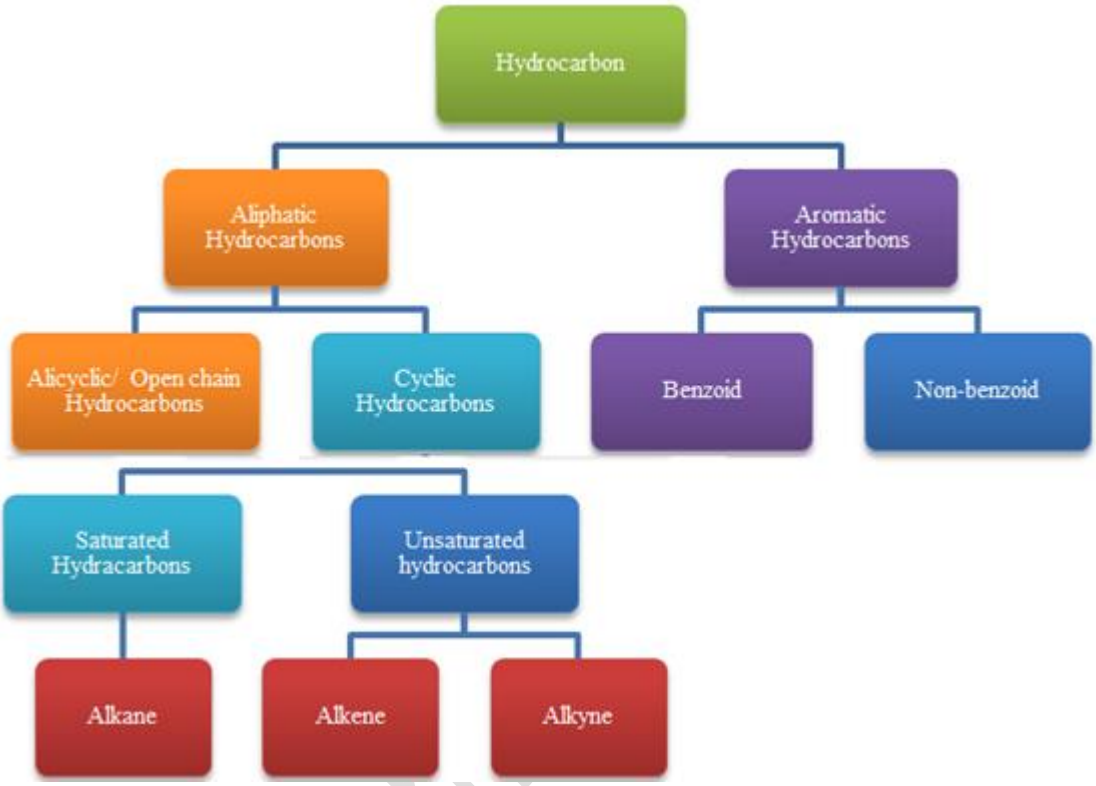
Compounds of carbon and hydrogen.

Classification of Hydrocarbons:



Alkane

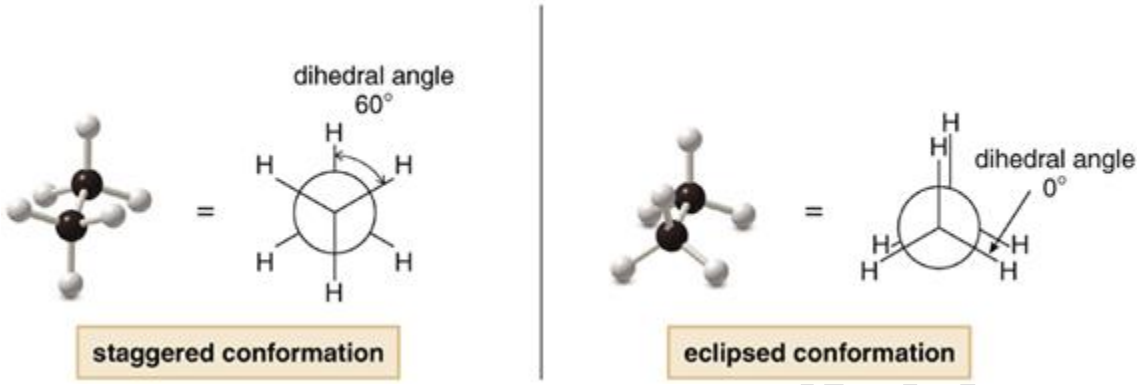
Open chain saturated hydrocarbon with general formula (C_nH_{2n+2}).

