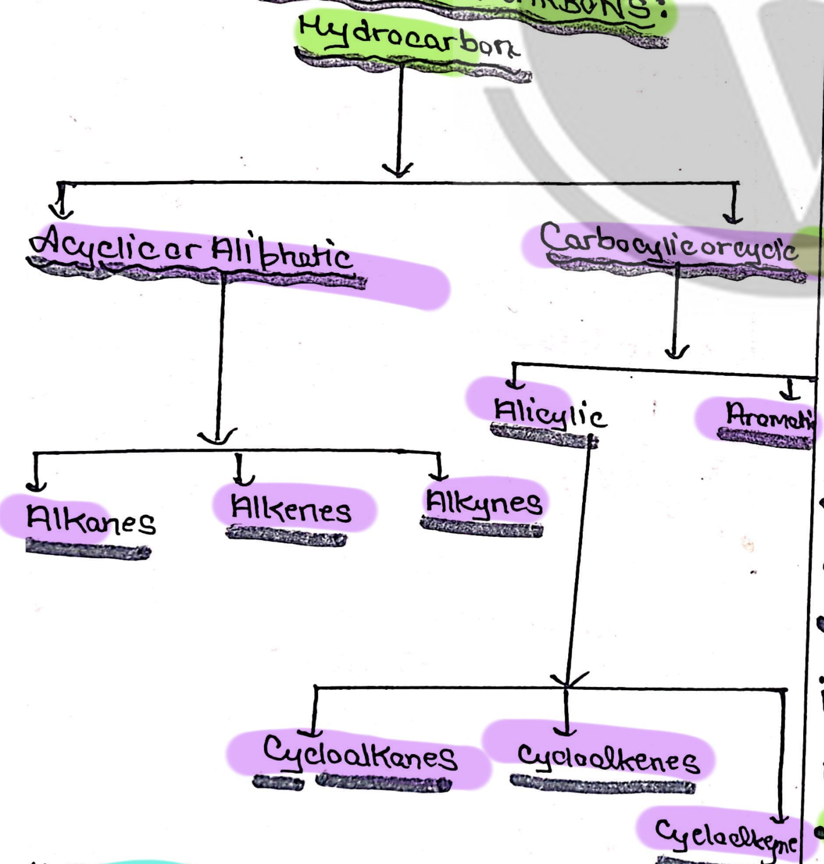
# HYDROCARBON

- **Hydrocarbons** are composed of Carbon and Hydrogen.
- The important fuel like petrol, kerosene, coal gas, CNG, LPG, etc. are all hydrocarbons or their mixture.
- **Sources:** Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons. The oil trapped the rock 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 consituterts of the natural gas are methane, ethane, probrane and butane.

## CLASSIFICATION OF HYDROCARBONS:

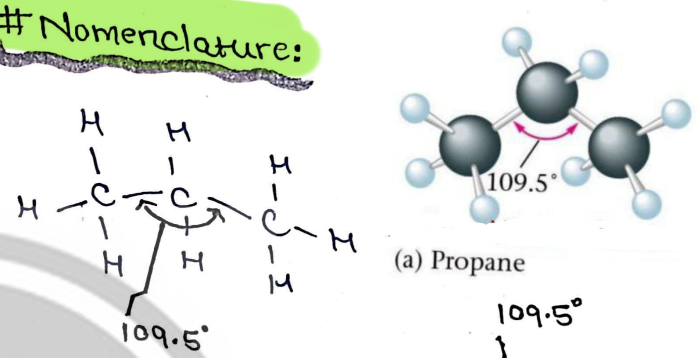


## # Alkanes:

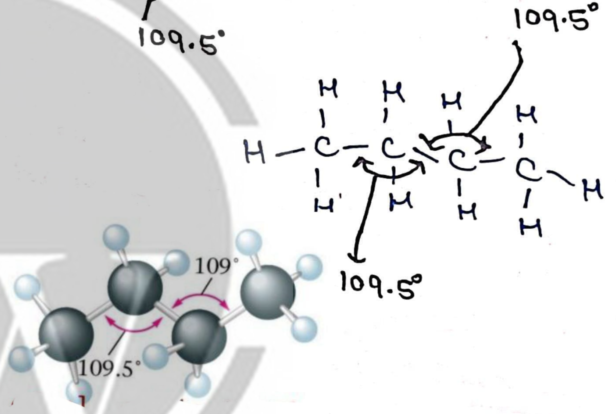
- Paraffins.
- General formula $C_nH_{2n+2}$

- $Sp^3$ hybridisation.
- C-C bond length 1.154 Å
- Chemically unreactive
- Show chain, position and optical isomerism
- Heptane has 9 isomer, Octane 18 and decane 75.

## # Nomenclature:



(a) Propane



(b) Butane

## # Prepration:

i) **Wurtz Reaction**:-

$$2CH_3CH_2Br + 2Na \xrightarrow{Dry} CH_3CH_2CH_2CH_3 + 2NaBr$$

- Follow mainly free radical mechanism.
- Useful in preparing an alkene containing even number of carbon atoms.
- Stepping up reaction.

ii) **Frakland - Reaction**:- $RX + Zn + RX \longrightarrow R-R + ZnX_2$.

