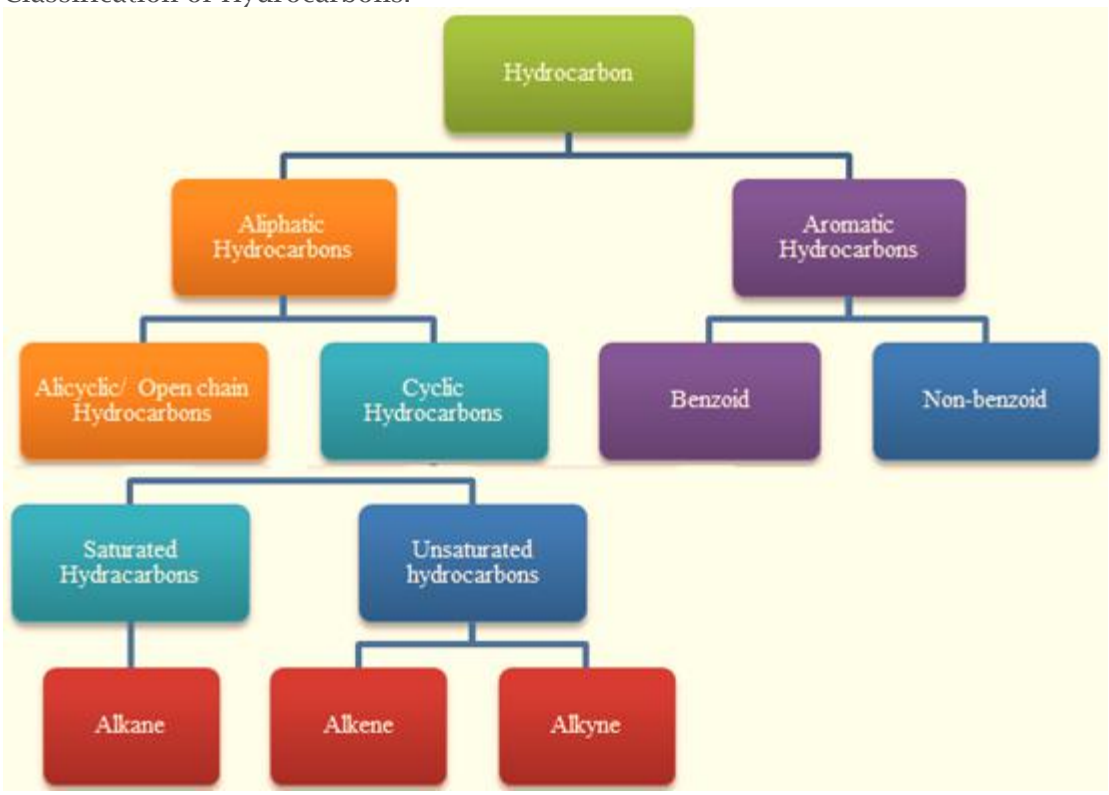
Hydrocarbons

- Compounds of carbon and hydrogen.
- Classification of Hydrocarbons:

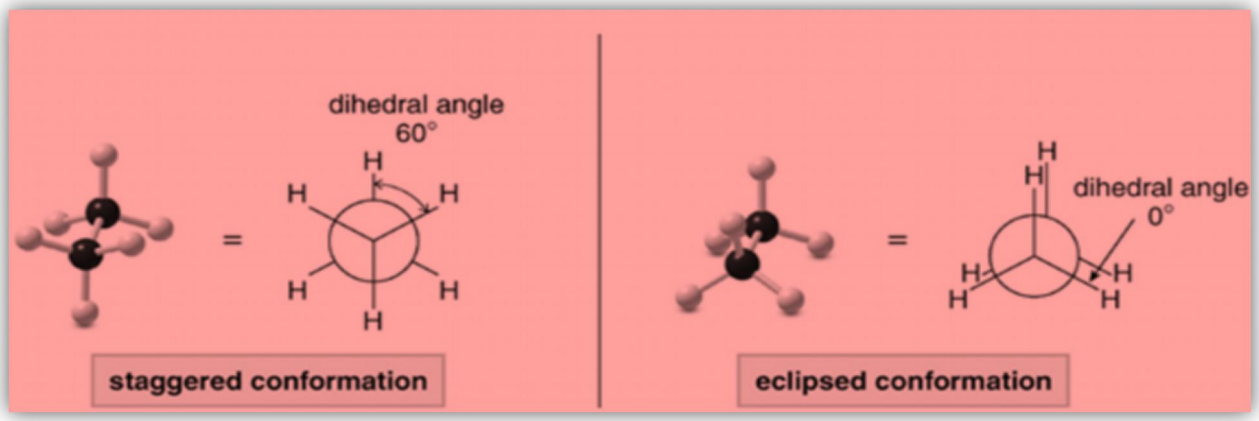


Alkane

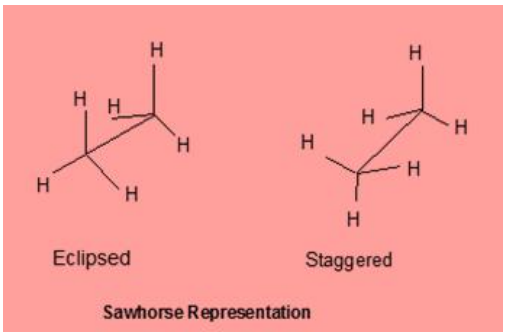
- Open chain saturated hydrocarbon with general formula (C_nH_{2n+2}).
- All the C atoms are single bonded i.e. sp^3 hybridised.