All the C atoms are single bonded i.e. sp^3 hybridised.

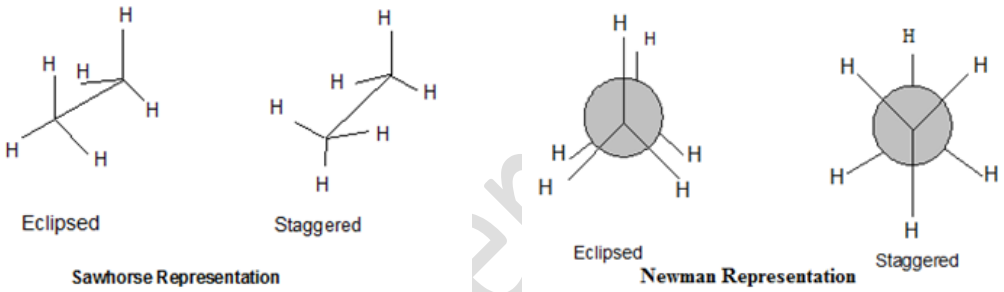
Conformations of Alkane

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:

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

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

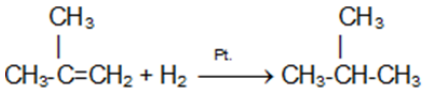
$RX + (n\text{-}C_4H_9)_3SnH \rightarrow R\text{-}H + (n\text{-}C_4H_9)_3SnX$

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:

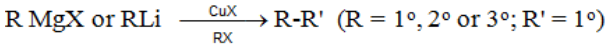


Wurtz Reaction:

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

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

Corey House Reaction:



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.

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

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.

$$\underset{\text{Hexane}}{C_6H_4} \xrightarrow[773K \text{ \& } 20\,atm]{V_2O_5/Cr_2O_3/Mo_2O_3} \underset{\text{Benzene}}{C_6H_6}$$

Oxidization of 3^0 alkane:?

Tertiary alkanes are oxidized to tertiary alcoholsby KMnO4

$R_3CH + KMnO_4 \rightarrow R_3COH$

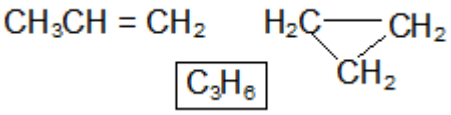
Alkene (olefins)

Open chain, Unsaturated hydrocarbons with general formula (CnH2n).

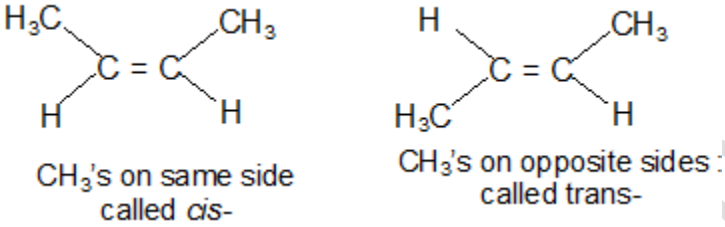
At least one >c=c< (double bond) group i.e. sp2 hybridisation, is present throughout the chain.

Allene: alkene molecule in which at least one C has double bonds with each of the adjacent carbon i.e. -c=c=c- group.