- **From Grignard Reagent:**

$RMgX + HOH \longrightarrow RH + Mg(OH)X$

$RMgX + R'OH \longrightarrow RH + Mg(OR')X$

$RMgX + R'NH_2 \rightarrow RH + Mg(NHR')X$

### iii) from unsaturated hydrocarbons:

$R-CH=CH_2+H_2 \xrightarrow{Ni/\Delta} R-CH_2-CH_3$

$R-C\equiv CH+H_2 \xrightarrow{Ni/\Delta} R-CH_2-CH_3$

### iv) From Carboxylic Acid: Decarboxylation-

$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4+Na_2CO_3$

Sodium ethanoate

**Kolbe's electrolyic Method-**

$2CH_3COO^-Na^+ + 2H_2O$

Sodium acetate

$\downarrow$ Electrolysis

$CH_3-CH_3+2CO_2+H_2+2NaOH$

# Physical-Properties:

i) **Nature:** Non-polar due to covalent nature of C-C bond and C-H bond. C-C bond energy = 83kj/Mole and C-H bond energy = 99kj/Mole.

ii) **Solubility:** Like dissolve like. Viz, polar compounds dissolve in polar solvent and Non-polar compound dissolve in non-polar solvent.

iii) **Boiling-Point:** Low boiling point due to non-polar in nature.

- The molecules are held together only by weak van der walls' forces.
- Since we know that the magnitude of vander wall's forces is directly proportion to Molecular size. Therefore, the boiling point increase with increase the molecular size i.e. with increase in number of carbon atoms.

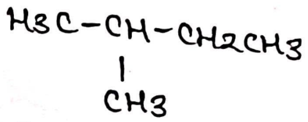
**#Noted:** The boiling points of the branched chain alkanes are less then the Straight chain isomers.

- This is due to the fact that branching of the chain makes the molecule more compact and thereby decrease the surface aria and consequently, the magnitudes of vander wall's forces also decreases.

$CH_3CH_2CH_2CH_2CH_3$

n-pentane

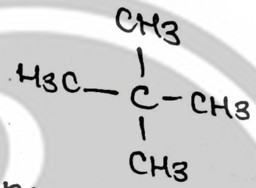
(boiling point = 309k)



$H_3C-\underset{\substack{|\\ CH_3}}{CH}-CH_2CH_3$

Iso-pentane

boiling point = 301k



$H_3C-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_3$

neo-pentane

boiling-point = 282.5k

# Chemically-Properties:

i) **Combustion:**

$CH_4+2O_2 \rightarrow CO_2+2HO$

$\Delta H = -217.0K\ cal/Mole$

ii) **Oxidation:** $CH_4+O_2 \xrightarrow[573k]{Cu} 2CH_3OH$

$CH_4+O_2 \xrightarrow{Mo_2O_3} HCHO+H_2O$

Methanel

iii) **Subsitution:** i) Halogenation:

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

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

**#Note:** Iodination is a reversible rxn. so it is carried out by heating alkane in the presence of some oxidising agent like iodic Acid ($HIO_3$) or nitric acid ($HNO_3$) or Mercuric oxide ($HgO$) which oxidizes HI formed during the reaction.

$CH_4 + I_2 \xrightarrow{Heat} CH_3I + HI$

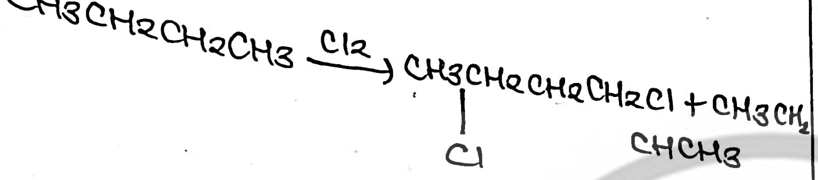
$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$

$2HI + 2HNO_3 \longrightarrow 2H_2O + I_2 + 2NO_2$

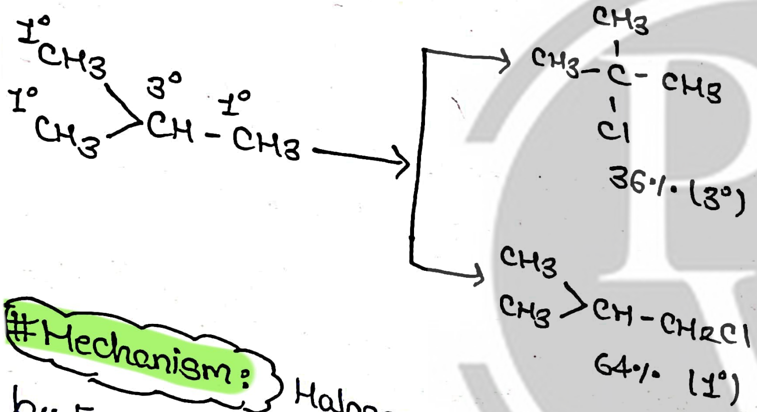
## • Features of Halogenations:

i) The reactivity of Halogens: $F_2 > Cl_2 > Br_2 > I_2$.

ii) The rate of replacement of Hydrogens of - Alkanes is: 3° > 2° > 1°



$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHCH_3$ (Cl)



## # Mechanism:

Halogenations rxn take place by free redical mechanism. The reaction - proceed into the following steps.

### i) Chain Initiation Step:

$Cl - Cl \xrightarrow{h\nu} 2Cl$

### ii) Chain Propagation step:

$CH_4 + Cl \longrightarrow CH_3 + HCl$

$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl.$

### iii) Chain termination step:

$Cl + Cl \longrightarrow Cl_2$

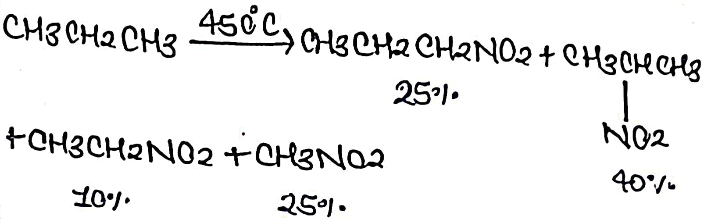
$CH_3 + CH_3 \longrightarrow CH_3 - CH_3$

$CH_3 + Cl \rightarrow CH_3Cl.$

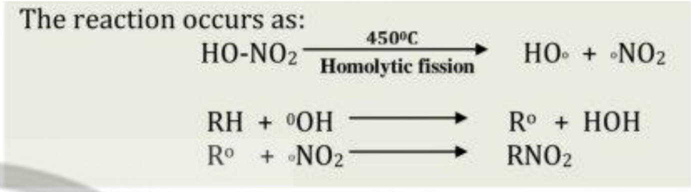
## (ii) Nitration:

The rxn takes places by free radicals mechanism at high temp (450°C).