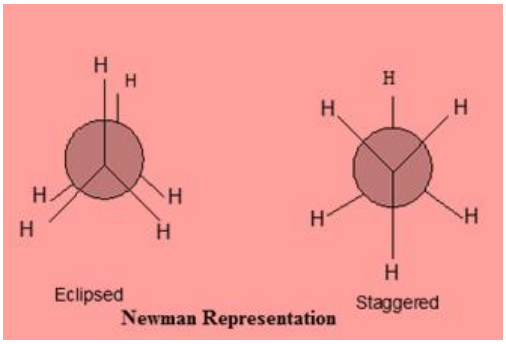
Conformations of Alkane

- Conformations are the different arrangement of atoms that can be converted into one another by rotation about single bonds.
- **Eclipsed Conformation:** H atoms on two adjacent carbon atoms are closest to each other i.e. dihedral angle is 0.



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





Preparation of Alkanes:

- **Reduction of Alkyl Halides:**

$RX + Zn: + H^+ \rightarrow RH + Zn^{2+} + X^-$

$4RX + LiAlH_4 \rightarrow 4RH + LiX + AlX_3 \quad (X \neq F)$

$RX + (n\text{-}C_4H_9)_3\ SnH \rightarrow R\text{-}H + (n\text{-}C_4H_9)_3\ SnX$

- **Grignard Reagent:**

$$RX + 2Li \xrightarrow{\text{dry ether}} R^-Li^+ + LiX \text{ then } R^-Li^+ + H_2O \longrightarrow RH + LiOH$$

$$RX + Mg \xrightarrow{\text{dry ether}} \underset{\text{(Grignard Reagent)}}{R^-(Mg^+X)} \quad \text{then,} \quad RMgX + H_2O \longrightarrow RH + Mg\begin{matrix}X\\OH\end{matrix}$$

?

- **Hydrogenation of Alkenes:**

$$CH_3\text{-}C(CH_3)=CH_2 + H_2 \xrightarrow{Pt.} CH_3\text{-}CH(CH_3)\text{-}CH_3$$

- **Wurtz Reaction:**

$2RX + 2Na \rightarrow R\text{-}R + 2NaX$

$2Na + 2CH_3CH_2CH_2Cl \rightarrow CH_3CH_2CH_2CH_2\text{-}CH_2CH_3 + 2NaCl$

- **Corey House Reaction:**

$$R\ MgX \text{ or } RLi \xrightarrow[RX]{CuX} R\text{-}R' \quad (R = 1^\circ, 2^\circ \text{ or } 3^\circ; R' = 1^\circ)$$

- **Decarboxylation of a mixture of the sodium salt of a carboxylic acid:**

$RCOONa + NaOH(CaO) \rightarrow RH + Na_2CO_3$

- **Kolbe's electrolytic method:**

$2\ RCOOK + 2H_2O \rightarrow R\text{-}R + 2CO_2 + H_2 + 2KOH$

Chemical Properties of Alkane

- **Direct Halogenation**

$RH + X_2 \rightarrow RX + HX$

Order of Reactivity of X_2: $F_2 > Cl_2 > Br_2$; I_2 does not react

?a. Initiation Step

$Cl\text{-}Cl \xrightarrow{uv} 2Cl^{\cdot}$

b. Propagation Step

$H_3C\text{-}H + Cl^{\cdot} \rightarrow H_3C^{\cdot} + H\text{-}Cl$

$H_3C^{\cdot} + Cl\text{-}Cl \rightarrow H_3C\text{-}Cl + Cl^{\cdot}$

c. Termination Step

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl\text{-}Cl$

$H_3C^{\cdot} + H_3C^{\cdot} \rightarrow H_3C\text{-}CH_3$

$Cl^{\cdot} + H_3C^{\cdot} \rightarrow Cl\text{-}CH_3$

- **Nitration**

Nitration of alkane is made by heating vapours of alkanes and HNO3 at about 400oC to give nitroalkanes.

¨This is also known as vapour phase nitration.

$$CH_{4(g)} + HNO_{3(g)} \xrightarrow{400^{o}C} CH_3NO_2 + H_2O$$

- **Combustion:**

?Alkanes burn readily with non luminous flame in presence of air or oxygen to give CO2 & water along with evolution of heat.

$C_2H_6 + 7O_2 \rightarrow CO_2 + 6H_2O$ + heat

- **Aromatization**

?¨Alkanes having six to 10 carbon atoms are converted into benzene and its homologues at high pressure and temperature in presence of catalyst.