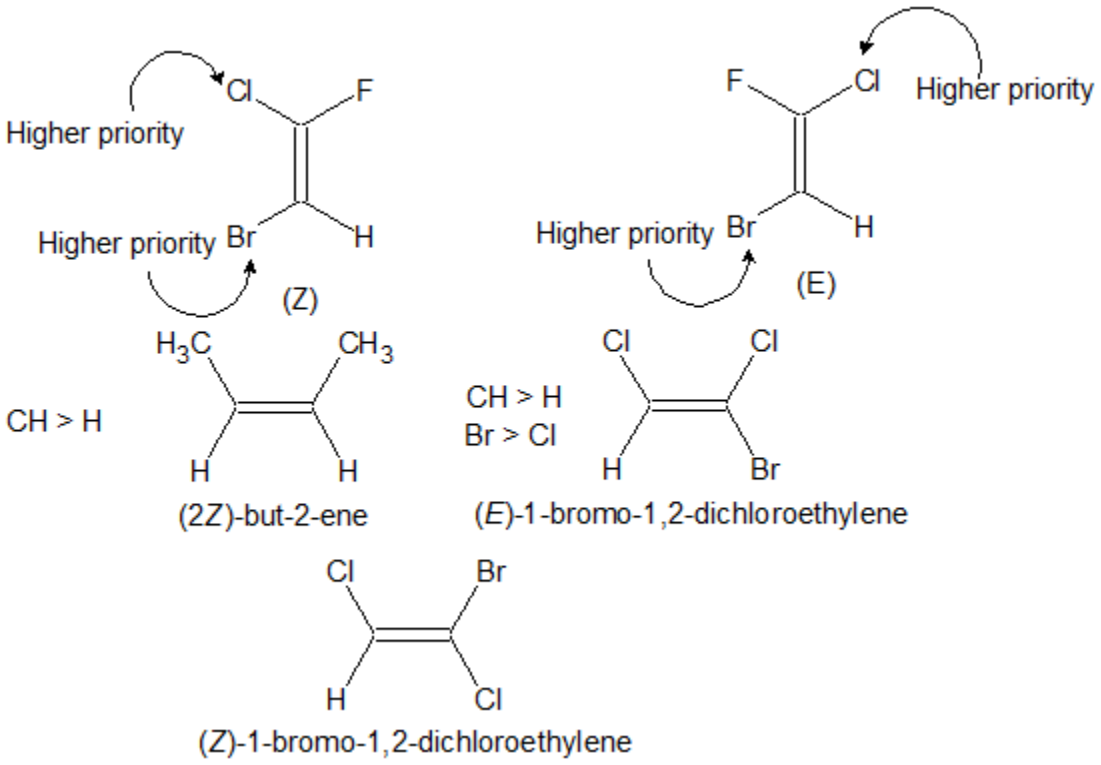
Isomeric with saturated cycloalkanes.



Geometric Isomers:



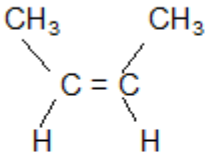
Z is used if the higher - priority substituents on each C are on the same side of the double bond.letter E is used if they are on opposite sides



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

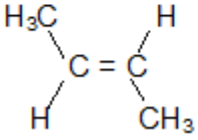
$CH_3CH_2CH=CH_2 + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -30.3 \text{ Kcal mol}^{-1}$

1 - Butene



$+ H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -28.6 \text{ Kcal mol}^{-1}$

cis –2 - Butene



$+ H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -27.6 \text{ Kcal mol}^{-1}$

trans –2 - Butene

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

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

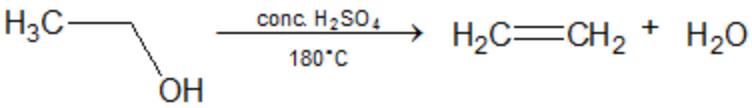
Preparation of Alkenes:

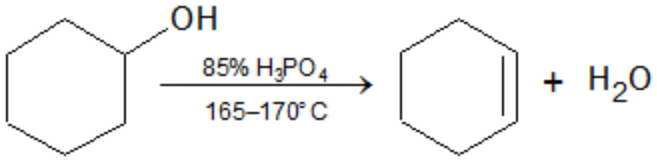
1. Cracking of petroleum: $R—CH_2—CH_3 \xrightarrow{Pt \text{ or } Pd} R—CH=CH_2 + H_2$