• At high temp C-C bond is also broken so that mixture of nitroalkanes is obtained.



$CH_3CH_2CH_3 \xrightarrow{450°C} \underset{25\%}{CH_3CH_2CH_2NO_2} + \underset{40\%}{CH_3CH(NO_2)CH_3} + \underset{10\%}{CH_3CH_2NO_2} + \underset{25\%}{CH_3NO_2}$



The reaction occurs as:

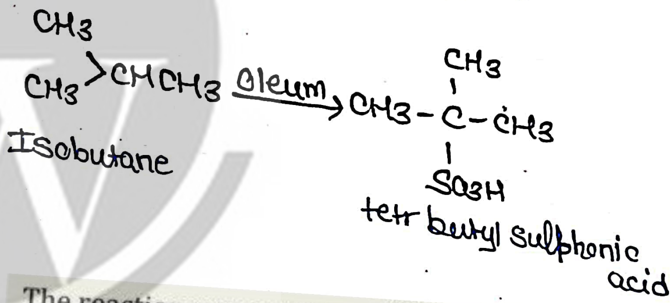
$HO\text{-}NO_2 \xrightarrow[\text{Homolytic fission}]{450^0C} HO^\circ + {}^\circ NO_2$

$RH + {}^0OH \longrightarrow R^o + HOH$

$R^o + {}^\circ NO_2 \longrightarrow RNO_2$

## (iii) Sulphonation:

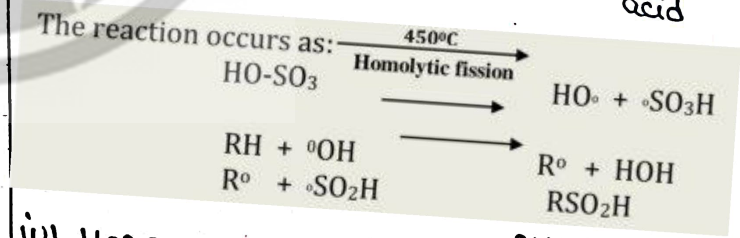
Replacement of hydrogen atom of alkane by - $SO_3H$ group.



$(CH_3)_2CHCH_3 \xrightarrow{Oleum} CH_3-C(CH_3)(SO_3H)-CH_3$

Isobutane

tetr butyl sulphonic acid

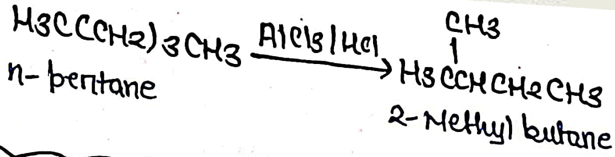


The reaction occurs as:

$HO\text{-}SO_3 \xrightarrow[\text{Homolytic fission}]{450^0C} HO^\circ + {}^\circ SO_3H$

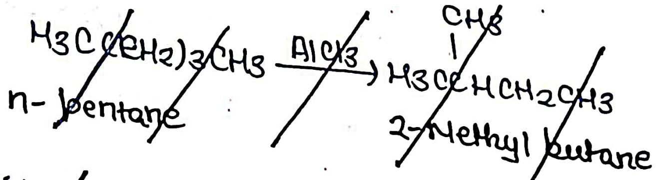
$RH + {}^0OH \longrightarrow R^o + HOH$

$R^o + {}^\circ SO_2H \longrightarrow RSO_2H$

iv) 

$\underset{n\text{-}pentane}{H_3C(CH_2)_3CH_3} \xrightarrow{AlCl_3/HCl} \underset{2\text{-}Methyl\ butane}{H_3CCH(CH_3)CH_2CH_3}$

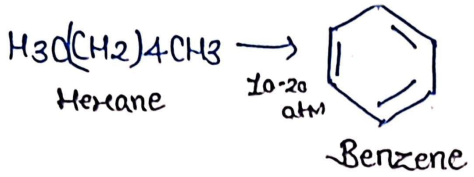
## (v) Aromatization:



~~$\underset{n\text{-}pentane}{H_3C(CH_2)_3CH_3} \xrightarrow{AlCl_3} \underset{2\text{-}Methyl\ butane}{H_3CCH(CH_3)CH_2CH_3}$~~

~~This method also called dehydrogenation or hydroforming.~~

## #Aromatization:


$H_3C(CH_2)_4CH_3 \xrightarrow[\text{atm}]{10\text{-}20}$ Benzene

Hexane

- This Method is also called dehydrogenation or hydroforming.

**vi) Thermal-decomposition:** When higher alkane are heated at high temp (about 700-800k) in the presence of alumina, the alkanes break down the lower alkanes and alkenes.