$$C_6H_4 \xrightarrow[773K\ \&\ 20\ atm]{V_2O_5/Cr_2O_3/Mo_2O_3} C_6H_6$$

Hexane Benzene

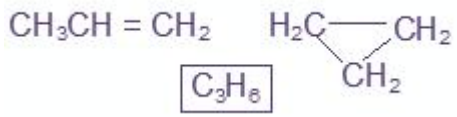
- **Oxidization of 3^0 alkane:?**

Tertiary alkanes are oxidized to tertiary alcoholsby KMnO4

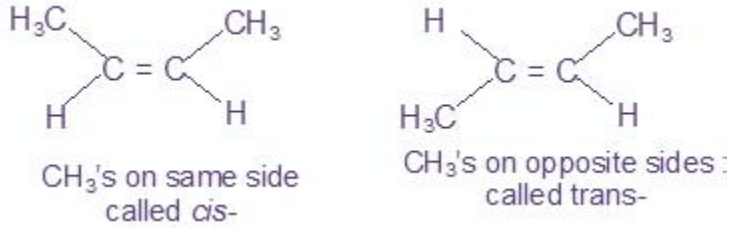
$R_3CH + KMnO_4 \rightarrow R_3COH$

Alkene (olefins)

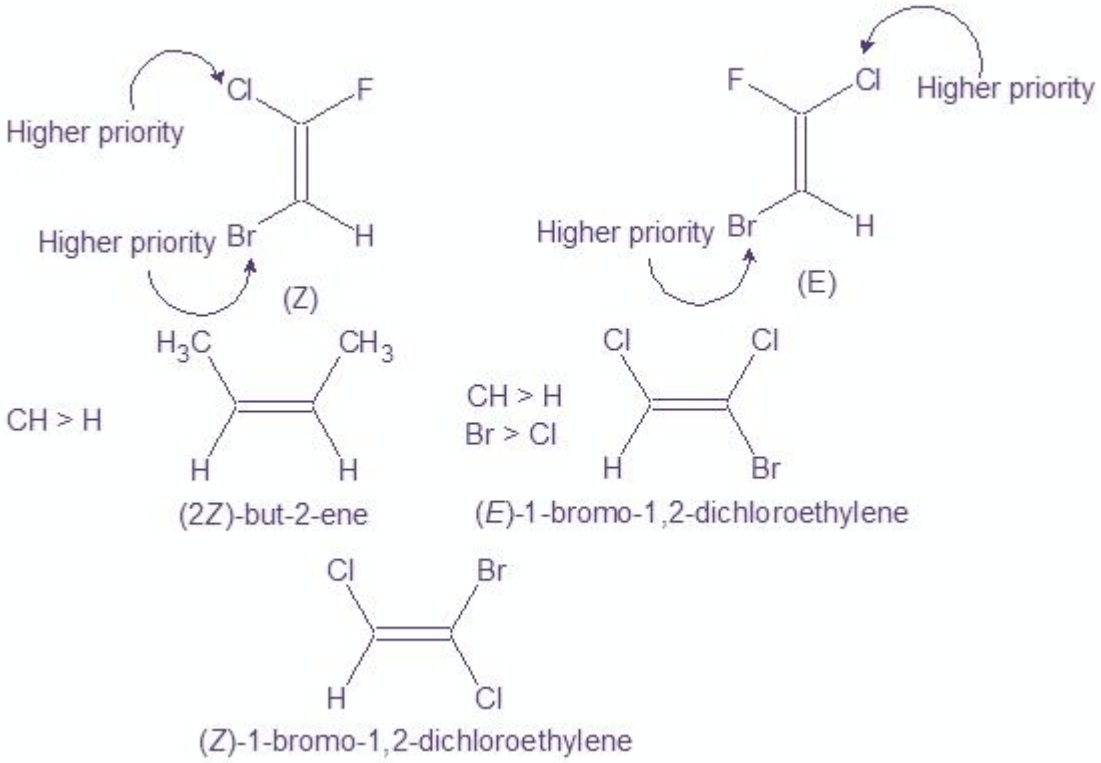
- Open chain, Unsaturated hydrocarbons with general formula (CnH2n).
- At least one >c=c< (double bond) group i.e. sp2 hybridisation, is present throughout the chain.
- Allene: alkene molecule in which at least one C has double bonds with each of the adjacent carbon i.e. -c=c=c- group.
- Isomeric with saturated cycloalkanes.



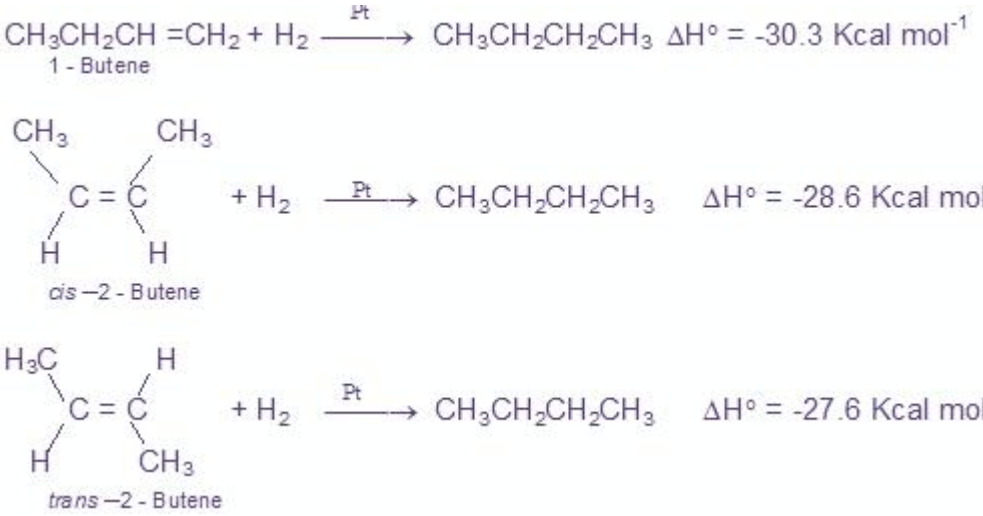
Geometric Isomers:



Z is used if the higher - priority substituents on each C are on the same side of the double bond.letter E is used if they are on opposite sides



Heats of Hydrogenation: Heat of hydrogenation increases with increase in stability of alkene.

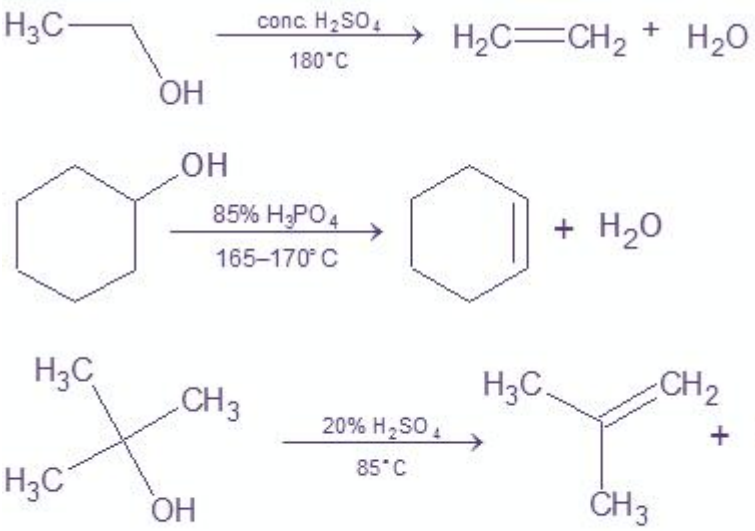


Order of heat of hydrogenation: 1-Butene> cis-2-Butene > trans-2-Butene
Order of stability: 1-Butene> cis-2-Butene > trans-2-Butene

Preparation of Alkenes:

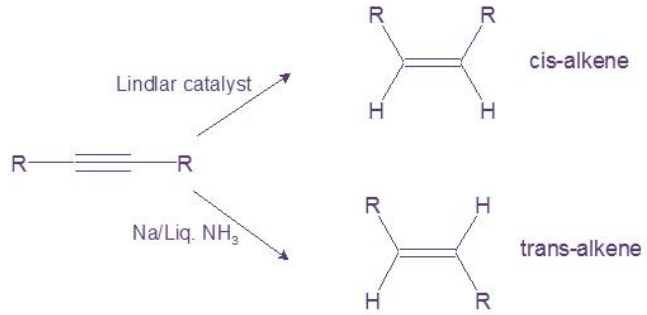
1. Cracking of petroleum: $R—CH_2—CH_3 \xrightarrow{Pt \text{ or } Pd} R—CH=CH_2 + H_2$
2. Dehydrohalogenating of alkyl halides: $RCH_2CH_2X + alc.KOH \rightarrow RCH = CH_2$
3. Dehydration of Alcohols:

Saytzeff Rule: In dehydration and dehydrohalogenating the preferential order for removal ofan H is $3^\circ > 2^\circ > 1^\circ$



Order of reactivity of alcohols: 1° >2° > 3°

4. Reduction of alkynes:



Chemical Properties:

1. Electrophilic Polar Addition Reactions

Reagent		Product	
Name	**Structure**	**Name**	**Structure**
Halogens (Cl_2, Br_2 only)	X:X	Ethylene dihalide	CH_2XCH_2X
Hydrohalic acids	H:X	Ethyl halide	CH_3CH_2X
Hypohalous acids	X:OH	Ethylene halohydrin	CH_2XCH_2OH
Sulfuric acid (cold)	$H:OSO_2OH$	Ethyl bisulfate	$CH_3CH_2OSO_3H$
Water (dil. H_3O^+)	H:OH	Ethyl alcohol	CH_3CH_2OH
Borane	$H_2B:H$	Ethyl borane	$(CH_3CH_2BH_2) \rightarrow (CH_3CH_2)_3B$
Peroxyformic acid	H:O-OCH=O (HCO_3H)	Ethylene glycol	CH_2OHCH_2OH

2. Addition of Hydrogen Halides to Alkenes: Markovnikov's Addition:

$R - CH = CH_2 + HBr \rightarrow R - CHBr - CH_3$

Mechanism:

$R - CH = CH_2 + HBr \rightarrow R - CH^+ - CH_3 \quad +Br^-$

$R - CH^+ - CH_3 + Br^- \rightarrow R - CHBr - CH_3$

Anit- Markovnikov's Addition (Peroxide Effect):

$R - CH = CH_2 + HBr + (C_6H_5CO)_2O_2 \rightarrow R - CHBr - CH_3$

Mechanism

Initiation:

$R - O - O - R \rightarrow 2RO^{\cdot}$

$RO^{\cdot} + HBr \rightarrow Br^{\cdot} + ROH$

Propagation

$CH_3CH = CH_2 + Br^{\cdot} \rightarrow CH_3{\cdot}CH - CH_2Br$

$CH_3{\cdot}CHCH_2Br + HBr \rightarrow CH_3CH_2CH_2Br + Br^{\cdot}$

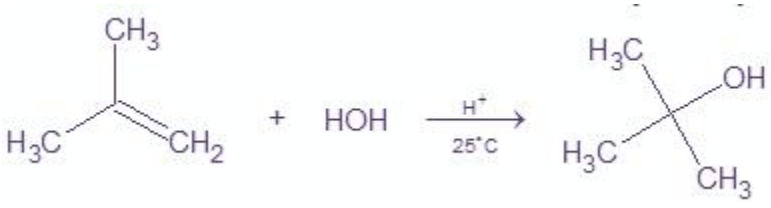
Termination:

$2RO^{\cdot} \rightarrow R - O - O - R$

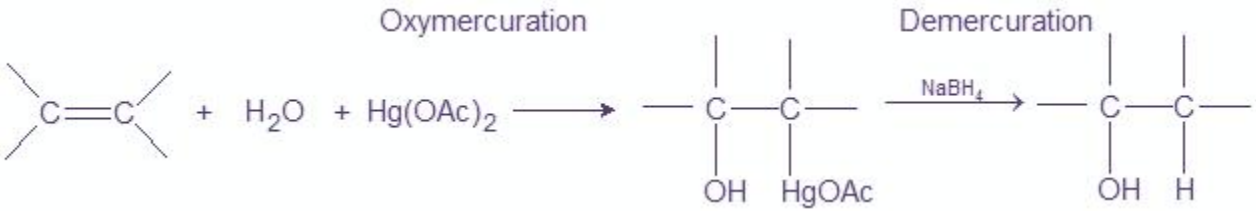
$Br^{\cdot} + Br^{\cdot} \rightarrow Br_2$

3. Addition of Water to Alkenes: Acid Catalyzed Hydration:

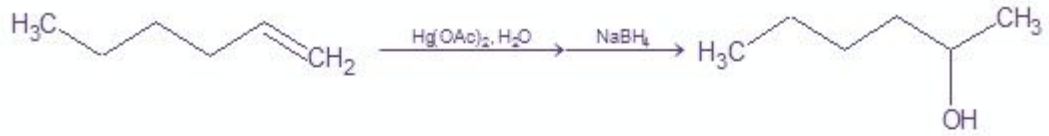
Reagent		Product	
Name	**Structure**	**Name**	**Structure**
Halogens (Cl_2, Br_2 only)	X:X	Ethylene dihalide	CH_2XCH_2X
Hydrohalic acids	H:X	Ethyl halide	CH_3CH_2X
Hypohalous acids	X:OH	Ethylene halohydrin	CH_2XCH_2OH
Sulfuric acid (cold)	$H:OSO_2OH$	Ethyl bisulfate	$CH_3CH_2OSO_3H$
Water (dil. H_3O^+)	H:OH	Ethyl alcohol	CH_3CH_2OH
Borane	$H_2B:H$	Ethyl borane	$(CH_3CH_2BH_2)^{®}(CH_3CH_2)_3B$
Peroxyformic acid	H:O - OCH = O (HCO_3H)	Ethylene glycol	CH_2OHCH_2OH

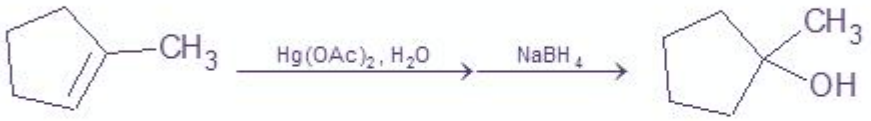


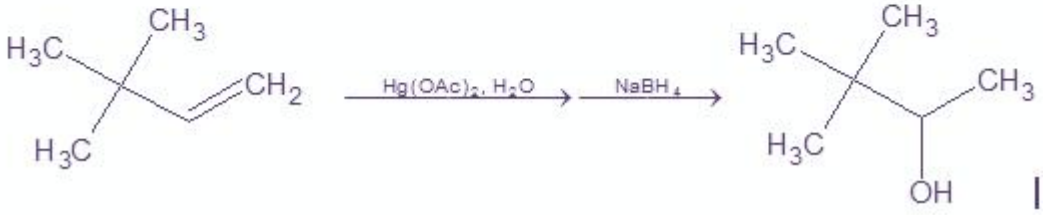
4. Oxymercuration-Demercuration:



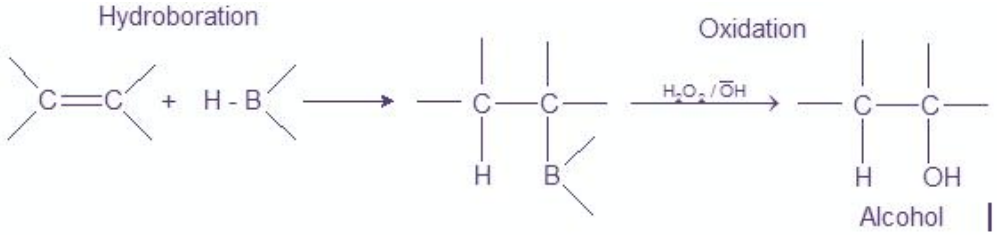
Examples:



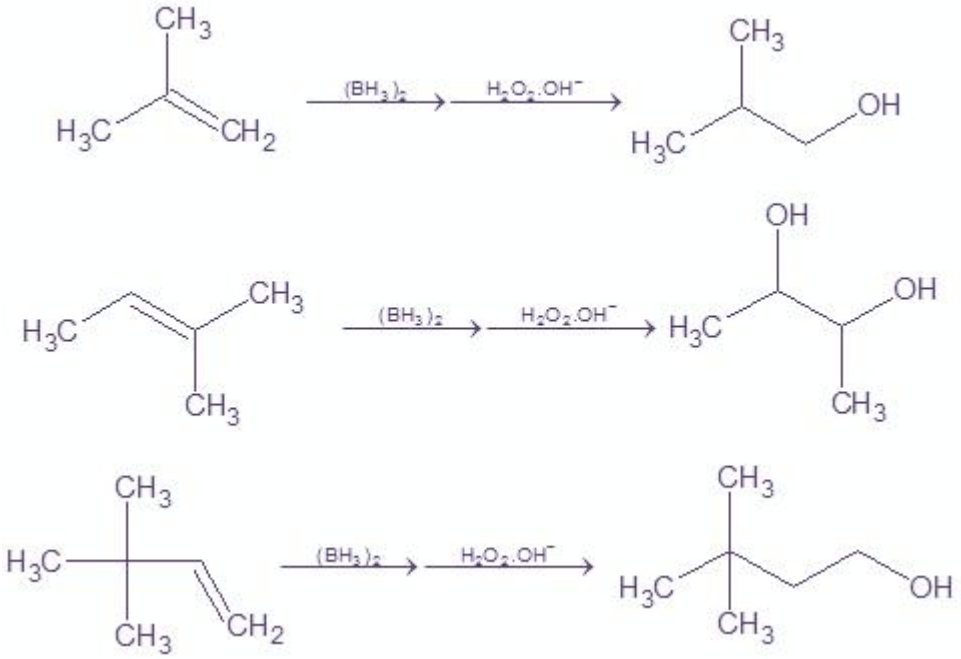




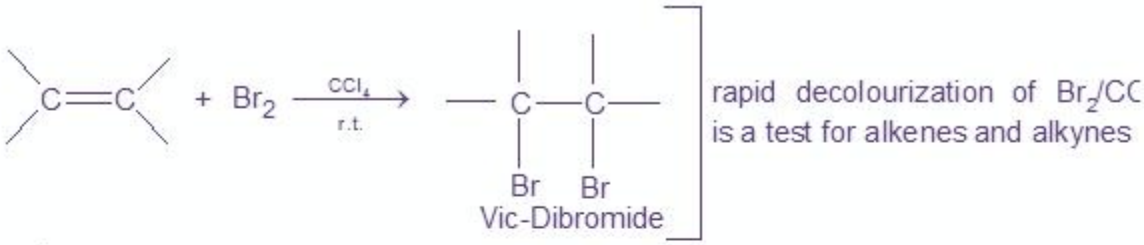
5. Hydroboration-Oxidation:



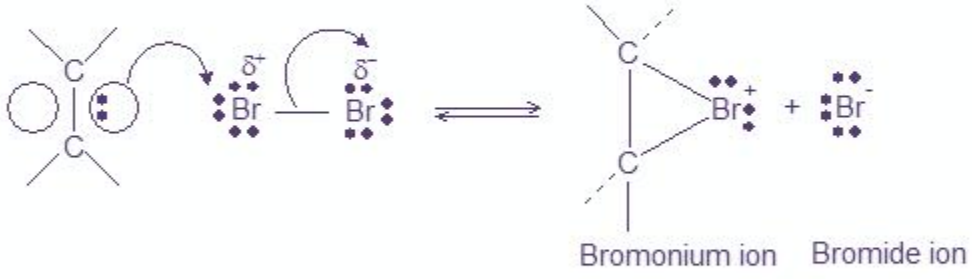
Examples:

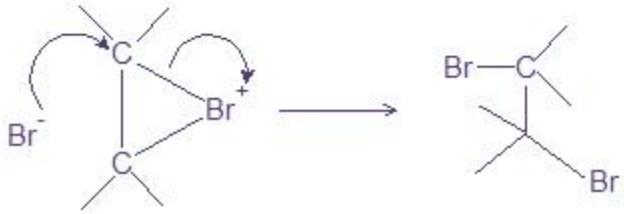


6. Halogen Addition in Non-polar Solvent:

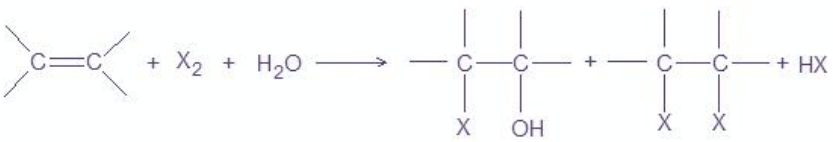


Mechanism:



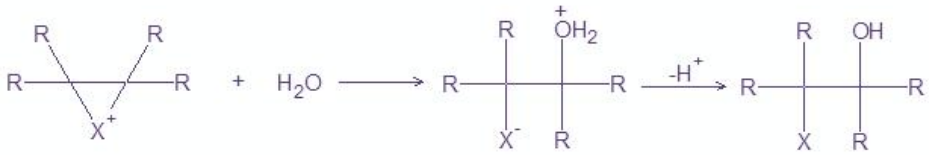


7. Halogen Addition in Aqueous Medium:

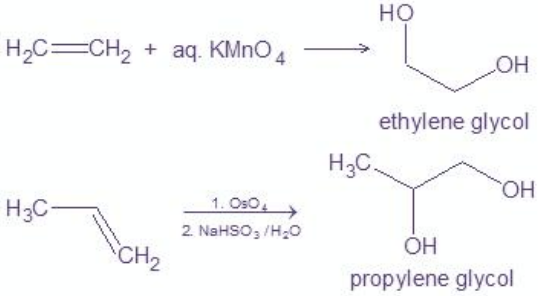


X = Cl_2 or Br_2

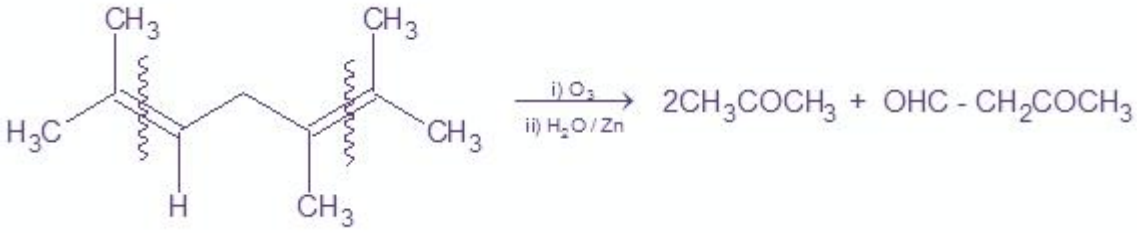
Mechanism:



8. Syn – Hydroxylation: Formation of di-oles.



9. Ozonolysis of Alkenes:

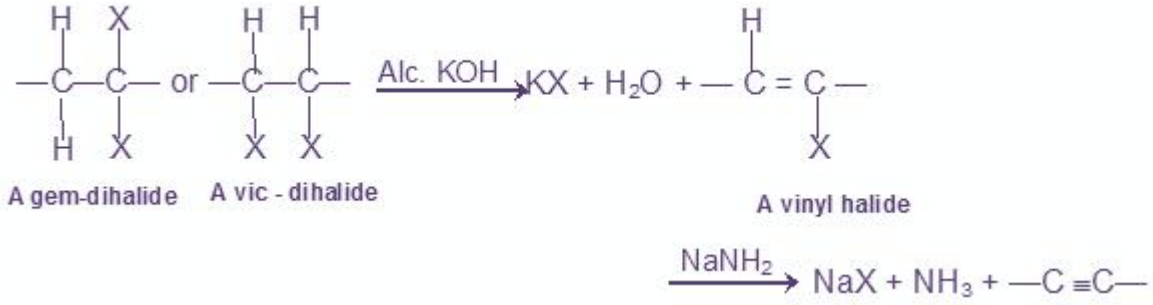


Alkyne

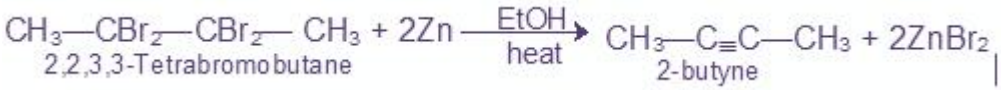
- Saturated open chain hydrocarbon with general formula (C_nH_{2n-2}).
- At least one -c≡c- (triple bond) group i.e. sp hybridisation, is present throughout the chain.
- Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



2. Dehalogenation of vic-Tetrahalogen Compounds

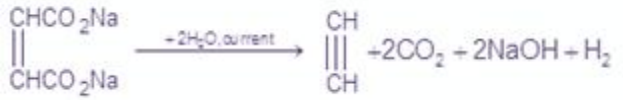


3. Alkyl Substitution in Acetylene; Acidity of º C-H

4. From Calcium Carbide:

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

5. Kolbe's Electrolysis:



Chemical Properties

1. Hydrogenation: $RC \equiv CCH_2CH_3 + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3$

2. Hydro-halogenation:

Markovnikov addition: $RC{\equiv}CH + HBr \rightarrow RCBr{=}CH_2 + HBr \rightarrow RCBr_2\text{-}CH_3$

Anti-markovnikov addition: $RC{\equiv}CH + HBr + \text{peroxide} \rightarrow RCH{=}CHBr$

3. Hydration:

$$CH \equiv CH + H_2O \xrightarrow[Hg^{2+}]{H_2SO_4} [CH_2 = CHOH] \longrightarrow CH_3CHO$$

4. Addition of boron hydride:

$$R'-C\equiv C-H + R_2BH \longrightarrow \underset{H}{\overset{R'}{C}} = \underset{BR_2}{\overset{H}{C}} \xrightarrow[\text{oxidation}]{H_2O_2, NaOH} R'CH_2CHO$$

$$\xrightarrow[\text{hydrolysis}]{CH_3COOH} R'CH = CH_2$$

5. Dimerization:

$$2\,H-C\equiv C-H \xrightarrow[H_2O]{Cu(NH_3)_2^+Cl^-} H_2C=CH-C\equiv CH$$

Vinylacetylene

6. Oxidation:

$$CH_3CH_2C\equiv C\text{-}CH_3 + 2KMnO_4 \rightarrow CH_3CH_2COOK + CH_3COOK + 2MnO_2 + 2H_2O$$

$$CH_3\text{-}\underset{CH_3}{CH}\text{-}C\equiv C\,CH_2\,CH_2CH_3 \xrightarrow{\text{ox dn.}} \underset{CH_3}{CH_3CH}\text{-}CO_2H + CH_3CH_2CH_2CO_2H$$

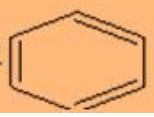
(Two isomeric acids each having M.F. $C_4H_8O_2$)

7. Ozonolysis-Hydrolysis:

$$CH_3C\equiv CCH_2CH_3 \xrightarrow[2.\ \text{hydrolysis}]{1.\ O_3} CH_3COOH + HOOCCH_2CH_3$$

2-Pentyne — Acetic acid — Propanoic acid

8. Cyclic polymerization:

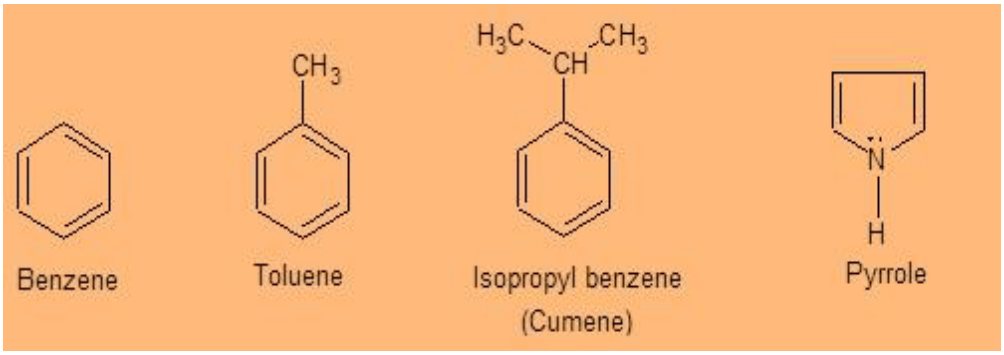
$$3\,HC\equiv CH \xrightarrow[\text{of Ni}]{\text{Red hot tube}}$$ 

Aromatic Hydrocarbons:

For being aromatic a hydrocarbon should

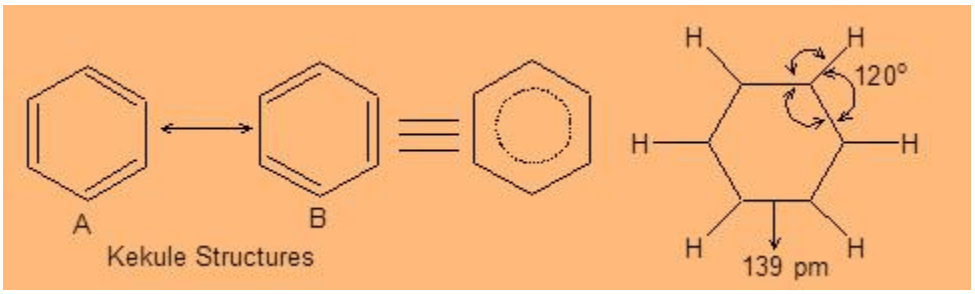
- be a cyclic compounds.
- have planarity in geometry.
- have complete delocalization of electrons over ring.
- follow Huckel Rule i.e. number of ?? electrons in ring = (4n+2).

:

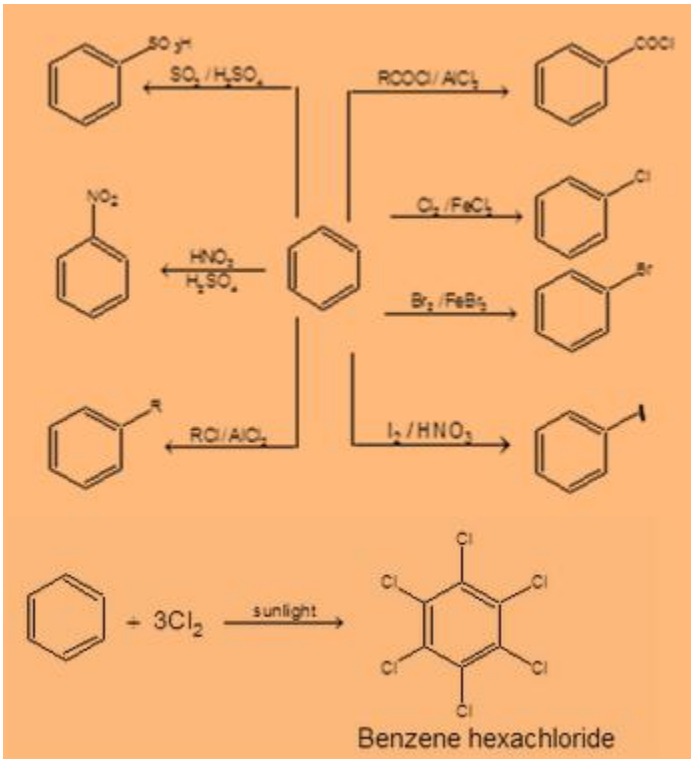


Benzene (C_6H_6)

1. Structure:



2. Chemical Reactions of Benzene:



Anti-aromatic Hydrocarbons:

Highly unstable compounds.

Number of π electrons in ring = 4n.

Example:

- by fractional crystallisation due to their difference in solubility;
- by chromatography due to their different molecular shapes and polarity.