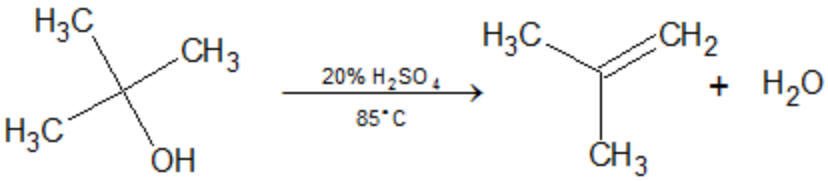
2. Dehydrohalogenation of alkyl halides: $RCH_2CH_2X + \text{alc.KOH} \rightarrow RCH=CH_2$

3. Dehydration of Alcohols :

Saytzeff Rule: In dehydration and dehydrohalogenation the preferential order for removal ofan H is 3° > 2° > 1°

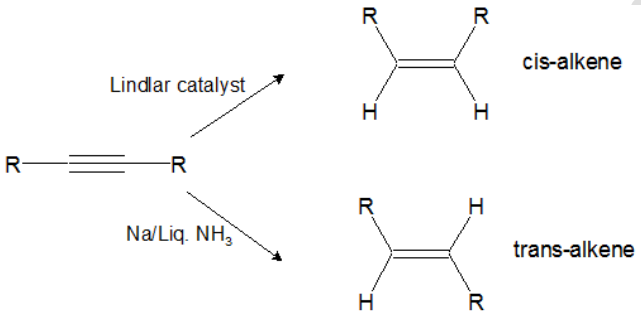






Order of reactivity of alcohols: 1° >2° > 3°

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:

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

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

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

$CH_3\cdot CHCH_2Br + HBr \rightarrow CH_3CH_2CH_2Br + Br\cdot$

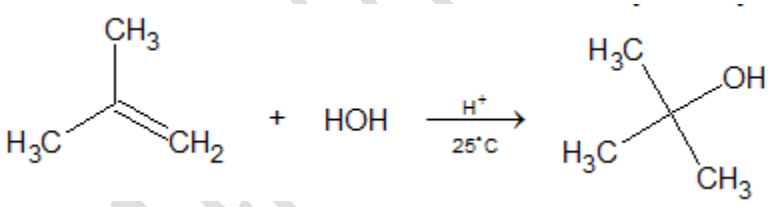
Termination:

$2RO\cdot \rightarrow R - O - O - R$

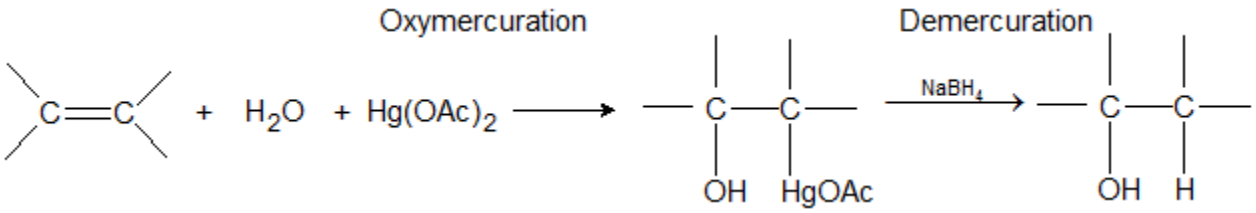
$Br\cdot + Br\cdot \rightarrow Br_2$

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

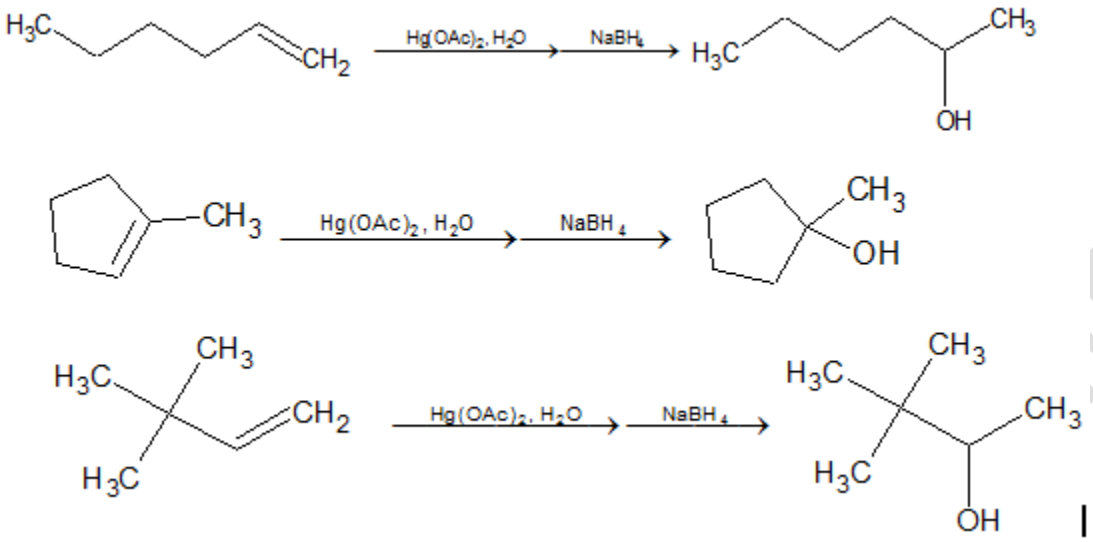
Reagent		Product	
Name	**Structure**	**Name**	**Structure**
Halogens (Cl_2, Br_2 only)	X:X	Ethylene dihalide	CH_2XCH_2X
Hydrohalic acids	H:X	Ethyl halide	CH_3CH_2X
Hypohalous acids	X:OH	Ethylene halohydrin	CH_2XCH_2OH
Sulfuric acid (cold)	$H:OSO_2OH$	Ethyl bisulfate	$CH_3CH_2OSO_3H$
Water (dil. H_3O^+)	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



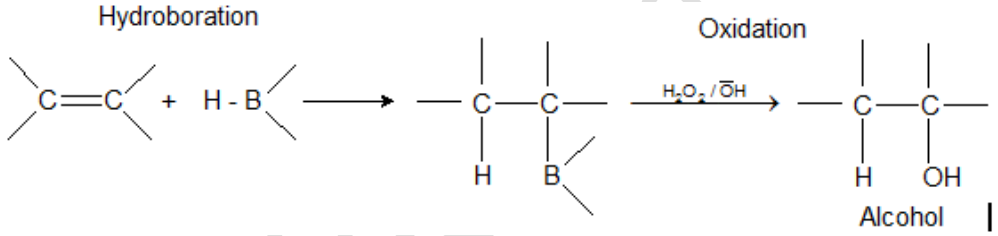
4. Oxymercuration-Demercuration:



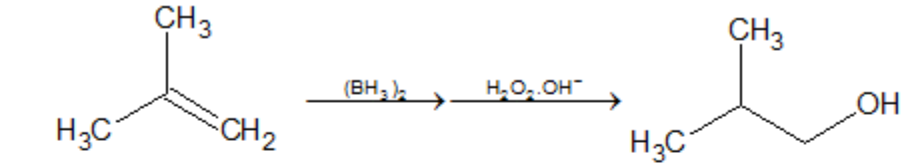
Examples:

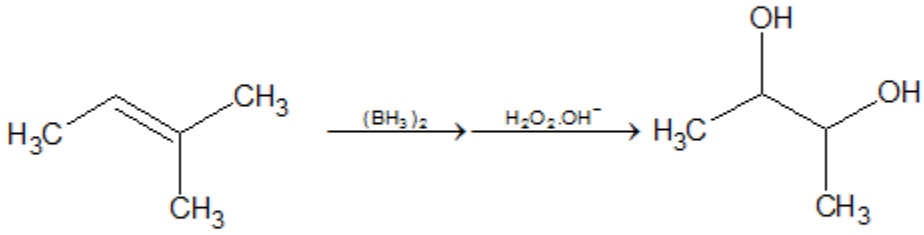


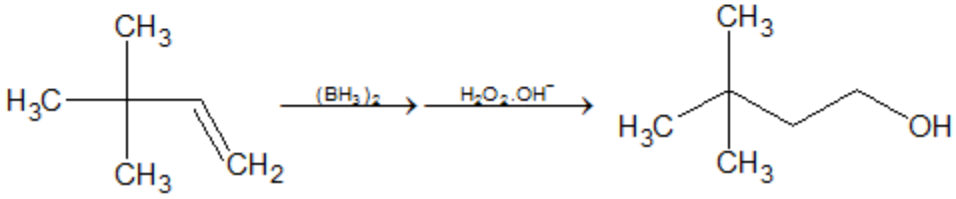
5. Hydroboration-Oxidation:



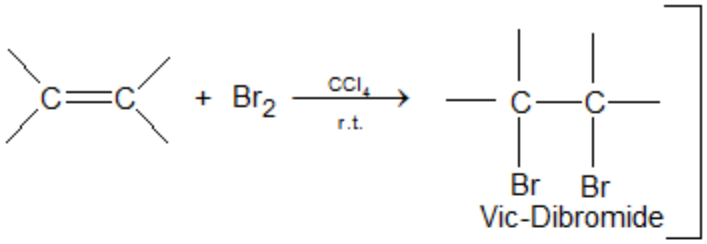
Examples:





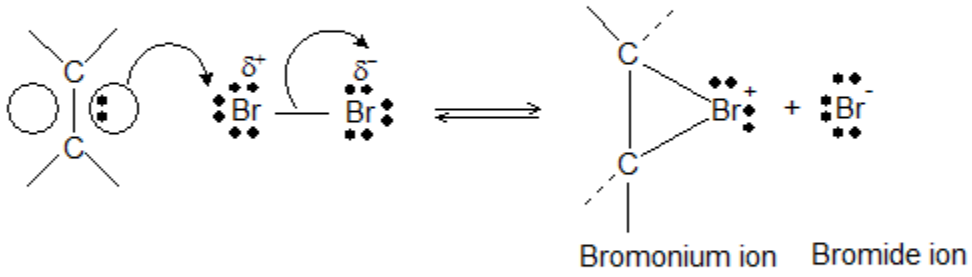


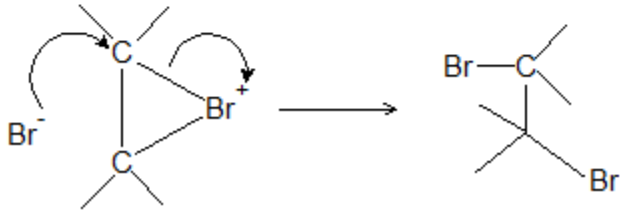
6. Halogen Addition in Non-polar Solvent:



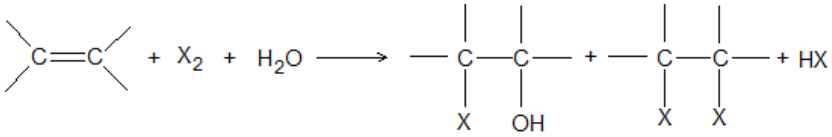
rapid decolourization of Br_2/CC is a test for alkenes and alkynes

Mechanism:



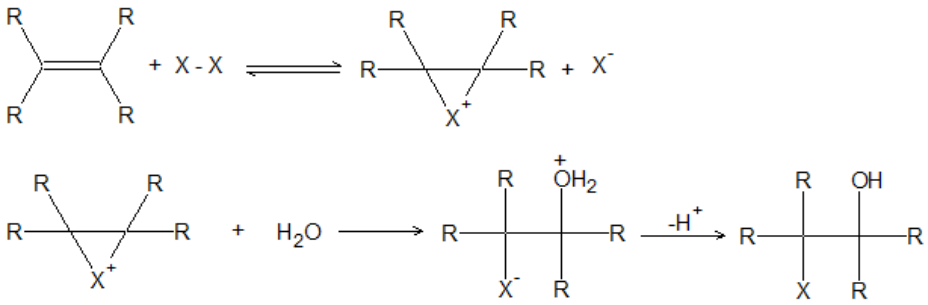


7. Halogen Addition in Aqueous Medium:

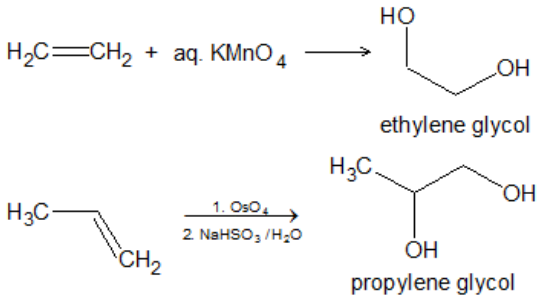


$X = Cl_2$ or Br_2

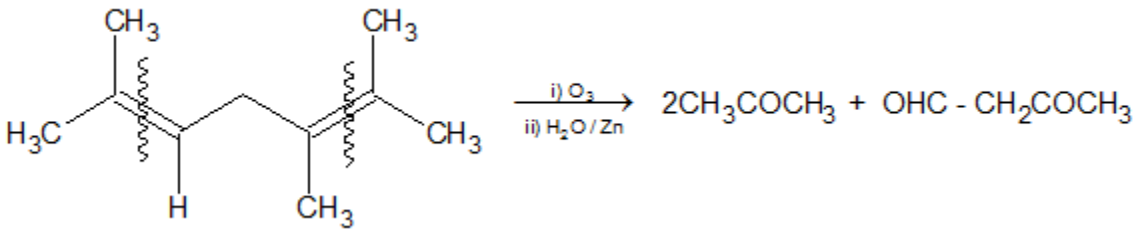
Mechanism:



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



9. Ozonolysis of Alkenes:



Alkyne

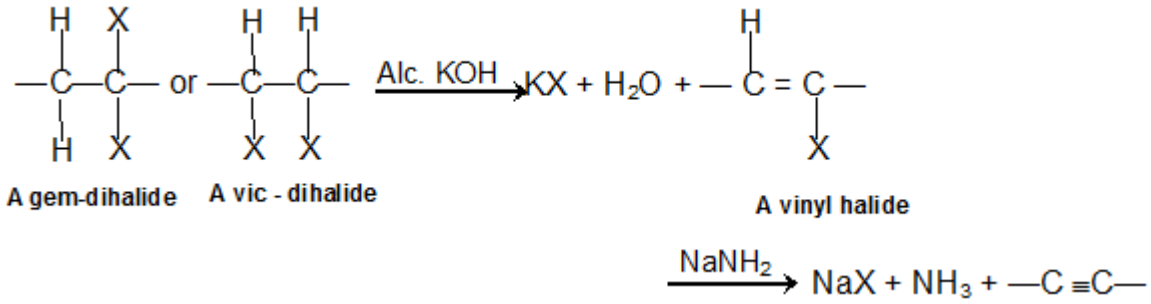
Saturated open chain hydrocarbon with general formula (C_nH_{2n-2}).

At least one -c≡c- (triple bond) group i.e. sp hybridisation, is present throughout the chain.

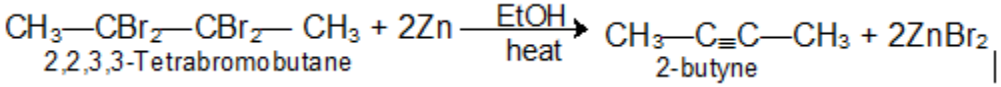
Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation

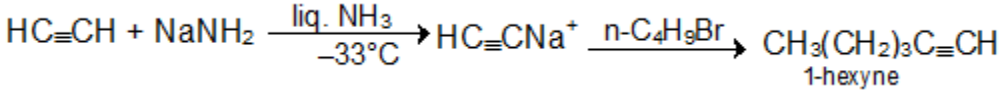
1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



2. Dehalogenation of vic-Tetrahalogen Compounds



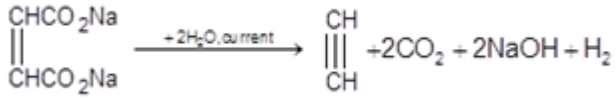
3. Alkyl Substitution in Acetylene; Acidity of º C-H