$CH_3-CH_2-CH_3 \longrightarrow CH_3-CH-CH_2 + CH_3-CH_3 + C_2H_4 + CH_4$

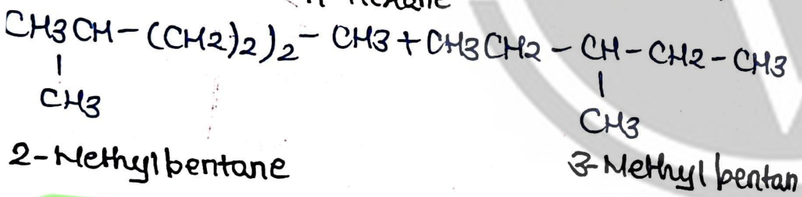
**vii) Action of Steam:** catalyst: Nickel, alumina $Al_2O_3$

$CH_4 + H_2O\,(\text{Steam}) \longrightarrow CO + 3H_2$

This reaction is used for the industrial prebration of hydrogen form natural gas.

**viii) Isomerism** $CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy. AlCl}_3}$

n-Hexane

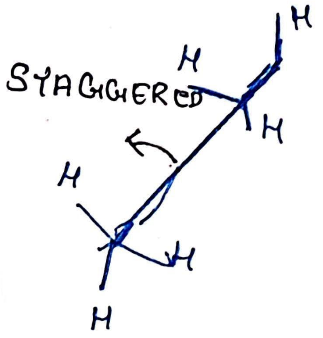

$\underset{\underset{CH_3}{|}}{CH_3CH}-(CH_2)_2)_2-CH_3 + CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

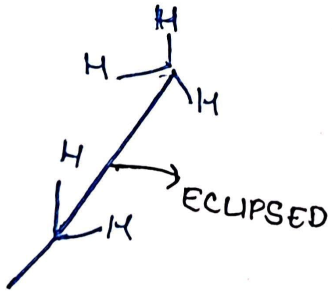
2-Methylbentane 3-Methyl bentan

## #Conformational Isomerism:

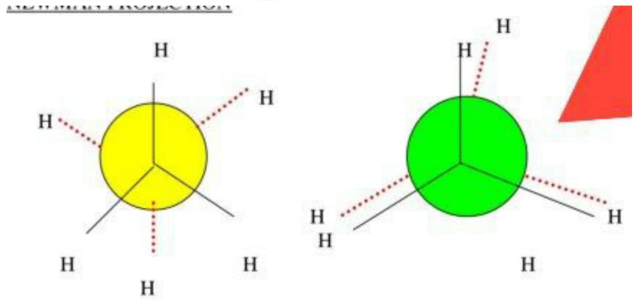
The different Molecular arrangements arising as a result of rotation around carbon carbon single bond are called Conformational Isomerism.

## #Sawhorse Representation





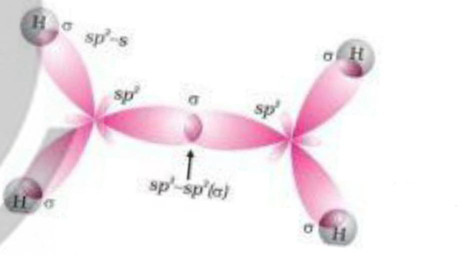
## #Newman Projection

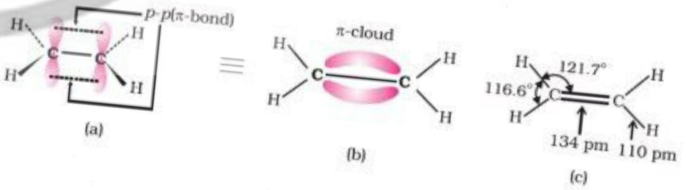


## #Alkenes:

Unsaturated hydrocarbon - which have double bond.

- General Molecular Formula $C_nH_{2n}$.
- C-C bond hybridization 1.34A.
- $sp^2$ hybridization
- When we treated alkane with chlorine, oily products are obtained. so Alkenes are called Olefins.
- Structure of Double bond :-





(a) (b) (c)

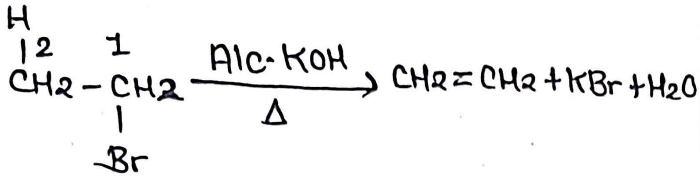
## #Prebration:

**i) From Alkynes:** Alkynes on partial reduction with bartially deactivated pallasid charcoal known as Lindlar's - catalyst give alkynes.

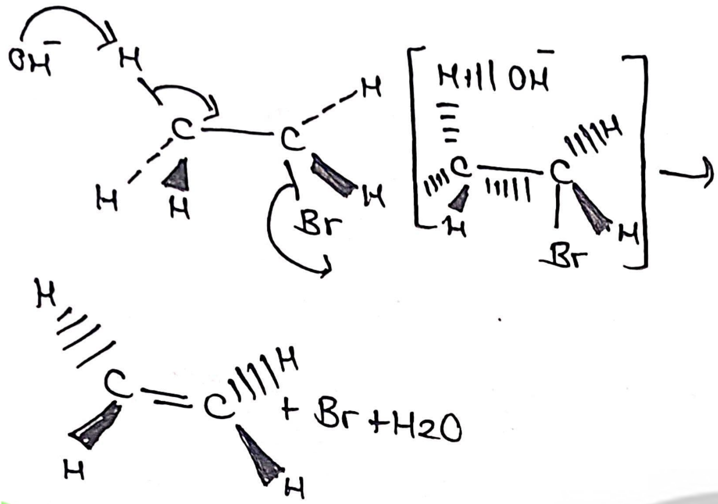
$CH\equiv CH + H_2 \xrightarrow{Pd/C} CH_2=CH_2$

Ethyne Ethene

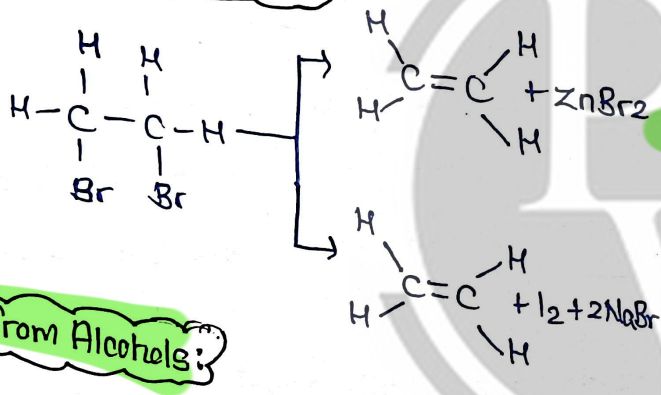
**ii) From Haloalkanes** - Dehydrohalogenation



$$\overset{H}{\overset{|2}{C}}H_2-\overset{1}{C}H_2(Br)\xrightarrow[\Delta]{Alc\cdot KOH}CH_2=CH_2+KBr+H_2O$$



## # from dihaloalkanes:



$$H-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H\rightarrow \begin{cases} CH_2=CH_2+ZnBr_2\\ CH_2=CH_2+I_2+2NaBr\end{cases}$$

## # from Alcohols:

$CH_3CH_2CH_2OH\xrightarrow{Conc\cdot H_2SO_4}CH_3CH=CH_2+H_2O$

## # Mechanism:

$CH_3-CH_2-CH_2-OH\underset{}{\overset{H^+}{\rightleftharpoons}}CH_3-CH_2-CH_2-\overset{+}{O}H_2$

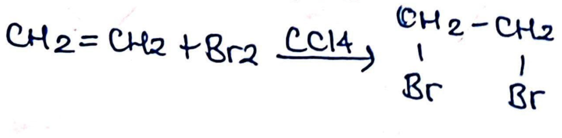
$\longrightarrow CH_3-CH_2-CH_2^+$

## # Chemical-Properties: Addition-Rxn:

### i) Addition of Hydrogen:

$RCH=CH_2\xrightarrow{H_2/Ni}RCH_2CH_3$

### ii) Addition of Halogens:

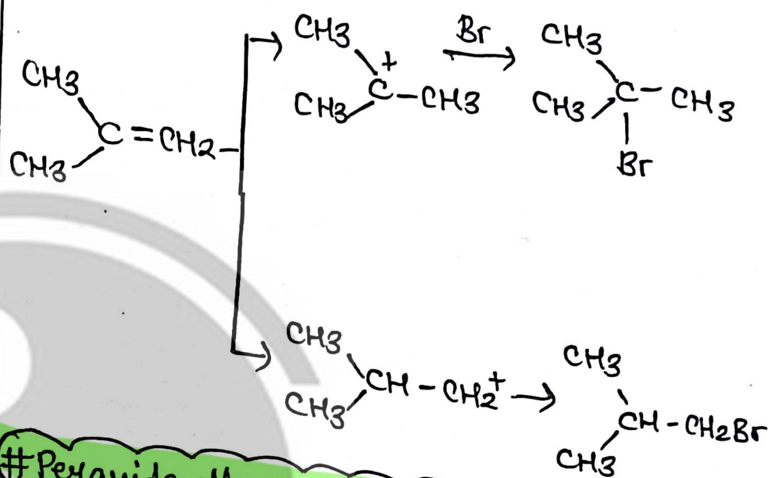


$$CH_2=CH_2+Br_2\xrightarrow{CCl_4}\underset{Br}{C}H_2-\underset{Br}{C}H_2$$

### iii) Addition of Hydrogen halides:

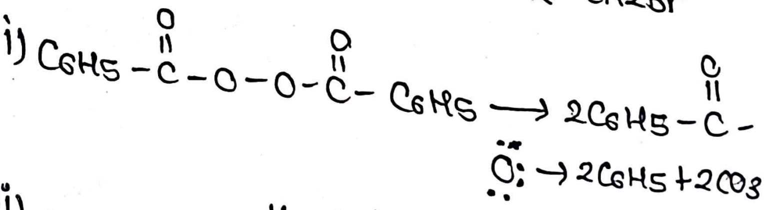
$CH_2=CH_2+H-Br\longrightarrow CH_3-CH_2-Br$

**# Markovnikov-Rule:** Negative part of the addendum gets attached to that carbon atom which posses lesser number of hydrogen atom.



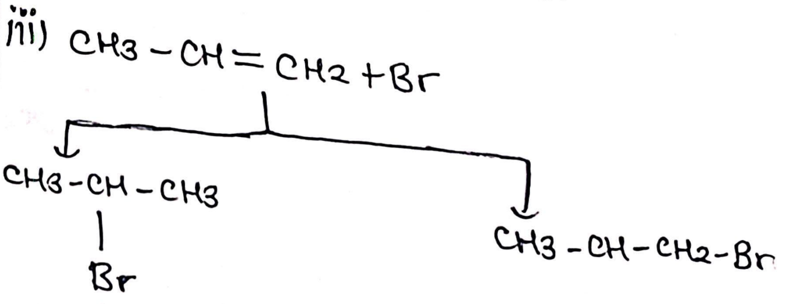
**# Peroxide effect of kharasch:** In 1933 kharasch and mayo observed that when HBr is added to an un symmetrical double-bond in the presence of organic peroxide the rxn take place opposite to the markovnikov rule.

$CH_3-CH=CH_2\xrightarrow{HBr}CH_3-CH_2-CH_2Br$



$$i)\ C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5\longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{O}{:}\longrightarrow 2C_6H_5+2CO_2$$

ii) $C_6H_5+H-Br\xrightarrow{Homolysis}C_6H_6+Br$



$$iii)\ CH_3-CH=CH_2+Br\rightarrow \begin{cases}CH_3-\underset{Br}{C}H-CH_3\\ CH_3-CH-CH_2-Br\end{cases}$$

iv) $CH_3-CH-CH_2Br + H-Br \longrightarrow CH_3-CH_3-CH_2Br + Br$

**iv) Addition of water:** Acid catalyzed addition of water.

$$CH_3-CH=CH_2 + H_2O \longrightarrow CH_3-\underset{\displaystyle CH}{\underset{|}{CH}}-CH_3$$

### 2) Oxidation: i) Combustion → $CO_2 + H_2O$

**i) Hydrobornation - Oxidation:** Alkanes react with diborane to form trialkyl boranes which on oxidation with alkaline $H_2O_2$ give alcohols.

$$3CH_2=CH_2 \xrightarrow{BH_3} \underset{\text{Triethyl borane}}{CH_3CH_{2\,3}B} \xrightarrow{H_2O_2} \underset{\text{Ethyl alcohol}}{3CH_3CH_2OH}$$

**iii) Oxymecuration - demercuration:**

$$H_2C=CH_2 \xrightarrow{Hg(OAC)_2} \underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_2-HgOAC \xrightarrow{NaBH_4} CH_3CH_2OH + Hg$$

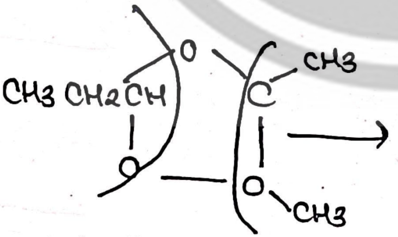
**iv) Oxidation with Pottasium bermangente:**

$$2KMO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

- This rxn also called Hydroxylation.
- Cis product I.e. cis Idol is obtained.

### # Oxidatation with Ozone: Ozonolysis — gives - carbonyl combounds.

$$CH_3CH_2CH=\underset{\displaystyle CH_3}{\underset{|}{CH_3}} \xrightarrow{O_3}$$



$$\longrightarrow CH_3CH_2\overset{\displaystyle O}{\overset{||}{C}}H + CH_3\overset{\displaystyle O}{\overset{||}{C}}CH_3 + Zn(OH)_2$$

### # Alkynes: → Unsaturated hydrocarbon which have trible band

→ General molecular formula.

→ SP hybridization.

### # Prebration: From vinical dihalides :- dihalogenation

$$CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{2KOH} CH_3-C\equiv CH + 2KBr + 2H_2O$$

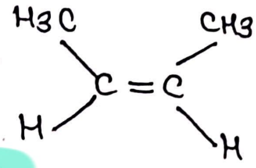
### # Chemical-Proberties:

**i) Addition Reaction** - Alkyne show electrophillic addition reaction.

**ii) Addition of Hydrogen** - Hydrogenation.

$$CH_3C\equiv CH + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

$$CH_3C\equiv CCH_3 \xrightarrow[\text{catalyst}]{H_2}$$



**iii) Addition of Halogens:**

$$HC\equiv CH \xrightarrow{2Br_2} H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H$$

**iv) Addition of hydrogen halides:**

$$HC\equiv CH + 2HBr \longrightarrow CH_3CHBr_2$$

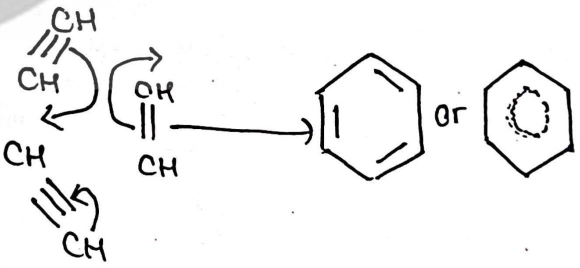
**v) Addition of water (Hydration):**

$$HC\equiv CH + H_2O \longrightarrow [CH_2=CHOH] \rightleftarrows CH_3CHO$$

### 5) Polymersitation: a) Linear Polymerisation:

of ethyne gives Polyacetylne or bolyethne which is a high molecular wieght bolyene containing rebeating unit of $(CH=CH-CH=CH)$ and can be represented as $-(CH=CH-CH=CH)$

**b) Cyclic-Polymerisation:** Result in the form of aromatic Compound.



### # Acidity of Alkynes: Terminal alkynes are acidic in nature.

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

- Akanes, Alkenes, alkynes follow the following trend in their acidic behaviour:

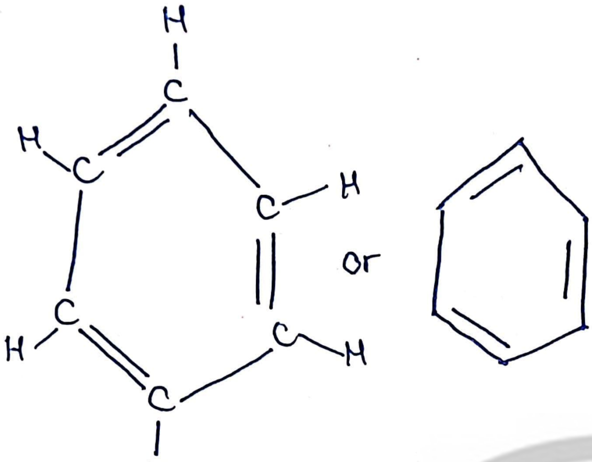
i) $HC\equiv CH > H_2C=CH_2 > CH_3-CH_3$

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

## # Aromatic- Hydrocarbon:

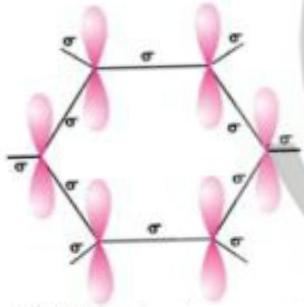
Aromatic combaund containing benzene ring are known as benzeniods and those not containing a benzone ring are known as non- bezeniods.

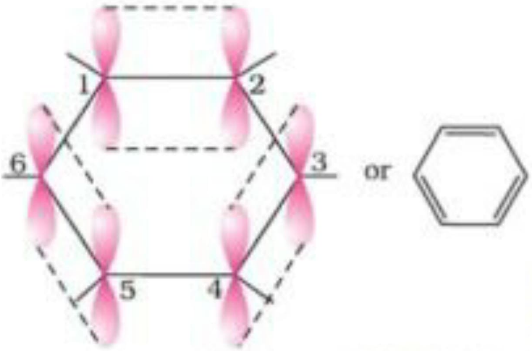
## #Structure of Benzene:

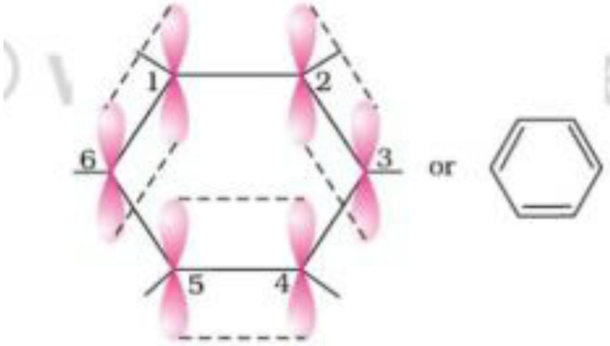


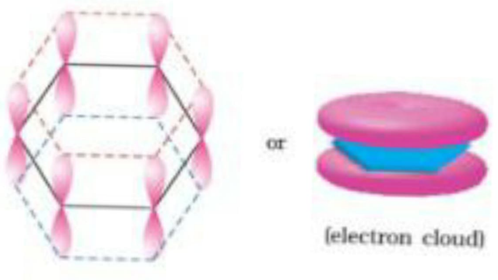
## # Resonance and Stabillity of Benzene:

All the six carbon atoms in benzene are $sp^2$ hybridized and these hybrid orbitals from sigma bonds.









## #Aromaticity:

The compounds that Follows the Following Features are to be considerd aromatic.

i) Planarity.

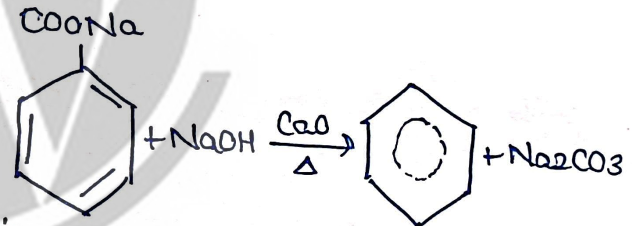
ii) Complete delocalisation of π electron in the ring.

iii) Presence of $(4n+2)\pi$ electron in the ring where n is an integer ($n=0,1,2-----$) This is often reffered to as Hückel Rule.

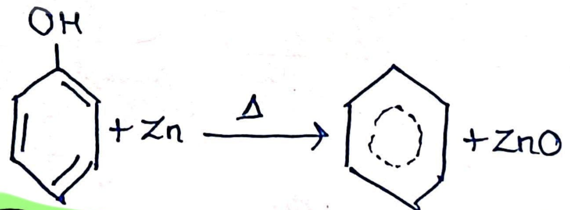
## #Prepration of Benzene:

i) Cyclic Polymerisation of ethyne:

ii) Decarboxylation of Aromatic acids:



iii) Reduction of Phenol:



## # Physical-Properties:

i) Aromatic hydrocarbon are non-polar molecules and are usually colourless liquid with character aroma

ii) Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solven.

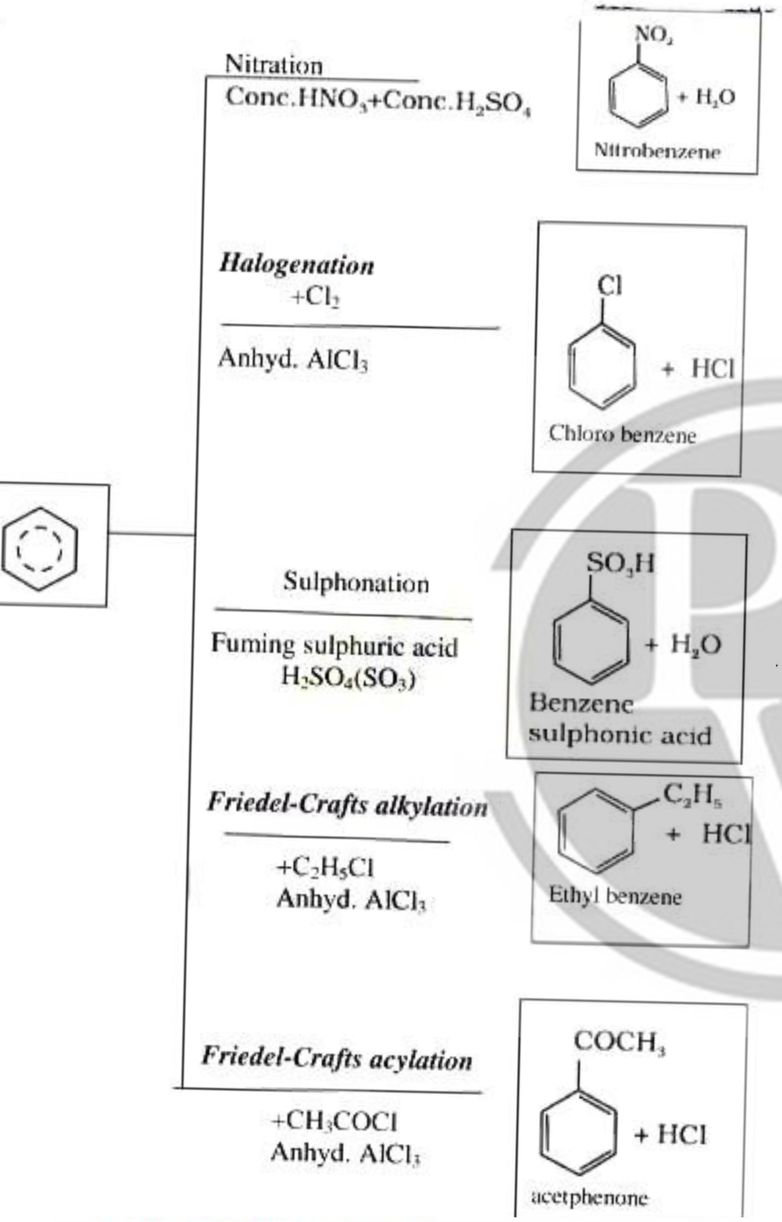
iii) They burn with sooty flame.

## #Chemical- Properties:

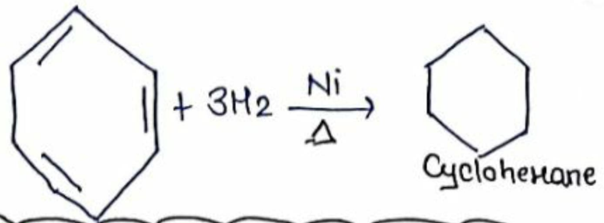
i) Generation of the electrophile.

ii) Formation of carbocation intermediate.

iii) Removal of Proton from the carbocation - intermidate.



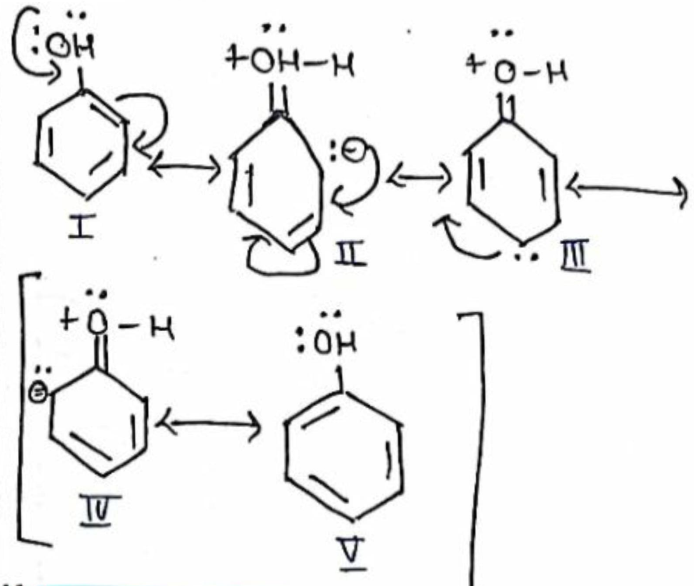
## #Addition of Benzene:



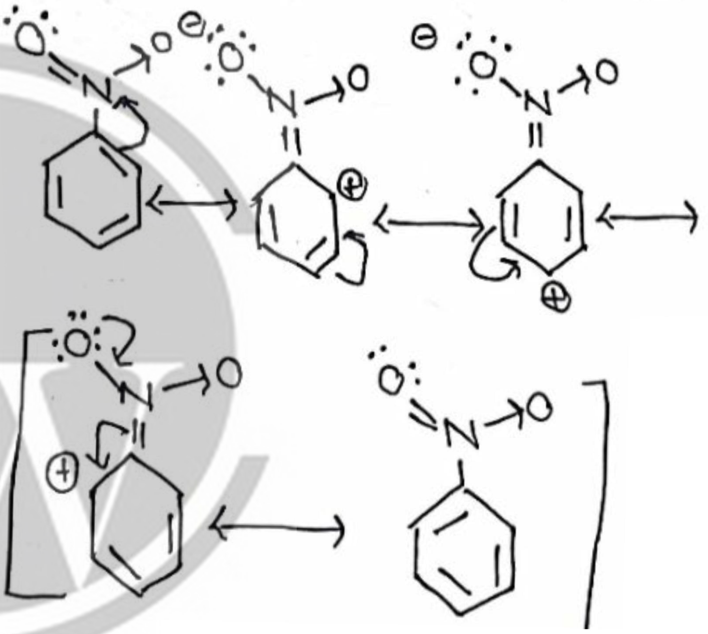
## #Directive influence of a functional group in Monosubsituted benzene:

i) Ortho and para directly group and activati

$-OH$, $-NH_2$, $-NHR$, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$, etc.



ii) Meta directing group of deactivating $-NO_2$ $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$, etc



iii) Ortho and para directing group of deactivating:

Halogens because of their strong -I effect, overall, electron density on benzene is decreasing.

#CARCINOGENICITY AND TOXICITY: Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing property.