atom. This polarizes the bond, causing the hydrogen atom to become slightly positive. This slight positive charge makes the hydrogen atom a weak proton, which can be removed by a strong base.
In the case of alkanes and alkenes, the ‘s’ character in the hybridized carbon bonds is less, resulting in fewer electronegative carbon atoms and a corresponding lesser shift toward those atoms in the overlap region of the σ bond.
Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour:

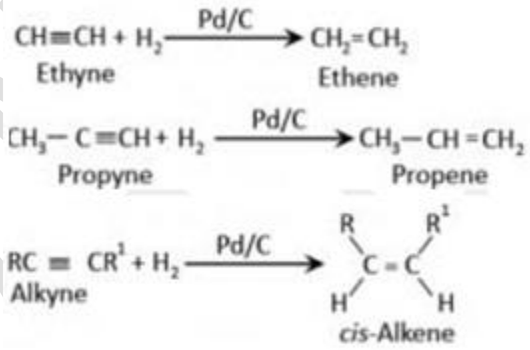
i) $HC{\equiv}CH > H_2C{=}CH_2 > CH_3{-}CH_3$

ii) $HC{\equiv}CH > CH_3{-}C{\equiv}CH >> CH_3{-}C{\equiv}C{-}CH_3$

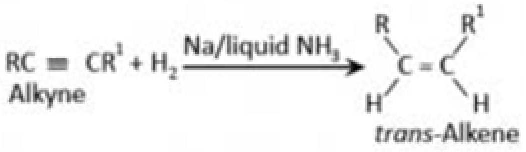
2) Addition Reaction: Alkynes show electrophilic addition reaction.
a) Addition of Hydrogen (Hydrogenation): Due to hydrogenation of alkynes it gives alkane and alkenes accordingly-

$$CH \equiv CH + 2H_2 \xrightarrow[573\,K]{Ni\ or\ Pt} CH_3 - CH_3$$

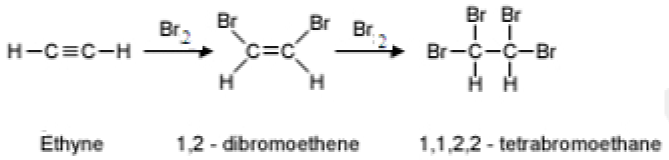
On partial reduction of Alkynes with partially deactivated palladised charcoal known as Lindlar’s catalyst give alkenes.



If alkynes reduction carried out in presence of sodium in liquid ammonia it gives trans –alkenes.

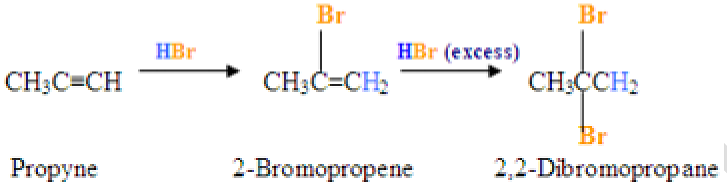


b) Addition of Halogen:

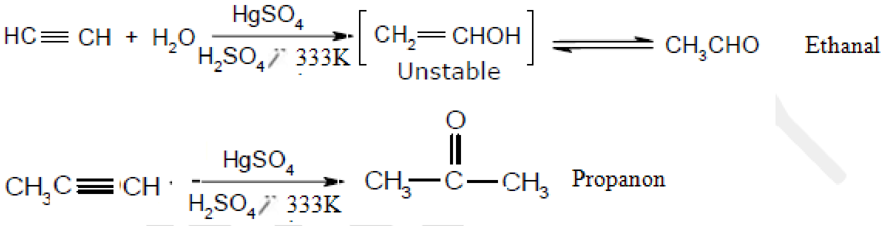


Note: This reaction also used as a test for unsaturation in hydrocarbon due to color of bromine change from orange to colorless.

c) Addition of Hydrogen halide: Addition carried out as per Markovnicov's rule and to form gem dihalides (in which two halogen are attached to the same carbon atom).



d) Addition of Water: It form carbonyl compound like as



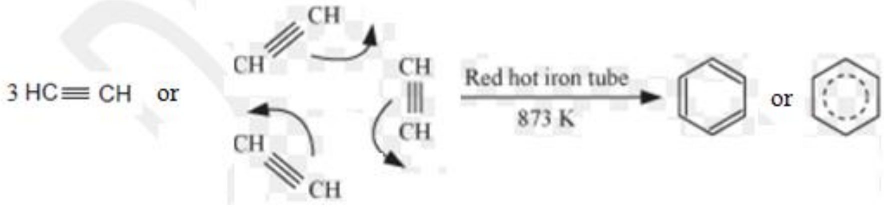
3) Polymerisation:

a) Linear polymerisation of Ethyne: It gives polyacetylene or polyethyne which is a high molecular weight polyethyne containing repeating units of (CH = CH – CH = CH) and can be represented as — (CH = CH – CH = CH) n —

$$n\ HC\equiv CH \longrightarrow —(CH=CH-CH=CH)_n—$$

Polyacetylene or polyethyne

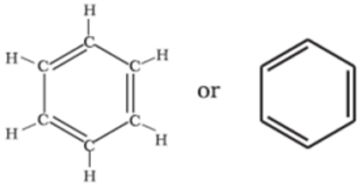
b) Cyclic polymerization- Results in the formation of aromatic compound.



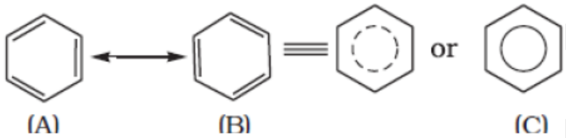
13.4 Aromatic Hydrocarbon

1. Introduction: Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**.

2. Structure of Benzene: Kekulé structure

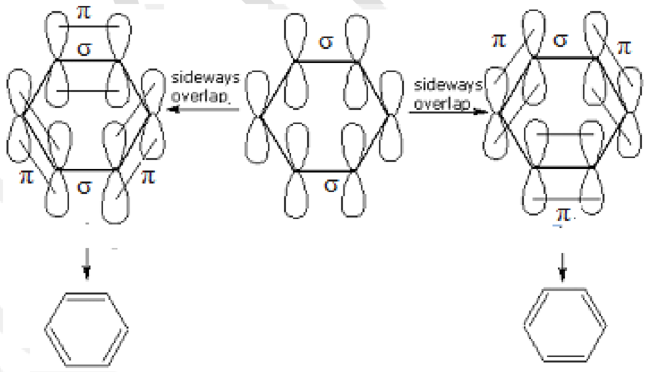


3. Resonance and stability of benzene: Benzene is a hybrid of various resonating structures.



4. The orbital overlapping picture benzene: All the six carbon atoms in benzene are sp^2 hybridized and these hybrid orbitals form sigma bonds.

The unhybridised *p* orbital of carbon atoms are close enough to form a π bond by lateral overlap. The six π electrons are thus delocalised and can move freely about the six carbon nuclei. The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable.



5. Aromaticity: The compounds that follow the following features are to be considered as aromatic.

(i) Planarity in geometry.

(ii) Complete delocalisation of the π electrons in the ring

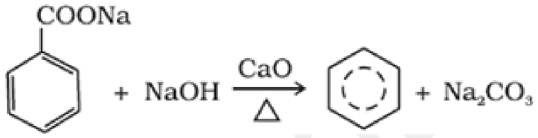
(iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots$). This is often referred to as **Hückel Rule**.

For ex in benzene 4n+2= 6 π electrons so value of n in benzene =1 so it is aromatic compound.

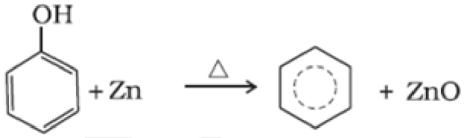
6. Preparation of Benzene:

1) Cyclic polymerisation of Ethyne: See chemical properties of Alkynes.

2) Decarboxylation of aromatic acids*:*



3) Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust



7. Physical properties:

1) Aromatic hydrocarbons are non- polar molecules and are usually colorless liquids or solids with a characteristic aroma.

2) They are immiscible with water but are readily miscible with organic solvents.

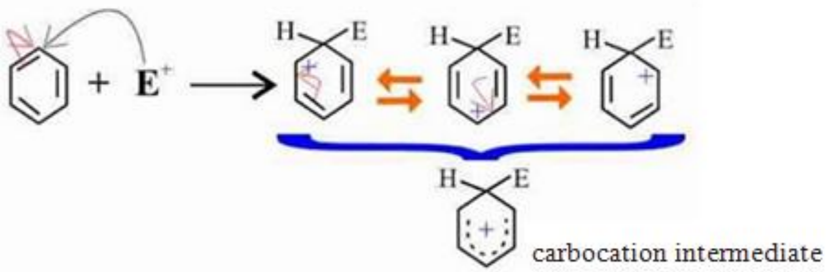
3) They burn with sooty flame.

8. Chemical properties:

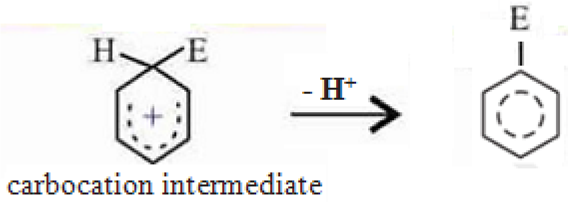
1) Electrophile substitution reaction: Arenes are characterized by electrophilic substitution reactions due to high stabilization of benzene ring by resonance (or delocalisation of pi electrons). So the substitution reactions in benzene are initiated by electrophile. Thus characteristic reactions of benzene are electrophile substitution reaction. It proceeds via the following three steps:

(a) Generation of the electrophile: $E\text{-}X + AlCl_3 \rightarrow \mathbf{E^+} + [AlCl_3X]^-$

(b) Formation of carbocation intermediate:

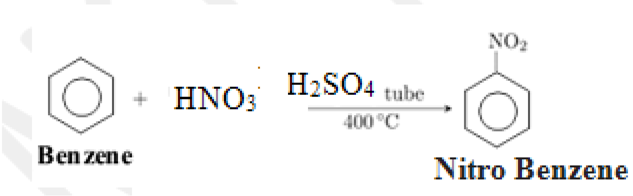


(c) Removal of proton from the carbocation intermediate:



Following are the examples of electrophile substitution reactions of benzene are as following-

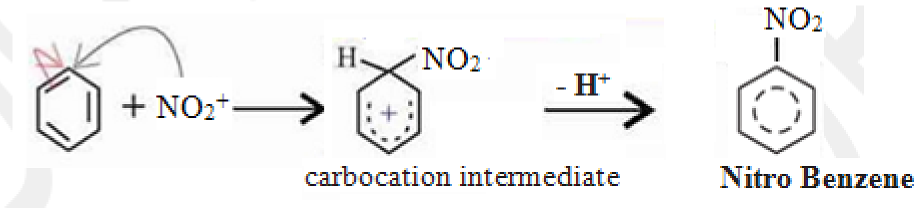
i) Nitration:



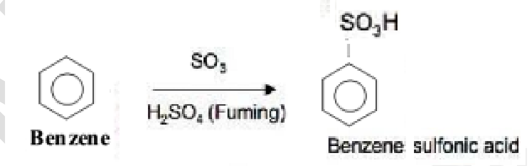
Mechanism:

Step 1) Formation of Electrophile: $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$ (Nitronium ion)

Step 2 & 3) Formation of carbocation intermediate and Removal of proton from the carbocation intermediate:



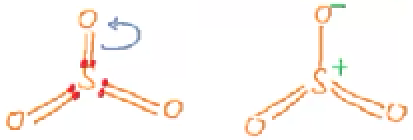
ii) Sulphonation: It is carried out with heating of benzene with fuming sulphuric acid (oleum). Fuming sulphuric acid release fumes of SO_3. Mixture of H_2SO_4+SO_3 = $H_2S_2O_7$ are also known as Oleum.



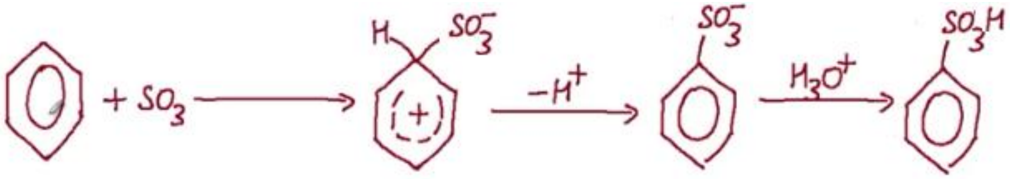
Mechanism:

Step 1) Formation of Electrophile: $2H_2SO_4 = SO_3 + HSO_4^- + H_3O^+$

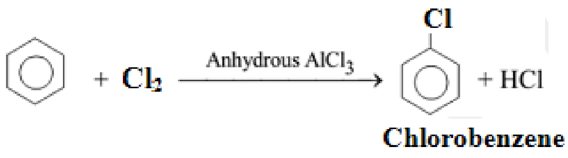
Here SO_3 is a electrophile, it can be explain as



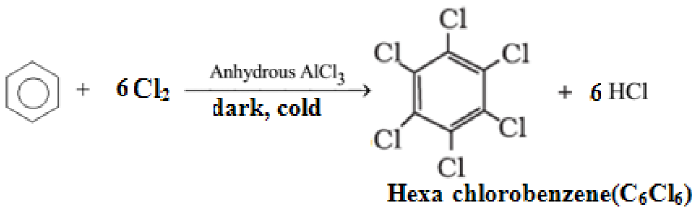
Step 2 & 3) Formation of carbocation intermediate and Removal of proton from the carbocation intermediate:



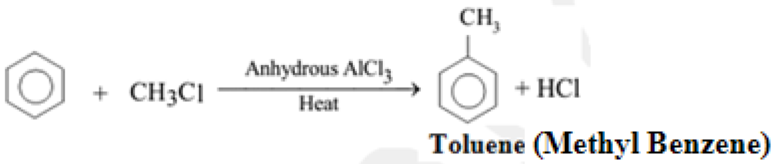
iii) Halogenation: This reaction is carried out in the presence of lewis acid like anhydrous BF_3, HF, $FeCl_3$ or $AlCl_3$



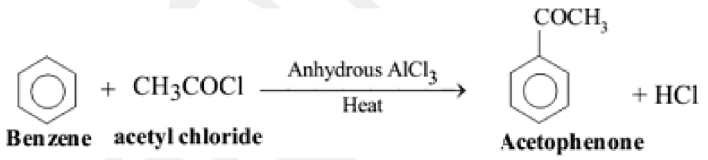
If excess of chlorine is used during the reaction, all other hydrogen of benzene ring is replaced by the chlorine (electrophile) and to form hexachlorobenzene.

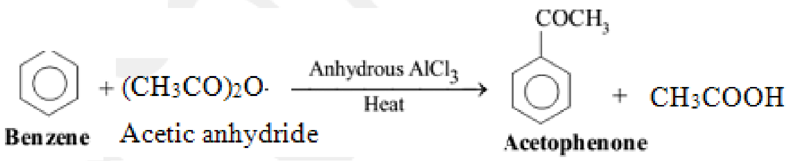


iv) Friedel Crafts alkylation reaction:



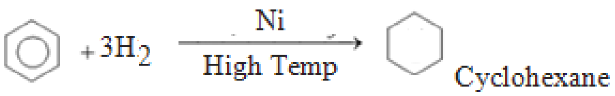
v) Friedel Crafts alcylation reaction:



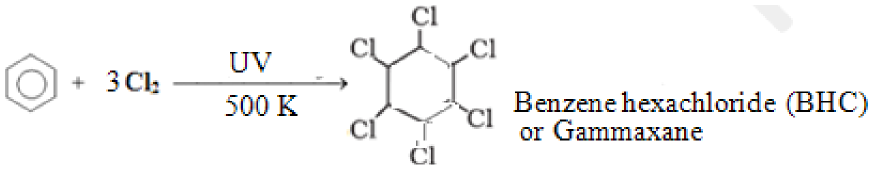


2) Addition Reaction:

i) Addition with Hydrogen (Hydrogenation):



ii) Addition with Chlorine:



3) Combustion: $C_6H_6 + 15/2\ O_2 \rightarrow 6CO_2 + 3H_2O$

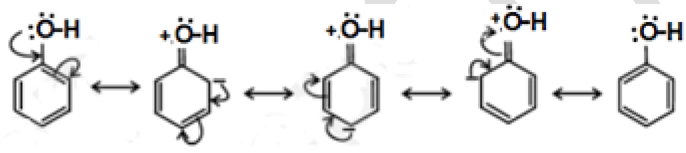
General combustion reaction of hydrocarbon may be given by the following chemical equation:

$$C_xH_y + (x + \frac{y}{4})\, O_2 \rightarrow x\, CO_2 + \frac{y}{2}\, H_2O$$

9. Directive Influence Of Functional Group in Mono Substituted Benzene: When mono substituted benzene undergoes an electrophilic attack, the rate of reaction and the site of attack vary with the functional group already attached to it. Some groups increase the reactivity of benzene ring and are known as **activating groups** while others which decrease the reactivity are known as **deactivating groups**.

We further divide these groups into two categories depending on the way they influence the orientation of attack by the incoming electrophile.

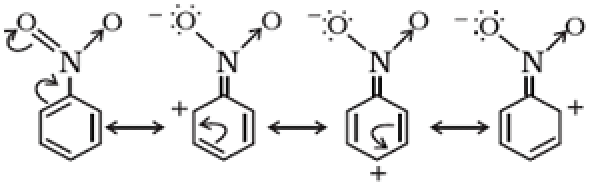
Ortho and para directing (activating) group: Those which increase the electron density at ”ortho” and “para” positions are known as **ortho and para directing groups.** These groups direct the electrophilic attack on “ortho” and “para” positions. All activating groups, which are “ortho-para” directing, for example –NH_2, –NHR, –$NHCOCH_3$, –OCH_3,–CH_3, –C_2H_5, etc.



From the figure, it is quite evident that the electron density at ortho and para position increases as compared to the “meta” position due to the resonance of benzene ring. As a result, we can say that “–OH” group is an ortho-para director.

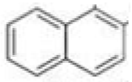
Ortho and para directing (deactivating) group: Halogens too are ortho-para directors, irrespective of the fact that they are **deactivating** due to “-I” effect.

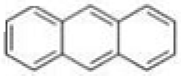
Meta directing (deactivating) groups: Those groups which increase the electron density at “meta” position are known as **meta directing groups**. These groups direct the electrophilic attack on “meta” positions of the associated benzene ring. Generally deactivating groups are meta directors, for example –NO_2, –CN, –CHO, –COR, –COOH, –COOR, –SO_3H, etc.

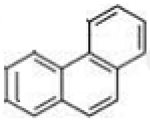


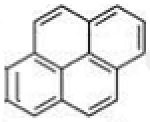
Nitro group is a ring deactivating group; they decrease the electron density of the attached benzene ring. As above figure the electron density at “meta” position is quite high in comparison to “ortho” and “para” position. Hence, these groups facilitate electrophilic substitution of the ring at “meta” positions and are called meta directors.

10. Carcinogenicity and toxicity: Aromatic hydrocarbons containing two or more fused rings are called polycyclic aromatic compounds or polynuclear aromatic hydrocarbons. Coal tar is the main source of polynuclear aromatic hydrocarbons. These hydrocarbons possess either a linear or an angular structure. For example hydrocarbon with a linear structure is naphthalene or anthracene, phenanthrene and pyrene.

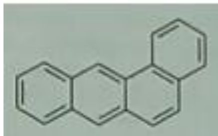

naphthalene

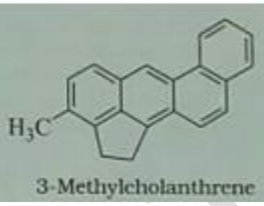

anthracene

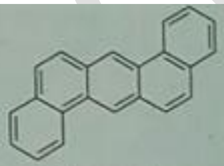

phenanthrene

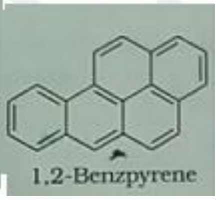

pyrene.

These following polycyclic aromatic hydrocarbons are carcinogenic as they cause cancer.

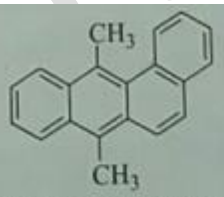

1,2-Benzanthracene


3-Methylcholanthrene


1,2,5,6-Dibenzanthracene


1,2-Benzpyrene

It is found that the number and position of certain groups such as methyl, hydroxide, cyanide and methoxy in these compounds give rise to carcinogenic tendencies.


9,10-Dimethyl-1,2-benzanthracene

These polynuclear aromatic hydrocarbons enter the environment due to the incomplete combustion of coal, petroleum, tobacco, etc. On entering the human body, these compounds undergo various biochemical reactions and damage DNA. This causes a sudden change in the DNA structure, leading to cancer.