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

Anti-markovnikov addition: RC≡CH +HBr +peroxide → 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:

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

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

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:

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

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

(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:

$$3\,HC{\equiv}CH \xrightarrow[\text{of Ni}]{\text{Red hot tube}} C_6H_6$$

Aromatic Hydrocarbons:

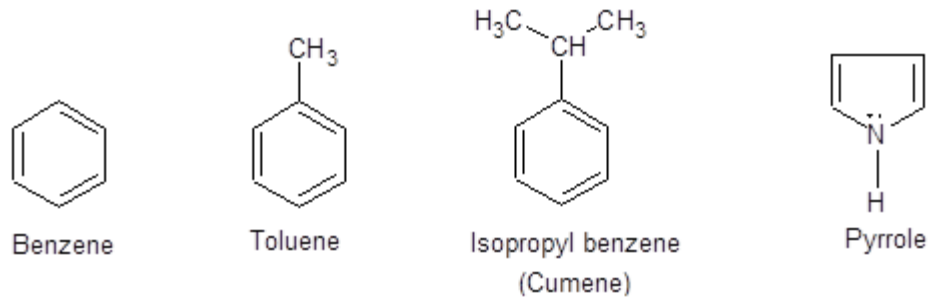
For being aromatic a hydrocarbon should

be a cyclic compounds.

have planarity in geometry.

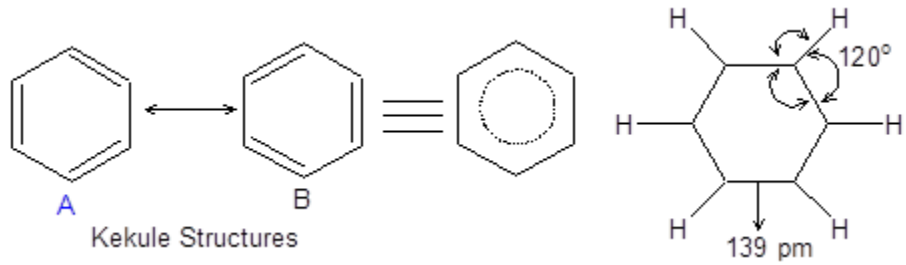
have complete delocalization of electrons over ring.

follow Huckel Rule i.e. number of ?? electrons in ring = (4n+2). :

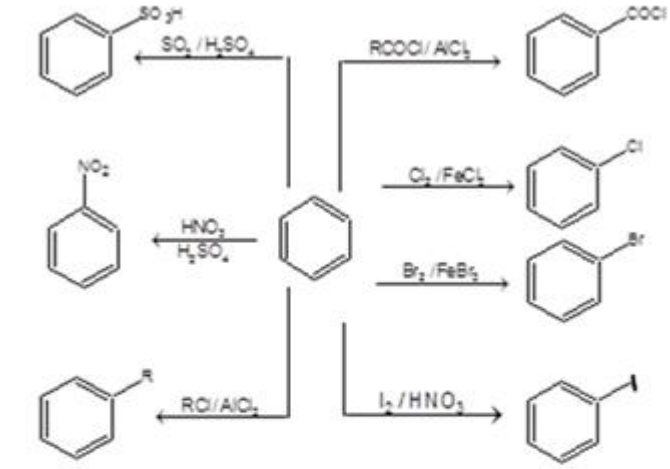


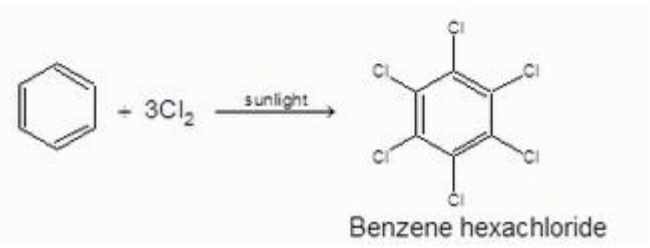
Benzene (C_6H_6)

1. Structure:



2. Chemical Reactions of Benzene:





Anti-aromatic Hydrocarbons:

Highly unstable compounds.

Number of π electrons in ring = 4n.

Example: