

HYDROCARBON

Introduction

Organic compounds containing carbon and hydrogen only are called hydrocarbons. These are widely distributed in nature in the form of petroleum, natural gas etc. Hydrocarbons are considered to be the parent organic compounds while all other compounds are thought to have been derived from them by replacement of one or more hydrogen atoms by other atoms or groups.

Classification

On the basis of carbon skeleton, hydrocarbons are mainly of two types

- I. Acyclic / open chain compound
- II. Cyclic / closed chain compounds

I. Acyclic / open chain compounds

Compounds contain open chains of carbon atoms in their molecules. They may be either straight or branched. Open chain compounds are also called aliphatic compounds

Aliphatic compounds are of two types

- i. saturated hydrocarbon: compounds containing $C-C$.

Also known as alkanes / paraffins

- ii. unsaturated

- a. Alkenes / olefins

compounds containing $C=C$

- b. Alkynes / Acetylenes

compounds containing $C\equiv C$

II. Cyclic / closed chain compounds

Compounds containing closed chains / rings of carbon atoms.

Mainly two types

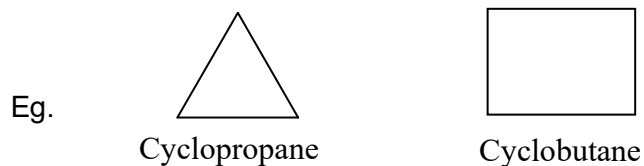
- 1) Homocyclic
- 2) Heterocyclic

1. Homocyclic

Rings are made up of only one kind of atom, mainly carbon atom so known as carbocyclic compounds; further divided in to

a) Alicyclic compounds

Rings are made up of 3 or more carbon atoms and properties resembles with aliphatic compounds



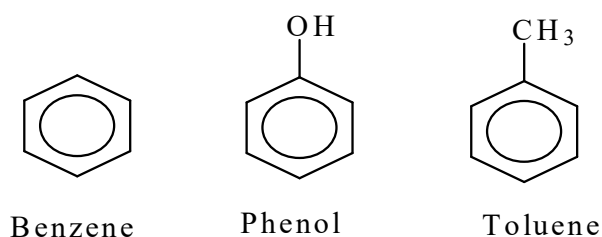
b) Aromatic compounds

From the word Aroma (Fragrant smell)

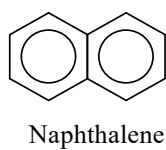
Two types

i) Benzenoid compound

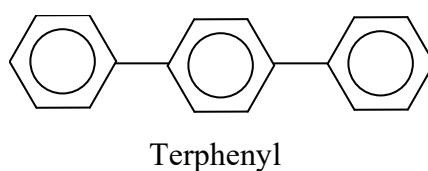
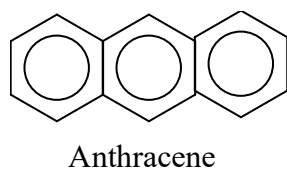
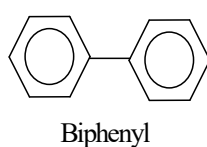
Compounds containing one or more fused or isolated benzene rings.



Fused

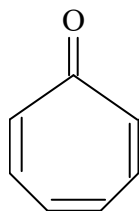


Isolated

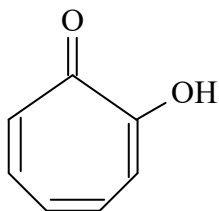


ii) Non Benzenoid aromatic compounds

Compounds does not contains benzene ring but contain other highly unsaturated rings.



Tropone



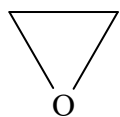
Tropolone

2. Heterocyclic compounds

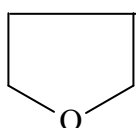
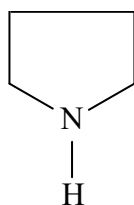
Rings contains carbon and hetero atoms

a) Alicyclic heterocyclic

Alicyclic compounds contains hetero atoms



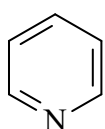
Oxirane

Tetrahydro
furan (THF)

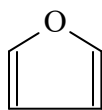
Tetrahydropyrrole

b) Aromatic hetero cyclic

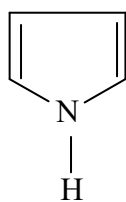
Aromatic compounds containing heteroatoms



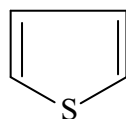
Pyridine



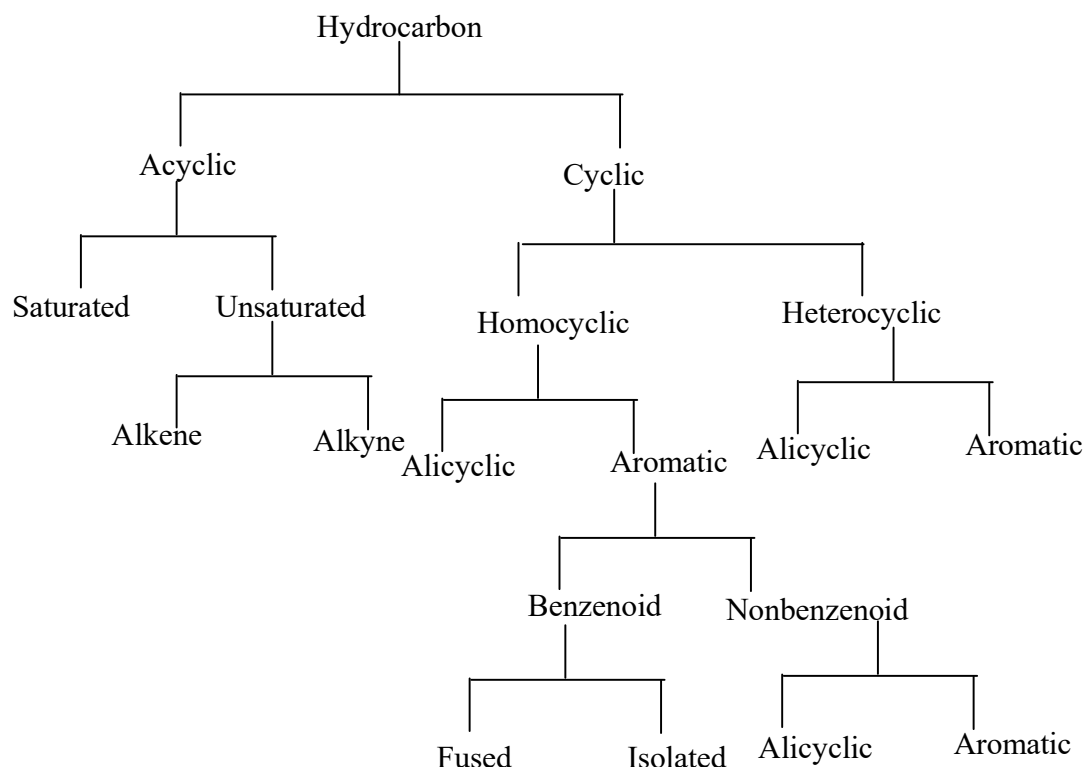
Furan



Pyrrole



Thiophene



I. ALKANES / Paraffins

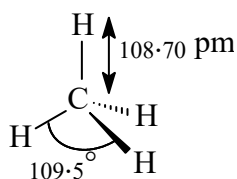
Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They are also called paraffins (Latin : Parum = little, affinis = affinity). They are unreactive towards most reagents.

Structure of Alkanes.

Carbon atoms in alkanes are sp^3 -hybridized, therefore, they have tetrahedral structures. The four bonds are directed towards the corners of a regular tetrahedron. The angle between any two adjacent bonds is 109.28° (tetrahedral angle).

Alkanes contain only carbon-carbon and carbon-hydrogen single bonds with average bond lengths of 154 pm and 110 pm respectively.

Structure of methane (CH_4)

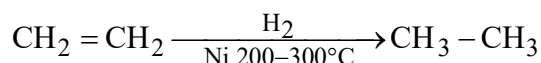


General formula C_nH_{2n+2}

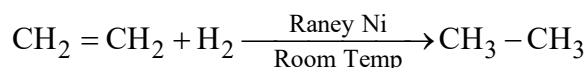
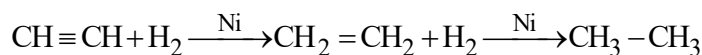
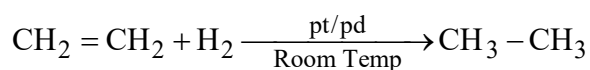
Preparation

1) From unsaturated hydrocarbon

Alkanes are obtained by hydrogenation of unsaturated hydrocarbons (alkenes / alkynes) in presence of catalyst.



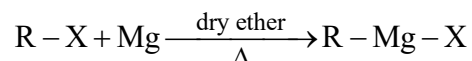
Reaction known as sabatier & senderen reaction



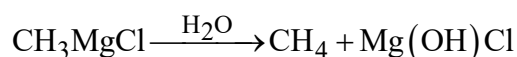
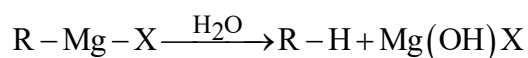
2) From alkyl halide

a) Using Grignard reagent (R-Mg-X)

$R - Mg - X \rightarrow$ First organometallic compound prepared by victor Grignard using R-X heated with Mg in present of dry ether.

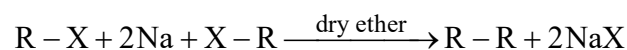


$\overset{8-}{R} - \overset{8+}{Mg} - \overset{8-}{X}$ is a source of carbanion so react with any H^+ medium to form Hydrocarbon

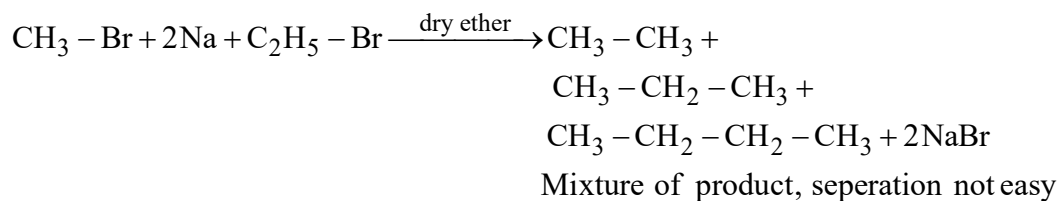


b) Wurtz reaction

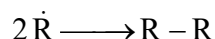
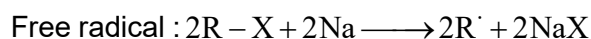
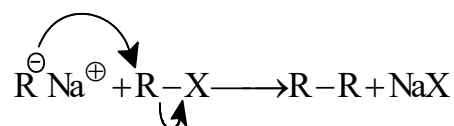
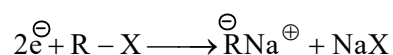
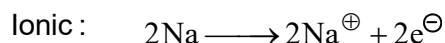
An ether solution of alkylhalide is treated with sodium form hydrocarbon



This reaction is not suitable for the synthesis of alkane containing odd number of carbon atoms but the method is useful for the preparation of symmetrical alkanes



Mechanism



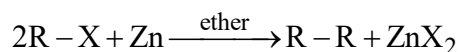
Limitation : 1) Methane cannot be obtained

2) Tert alkylhalide does not give the reaction

3) Only for the preparation of symmetrical alkanes.

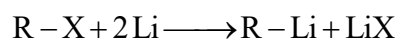
c) **Frankland's reaction**

Alkylhalide heated with Zn in presence of ether

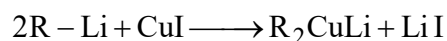


d) **Corey-House synthesis**

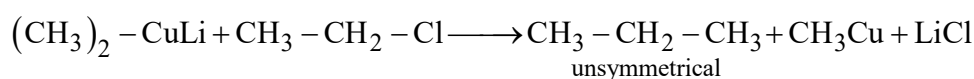
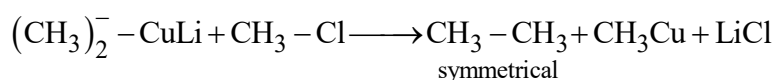
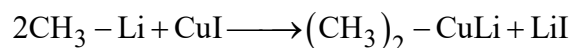
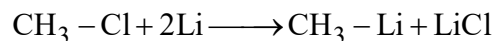
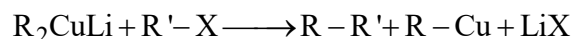
Halo alkane react with Li form alkyl lithium



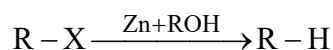
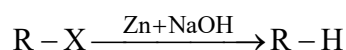
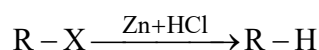
Alkyl lithium react with cuprous iodide form Lithium dialkylcuprate



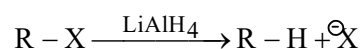
R_2CuLi react with $\text{R}-\text{X}$ form hydrocarbon.

Gilman's reagent R_2CuLi **e) Reduction of alkyl halide**

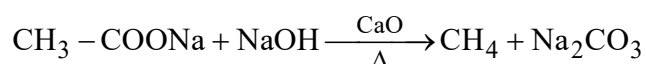
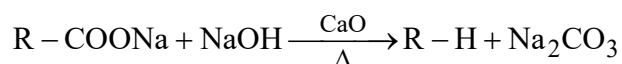
Haloalkane react with metals dissolving in acid / base / alcohol



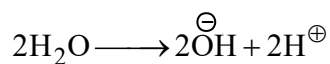
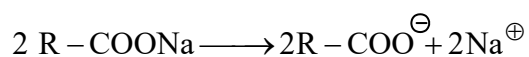
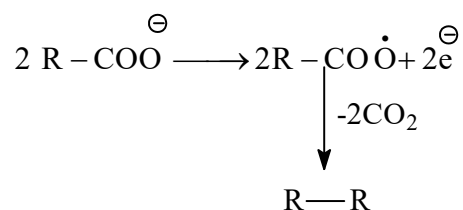
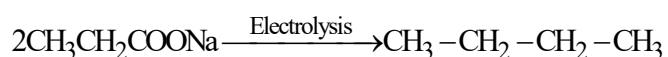
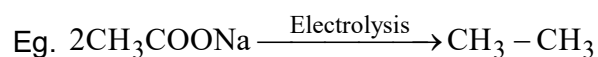
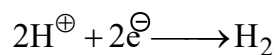
Haloalkane reduce with strong reducing agent $LiAlH_4$, $R-H$ is formed

**3) From carboxylic acid****a) using sodalime**

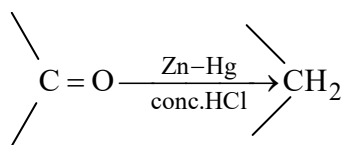
Sodium salt of carboxylic acid decarboxylated with sodalime ($NaOH + CaO$), hydrocarbons having, one carbon less than parent acid is formed.

**b) Kolbe's electrolytic decarboxylation**

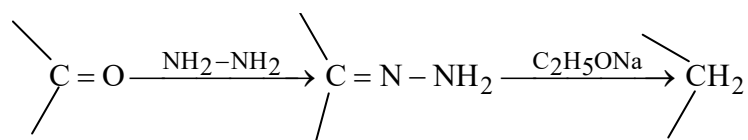
Aqueous sodium / potassium salt of mono carboxylic acid electrolysis, hydrocarbons are formed having twice the number of carbon atom in the parent alkyl group

**At Anode****At Cathode****4) Reduction of carbonyl compounds****a) Clemmensen reduction**

Aldehyde and ketones reduced with amalgamated Zn and conc:HCl alkanes are formed

**b) Wolf-Kishner reduction**

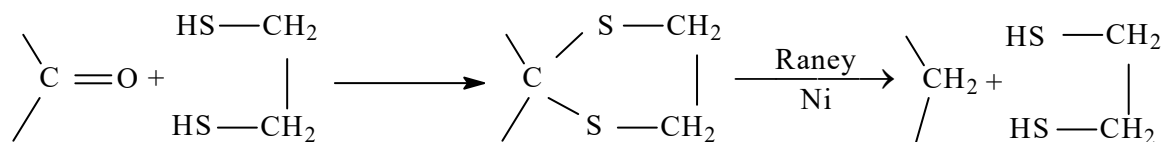
Aldehydes and ketones reduced to hydrocarbon in presence of excess hydrazine and sodium alkoxide on heating

**c) Mozingo method**

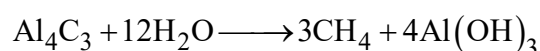
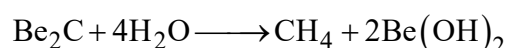
$\begin{array}{c} \diagup \\ \text{C} = \text{O} \\ \diagdown \end{array}$ is converted into its dithioacetal or ketol using ethanedithiol in presence of Lewis

acid. Dithioacetal hydrogenated

get hydrocarbon in presence of Raney Ni



5) By action of water on Be / Al carbide



Physical properties

Amongst straight chain alkanes, the first four members (C1-C4) are gases, the next thirteen are liquids (C5-C17) and the higher members (C18 onwards) are colourless waxy solids.

Boiling points

The boiling points of straight chain alkanes increase fairly regularly by 20–30 K for the addition of each carbon atoms. This regular increase in the boiling point of straight chain alkanes is due to increase in molecular size and hence the surface area of the molecules. As result, the magnitude of the van der Waals forces of attraction increases.

Amongst isomeric alkanes, the branched chain isomer has lower boiling point than the corresponding n-alkane. This is due to the fact that with branching the shape of the molecule tends to approach that of a sphere. As a result, the surface area decreases and van der Waals forces of attraction become weaker. In case of isomeric alcohols branching increases boiling point decreases.

Melting points

The melting points of alkanes increase with increase in carbon content but the variation is not regular due to alternation effect.

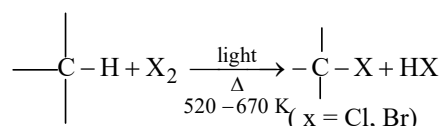
Chemical Reactions

I. Substitution reaction

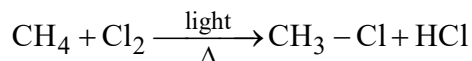
Replacement of H by another atoms / group

i) Halogenation

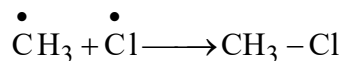
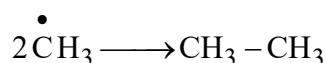
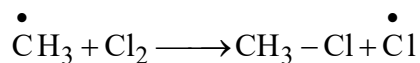
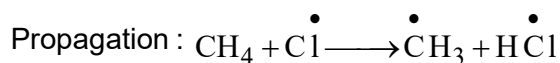
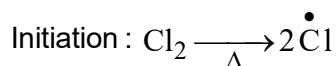
Replacement of H by halogen



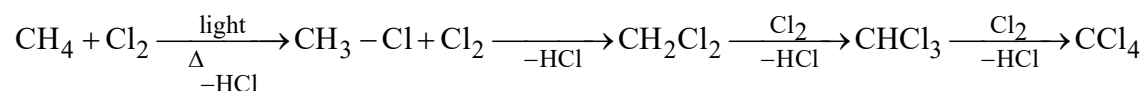
Halogenation reaction depends on nature of halogen and type of H



Mechanism



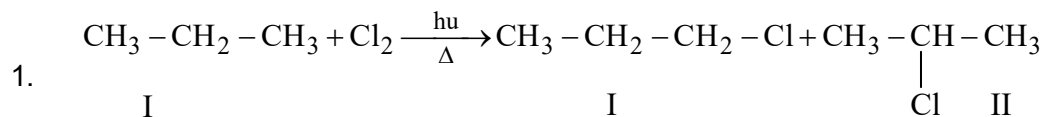
In presence of excess Cl_2 all hydrogens are replaced by Cl,



The relative reactivity of 1° , 2° and 3° H towards Cl_2 in the ratio $1^\circ : 2^\circ : 3^\circ = 1 : 3.8 : 5$

Towards bromination in the ratio $1 : 82 : 1600$

$$\text{The \% yield of chlorination or bromination} = \frac{\text{Relative amount}}{\text{Total amount}} \times 100$$

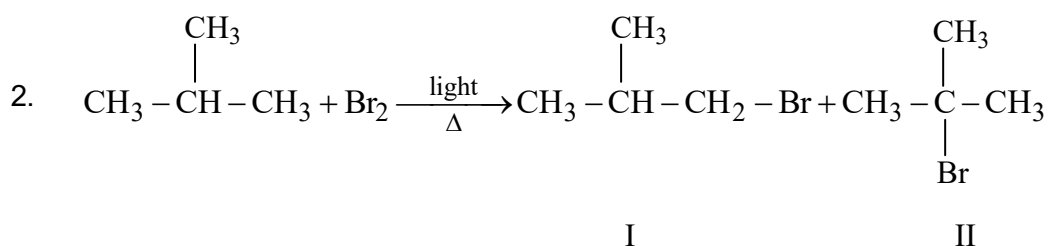


No. of $1^\circ H = 6$

$$\text{Relative amount} = 6 \times 1 = 6\% = \frac{6}{13.6} \times 100 = 44\%$$

II No. of $2^\circ\text{H} = 2$

$$\text{R.A} = 2 \times 3.8 = 7.6 \quad \% = \frac{7.6}{13.6} \times 100 = 56\%$$

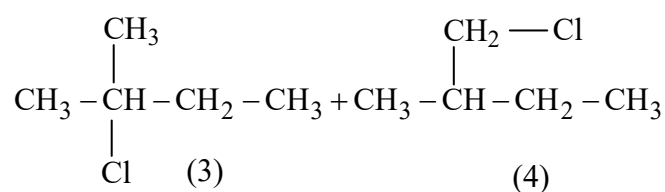
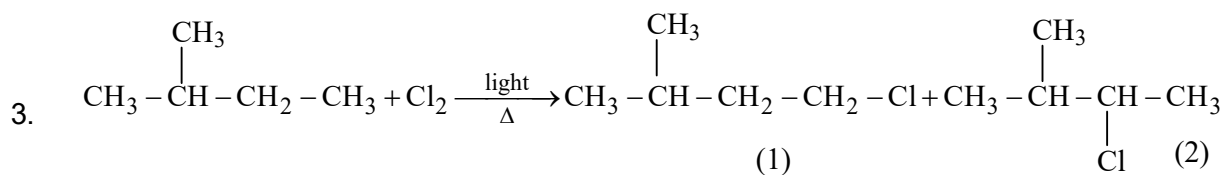


I. No. of $1^\circ\text{H} = 9$

$$\text{R.A} = 9 \times 1 = 9 \quad \% \text{ yield} = \frac{9}{1609} \times 100 = 0.6\%$$

II. No of $3^\circ\text{H} = 1$

$$\text{R.A} = 1 \times 1600 = 1600 \quad \% \text{ yield} = \frac{1600}{1609} \times 100 = 99.4\%$$



1) No. of $1^\circ\text{H} = 3$

$$\text{R.A} = 3 \times 1 = 3 \quad \% \text{ yield} = \frac{3}{21.6} \times 100 = 14\%$$

2) No. of $2^\circ\text{H} = 2$

$$\text{R.A} = 2 \times 3.8 = 7.6 \quad \% \text{ yield} = \frac{7.6}{21.6} \times 100 = 35\%$$

3) No. of 3° H = 1

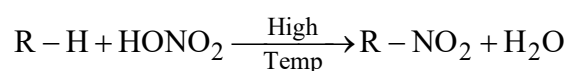
$$R.A = 1 \times 5 = 5 \quad \% \text{ yield} = \frac{5}{21.6} \times 100 = 23\%$$

4) No. of 1° H = 6

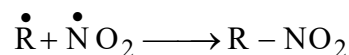
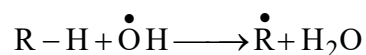
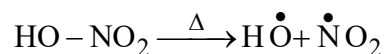
$$R.A = 1 \times 6 = 6 \quad \% \text{ yield} = \frac{6}{21.6} \times 100 = 28\%$$

ii) Nitration

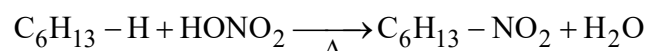
H atom replaced by nitro group



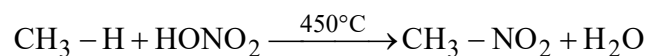
Mechanism



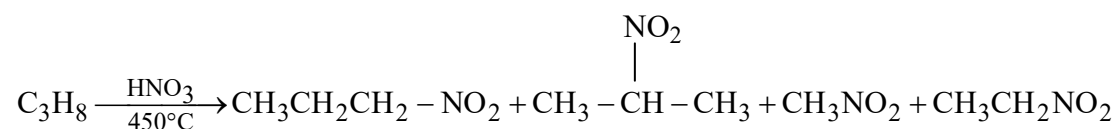
Alkanes contain 6 or more carbon atom heating with fuming nitric acid yield nitroalkane



Mixture of vapour of an alkane and nitric acid is heated at 400° – 500°C nitro alkane is formed. This method is known as vapour phase nitration.



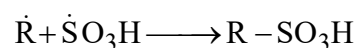
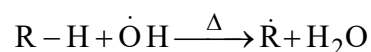
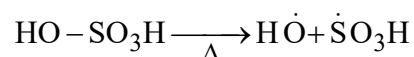
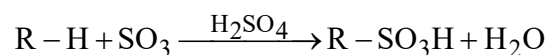
In alkane having 2 or more carbon atom, there is possibility of C-C bond breakage



iii) Sulphonation

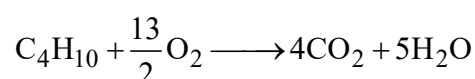
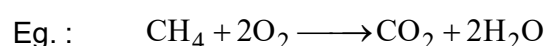
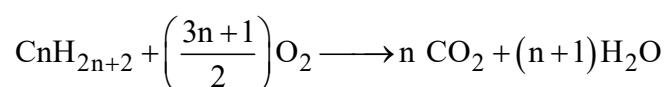
H atom replaced by SO₃H group

Higher alkanes contains six or more carbon atom heated with fuming H_2SO_4 at about 400°C



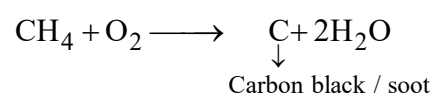
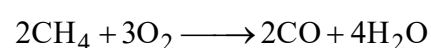
II. Oxidation reaction

a) Complete oxidation / combustion reaction



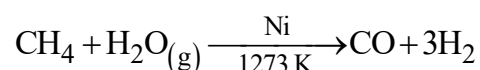
b) Incomplete oxidation

In presence of limited supply of air / oxygen, alkanes give CO along with some unburnt carbon (soot) in the form of carbon black.



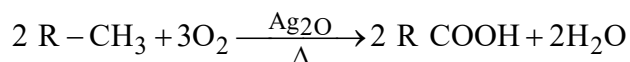
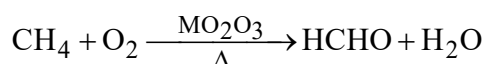
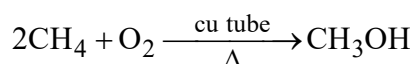
Carbon black is used for the preparation of black ink, paint etc.

When methane is react with superheated steam in presence of Ni at high temp, water gas is formed

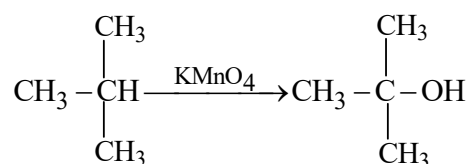


c) Catalytic oxidation

Different catalyst give different product

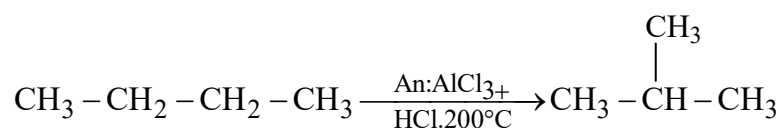


Alkanes having 3°H are oxidised by oxidising agents to corresponding alcohol.



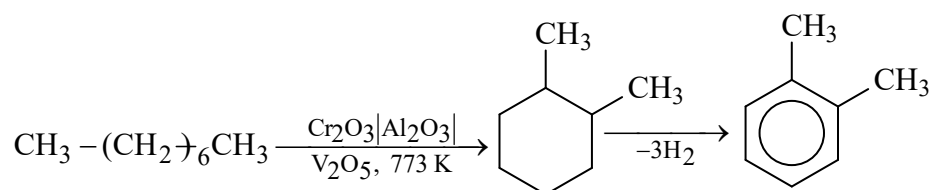
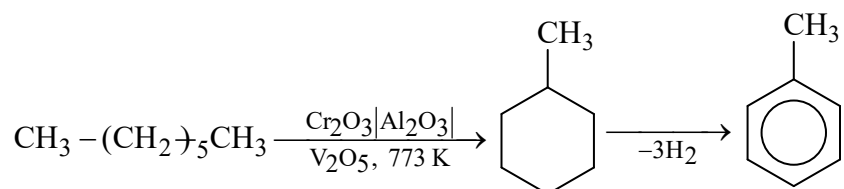
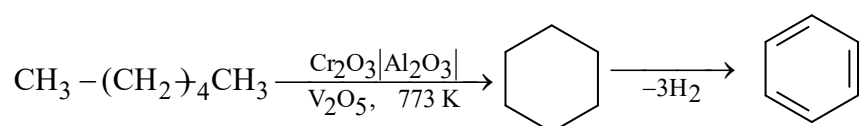
III. Isomerisation

When n-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under pressure (about 35 atmospheres) they are converted into branched chain alkanes.



IV. Aromatisation

Alkanes containing 6 - 10 carbon atoms are heated with metallic oxides and followed by dehydrogenation to form aromatic compounds

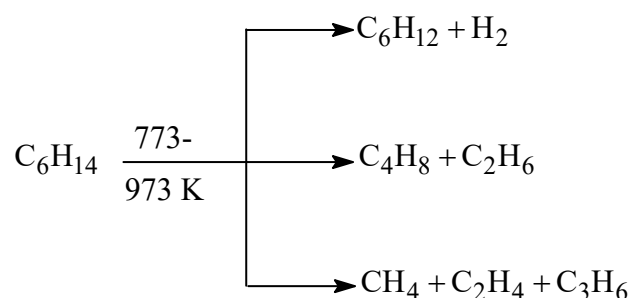


xylene

V. Pyrolysis

Decomposition of a compound by applying heat is known as pyrolysis

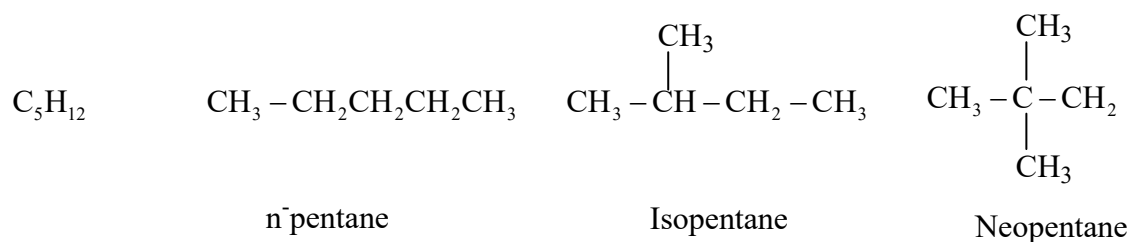
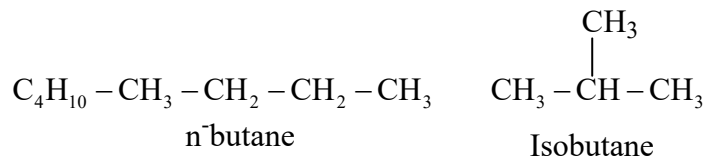
Pyrolysis of higher alkanes to give a mixture of lower alkanes, alkenes, etc. is called cracking. It is usually carried out by heating higher alkanes to high temperature (773–973 K) under a pressure of 6–7 atmospheres in presence or absence of a catalyst.



Isomerism in alkanes

Structural isomerism

Chain isomerism

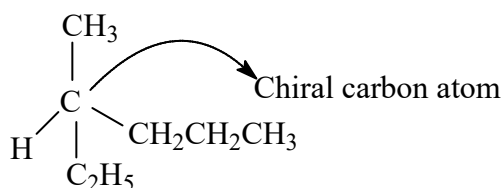


Stereo isomerism

Isomers having the same structural formula but different relative arrangement of atoms or groups in space are called stereoisomers (Greek : stereo = space, meros = part) and the phenomenon is called stereoisomerism. Stereoisomers have the same molecular structure but different configurations. Stereoisomerism is of three types : (i) conformational isomerism (ii) geometrical isomerism and (iii) optical isomerism.

Optical isomerism

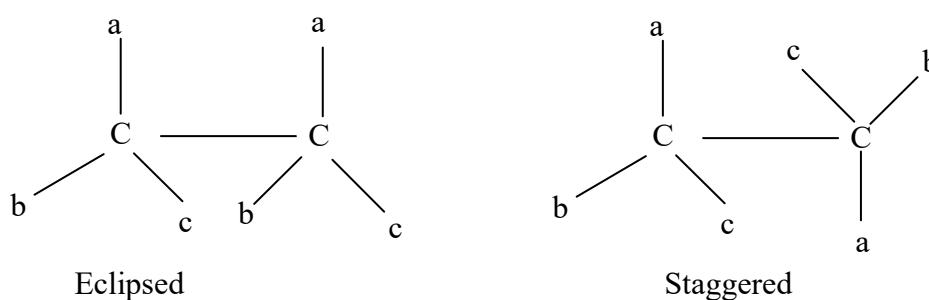
Alkanes with minimum 7 carbon atoms can show optical isomerism.



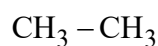
Conformational isomerism

The infinite no. of spatial arrangements obtained due to the rotation around a C-C single bond is known as conformers. The phenomenon is known as conformational isomerism

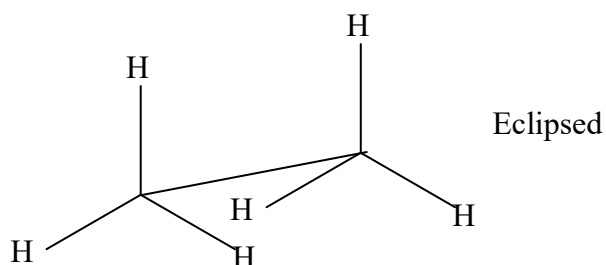
- It arises due to the free rotation around a C-C
- The energy of arrangement is max when bond pairs are very close to each other, such forms are called eclipsed conformation (Least stable)
- The energy of arrangement is min when bond pairs are far apart, such forms are called staggered conformation (more stable)
- Conformations between eclipsed and staggered is known as skew conformation



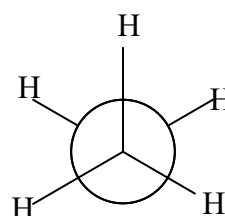
Conformations of ethane

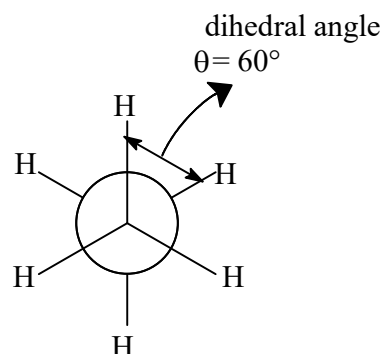
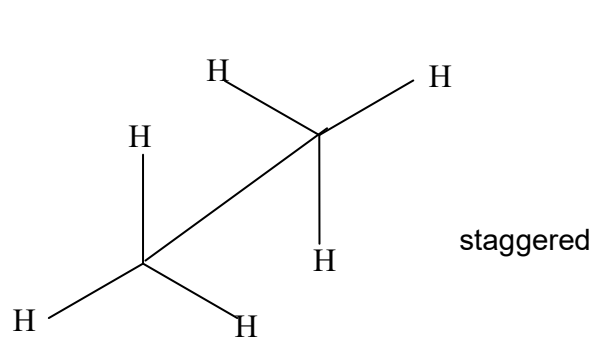


1) Saw - House projection

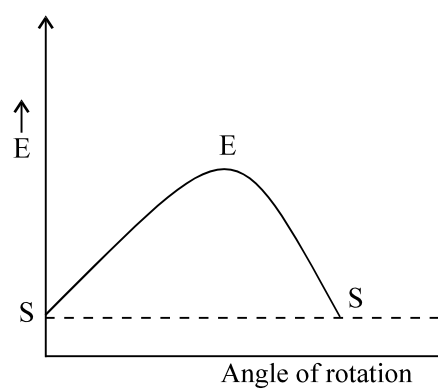


2) New - man projection

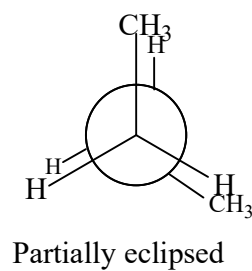
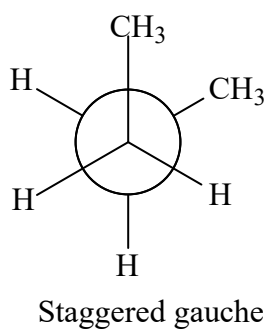
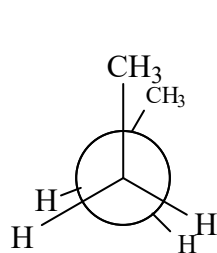
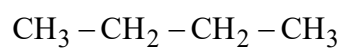


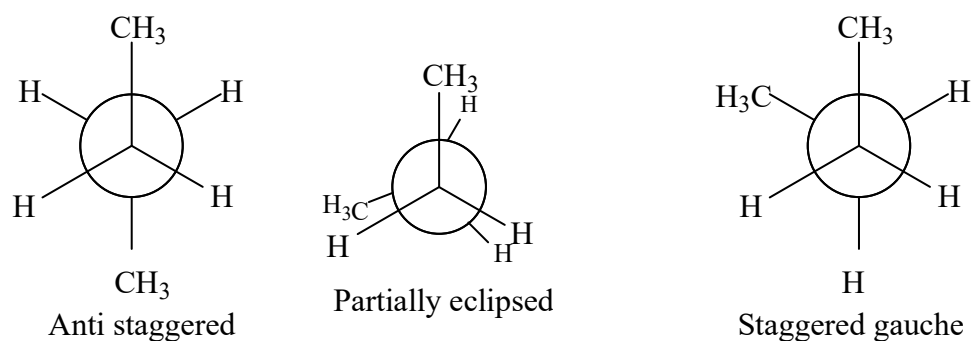


Energy level diagram

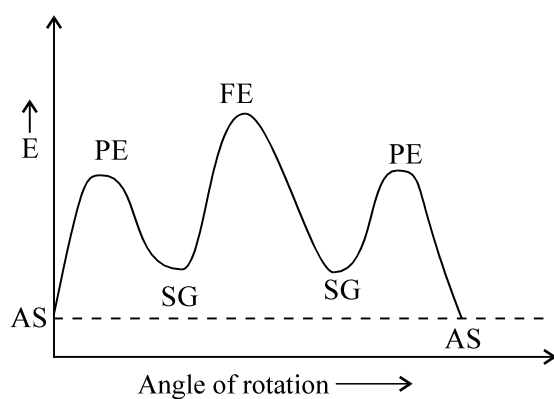


Conformations of butane





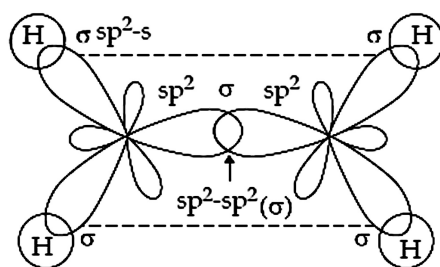
Energy level diagram



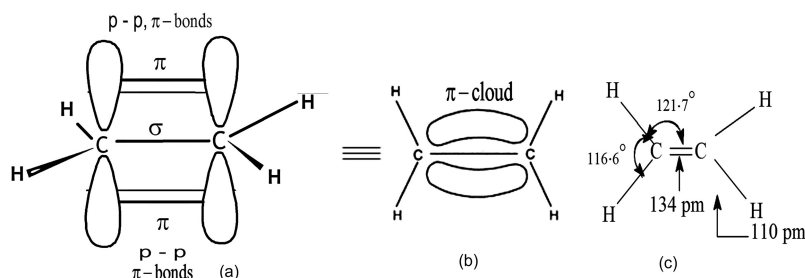
ALKENE

General formula C_nH_{2n}

3.1 Structure of Double Bond. The double bond in alkenes consists of one carbon-carbon σ -bond formed by head-on overlap of sp^2 -hybridised orbitals and a π -bond (284 kJ mol^{-1}) formed by lateral or sideways overlap of the two 2p-orbitals of the two carbon atoms



Orbital picture of ethene showing σ -bonds only



Orbital picture of ethene showing formation of (a) π -bonds (b) π -cloud and (c) bond angles and bond lengths

To have effective overlap, the p-orbitals move closer, therefore, a double bond is shorter (134 pm) than a single bond (154 pm). The presence of π -bond makes alkenes less stable and more reactive than alkanes. Therefore, alkenes are readily attacked by (electrophiles) electrophilic reagents.

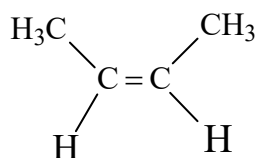
Isomerism in alkene

Geometrical isomerism

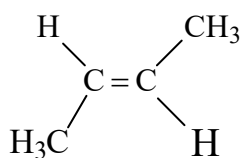
Two compounds having same molecular formula but different spatial arrangement around a carbon - carbon double bond. Such isomers are called geometrical isomers and the phenomenon is known as geometrical isomerism.

- If the identical atoms or groups are on same side of $C = C$ is called cis isomer and they are on opposite side trans isomers

Eg. But - 2 - ene



Cis



Trans

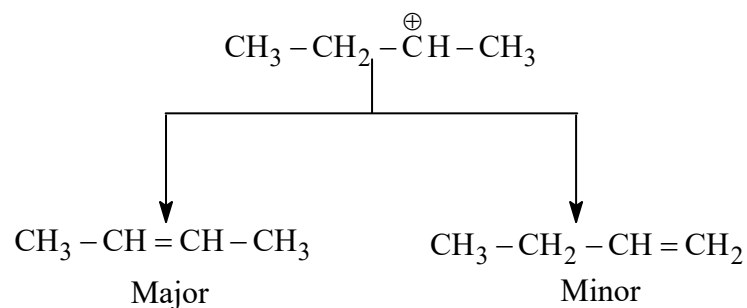
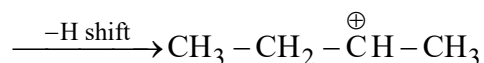
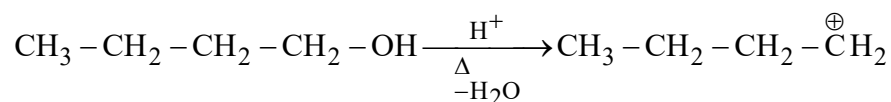
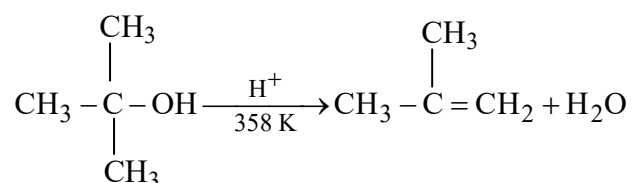
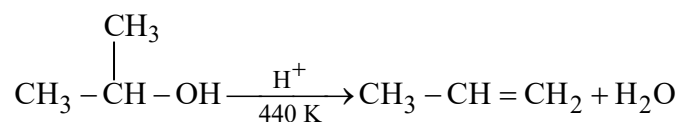
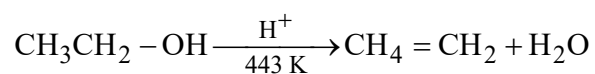
Conditions :

- Should contain at least 1 double bond
- No identical atoms or group are on same double bonded carbon atom

Preparation

I. From alkynes

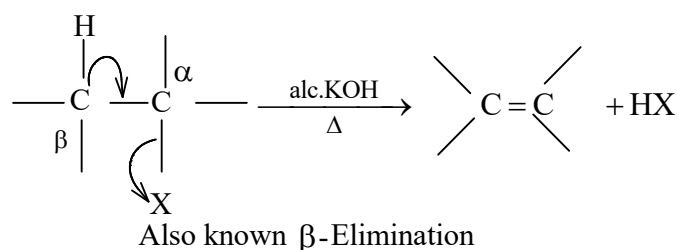
Alkynes undergo partial reduction to form alkenes, Alkynes reduced with H₂ in presence of Pd over CaCO₃ or BaSO₄ with added lead acetate and quinoline - is known as Lindlar catalyst

Order of dehydration $3^\circ > 2^\circ > 1^\circ$ 

In this case more than one product is formed, major product is determined by Saytzeff's rule i.e. more substituted alkenes are the major product.

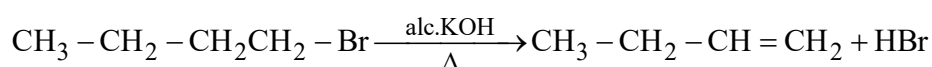
III. From alkylhalide

Haloalkane heated with strong bases such as sodium methoxide, alc. KOH, tert -butoxide undergoes dehydrohalogenation to form alkenes

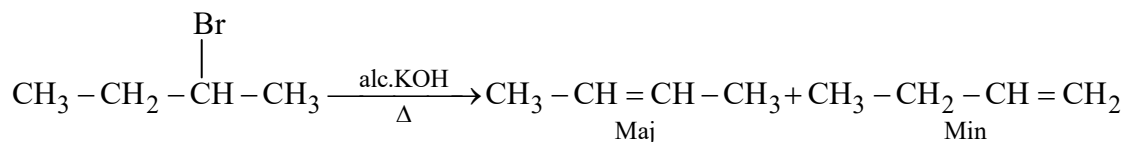


The leaving nature of halogens $F < Cl < Br < I$ order of reactivity of $R-X$ $3^\circ > 2^\circ > 1^\circ$

Reaction follows E^2 Mechanism.

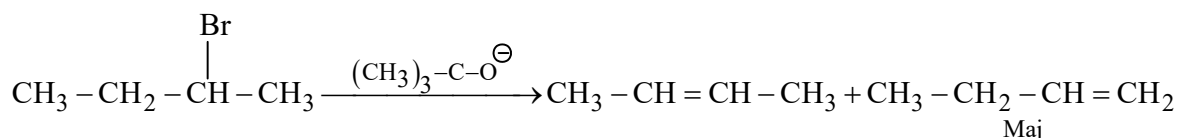


In case of terminal halide, terminal alkenes are formed



In case of non terminal halides major product is determined by saytzeff rule.

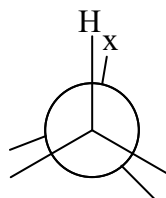
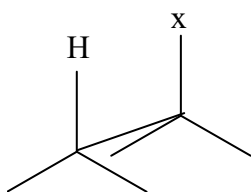
If the elimination carried out in presence of a bulky bases Hoffmann's elimination follows



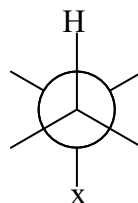
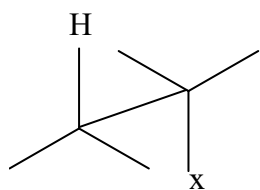
E^2 elimination depends on periplanar geometry

Two types of periplanar

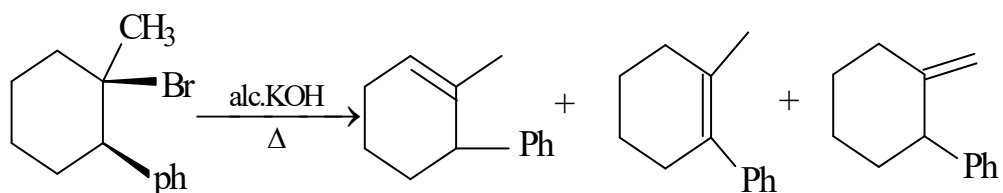
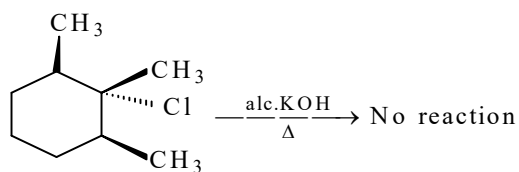
1. Syn periplanar - Both H and halogen are on same side



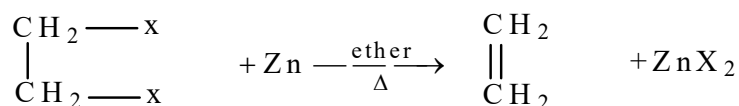
2) Anti periplanar - Both H and halogen are on opposite side



E₂ eliminations are always antiperiplanar

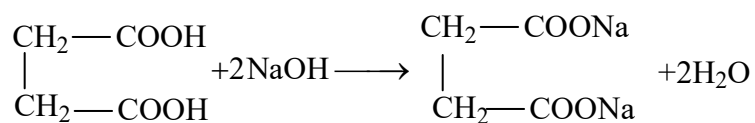


4) From vicinal dihalides

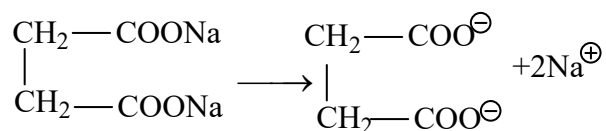


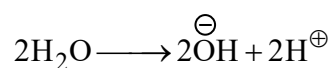
5) From saturated dicarboxylic acids

Aqueous solution of sodium / potassium salt of succinic acid undergo Kolbe's electrolytic decarboxylation to form alkene



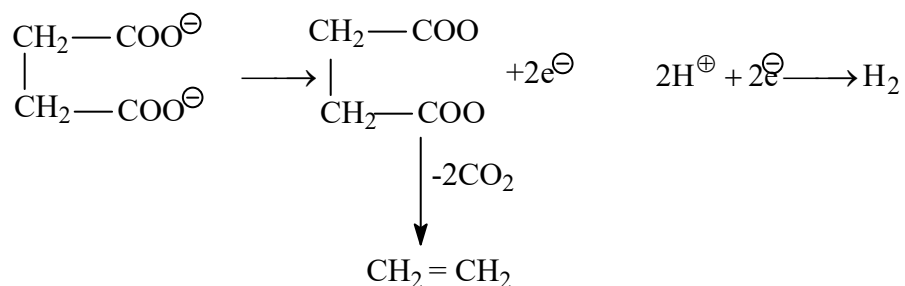
succinic acid



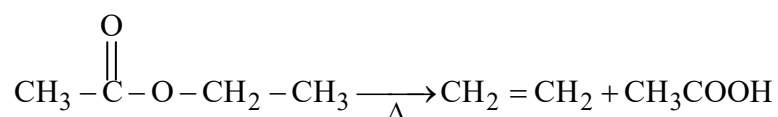


At Anode

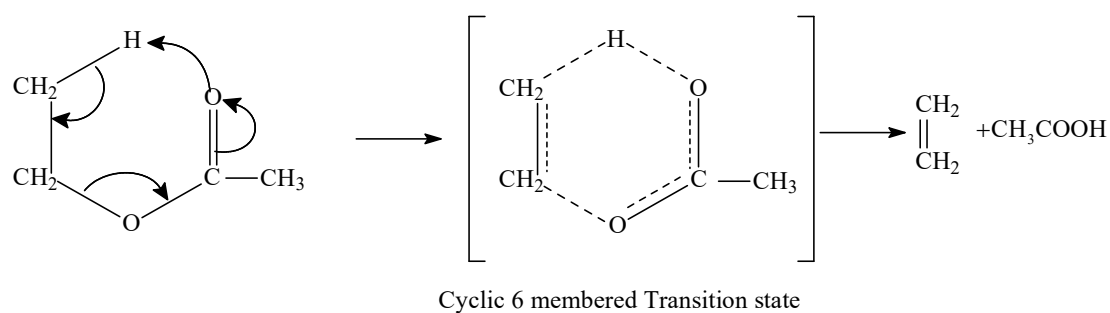
At cathode



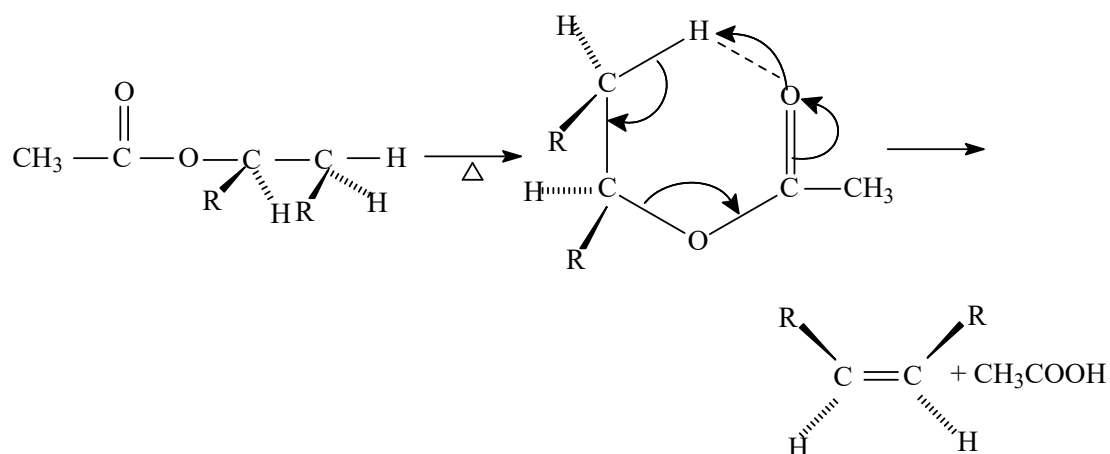
6) Pyrolysis of ester



Mechanism

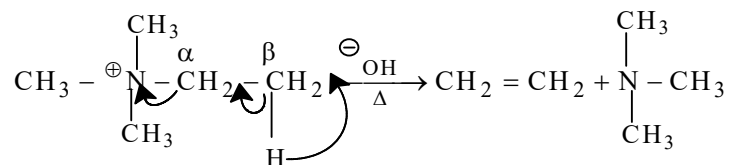


Pyrolysis of esters are syn elimination reaction



7) Pyrolysis of Quaternary ammonium salts

When quaternary ammonium salts are heated in presence of a base alkenes are formed.



Properties

Physical properties

i) Physical state :

The first three members i.e., ethene, propene and butenes are colourless gases; the next fourteen (C₅–C₁₈) are liquids while the higher ones are solids. Except ethene which has pleasant smell, all other alkenes are colourless and odourless gases.

ii) solubility:

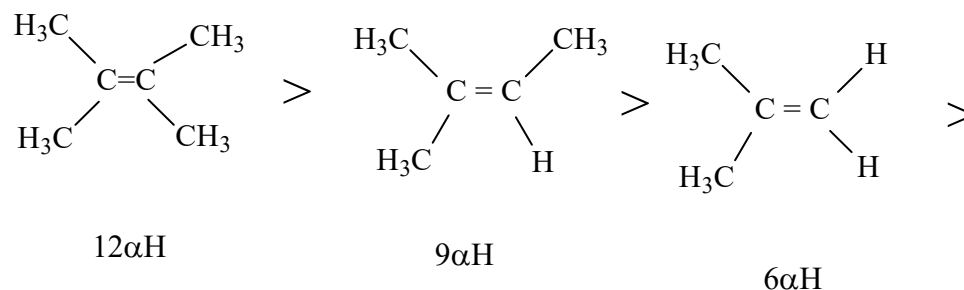
They are insoluble in water, buffairly soluble in non polar solvents such as benzene, petroleum ether, etc.

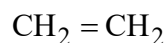
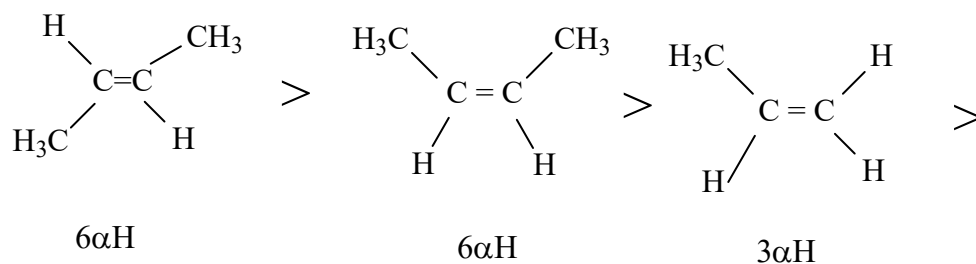
iii) Boiling points: Their boiling points increase regularly with increase in molecular mass. The boiling points generally increase by 20–30 K for the addition of each CH₂ group to the chain. Like alkanes, straight chain alkenes have higher boiling points than isomeric branched chain alkenes.

Stability

$$\text{Stability of alkenes} \propto \text{No of alpha H atom} \propto \frac{1}{\text{Heat of Hydrogenation}}$$

Heat of Hydrogenation - The amount of energy release when an alkene is hydrogenated to form alkane

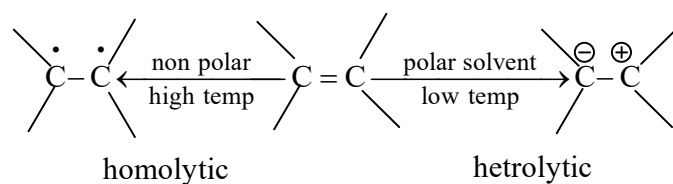




Chemical Reactions

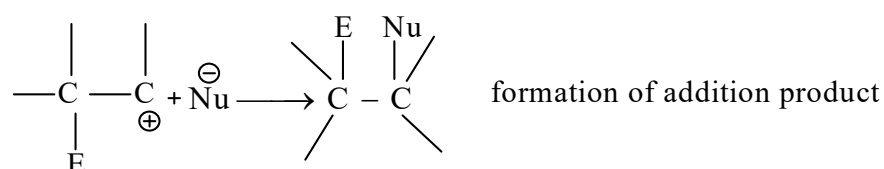
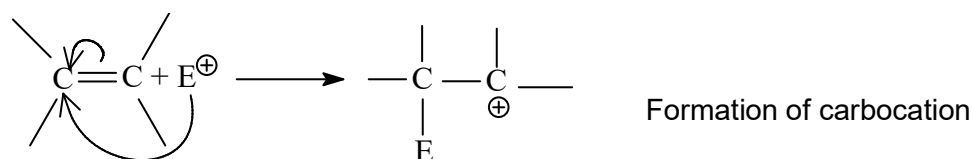
The π electrons in alkenes are loosely held and easily polarisable in presence of a polar solvent at low temperature heterolytic cleavage takes place and favours ionic mechanism.

In presence of a non polar solvent at high temperature homolytic cleavage takes place and favours free radical mechanism



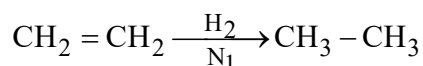
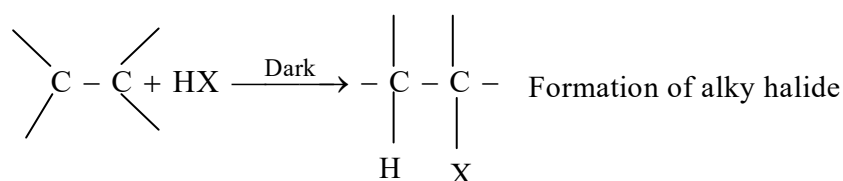
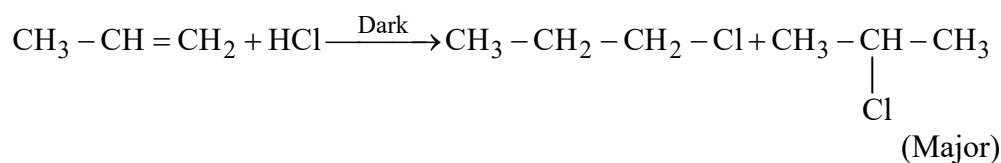
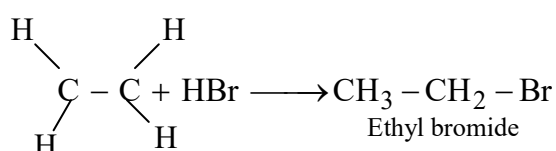
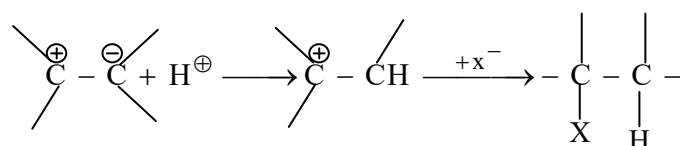
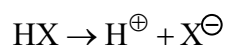
IONIC MECHANISM

Alkenes show electrophilic addition reaction through 3 steps



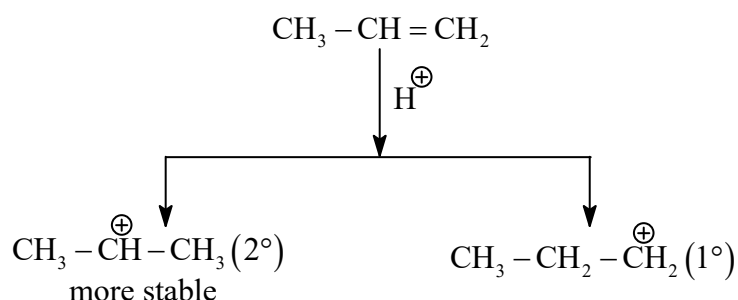
Important Addition Reactions**1) Addition of Hydrogen**

Alkenes readily add dihydrogen in presence of Raney nickel (an active form of nickel), platinum or palladium as catalyst at room temperature or ordinary nickel at 523 – 573 to form alkanes (Sabatier and Senderen's reduction)

**2) Addition of hydrogen halide****Mechanism**

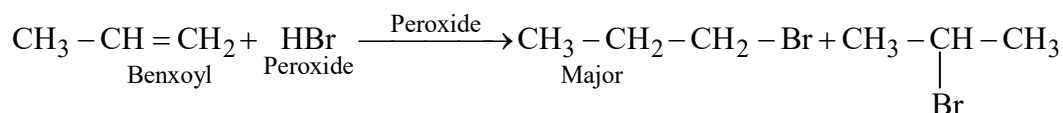
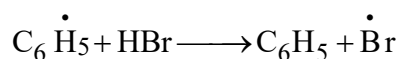
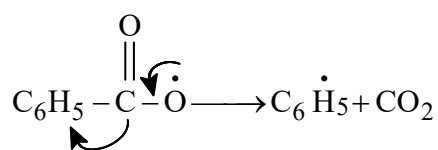
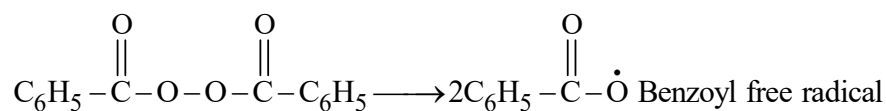
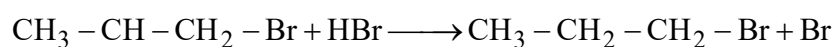
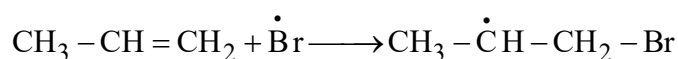
In this reaction more than one product is formed therefore reaction is a regioselective reaction so the major product is determined by using "Markovnikov rule"

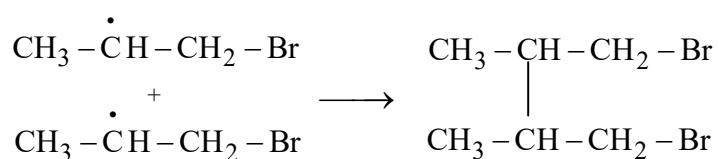
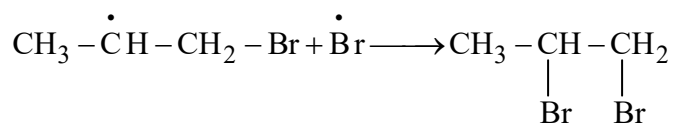
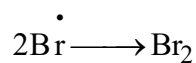
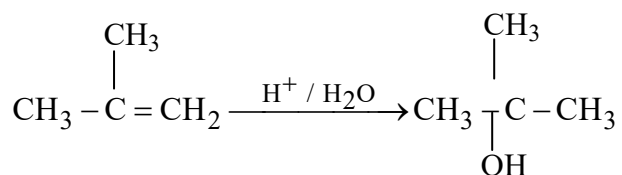
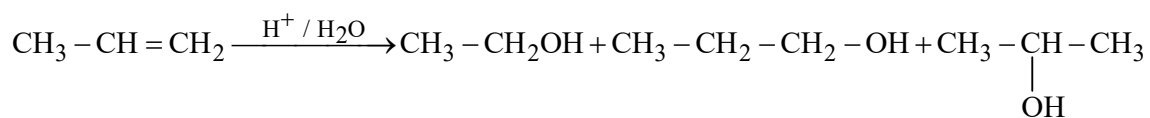
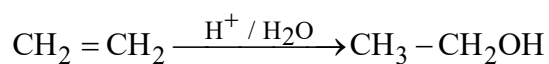
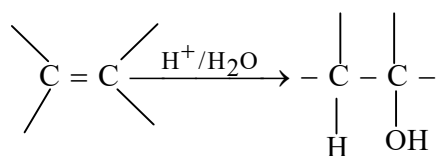
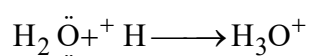
The rule states that addition of unsymmetrical reagent to an unsymmetrical alkene the negative part of the adding molecule attached to the carbon containing lesser number of H-atom

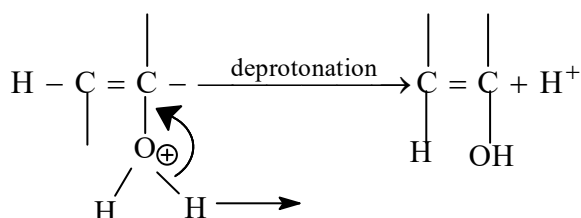
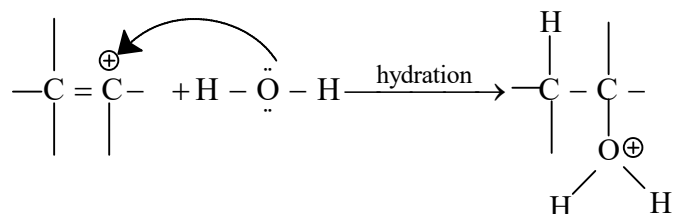
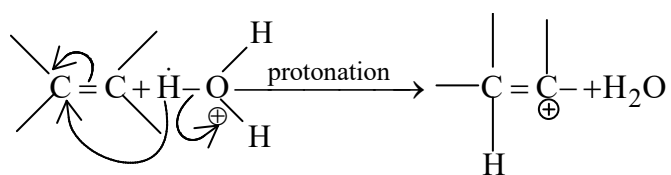
Proof for Markovnikov rule:

2° C is more stable hence it forms the major one. This reaction occurs due to electromeric shift. The reason for the repulsion of electrons to the next is due to +I effect of methyl thus providing a pushing force.

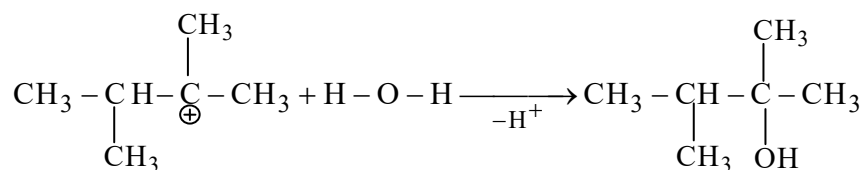
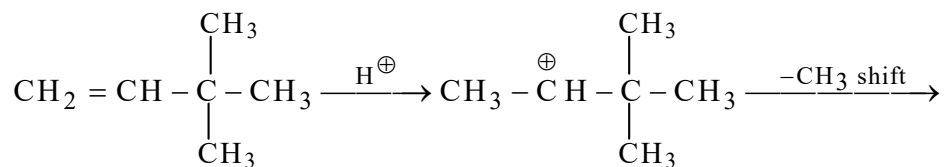
• Addition of HBr [not HF, HCl and HI] to an unsymmetrical alkene in presence of peroxide addition takes place against to Markovnikov rule known as Anti Markovnikov's Addition/ Peroxine Effect / Kharasch Effect.

**Initiation****Propagation**

Termination**3) Addition of H₂O****1. Acidic Hydration of Alkene****Mechanism**

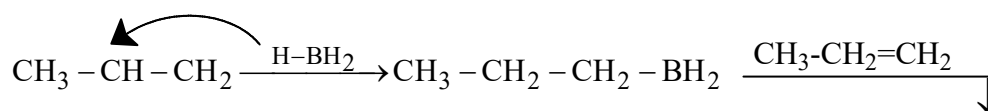
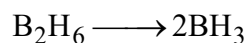


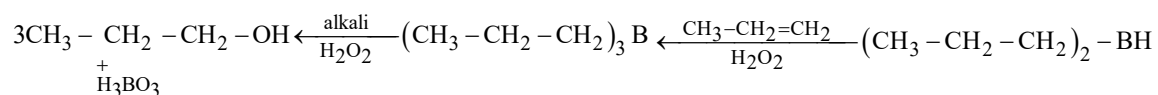
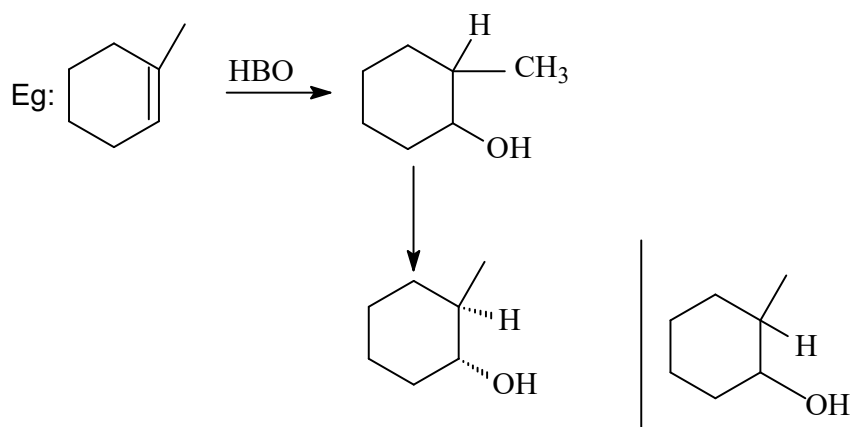
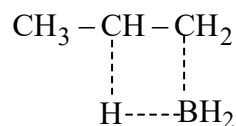
Eg: 3, 3 dimethyl but -1- ene + dilute H_2SO_4



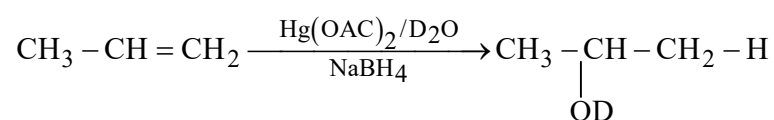
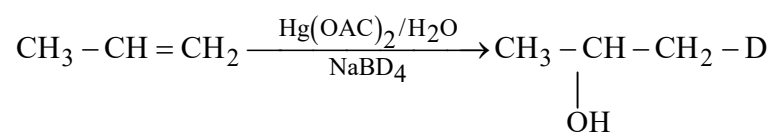
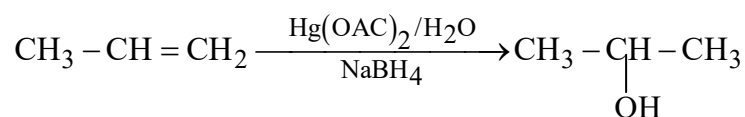
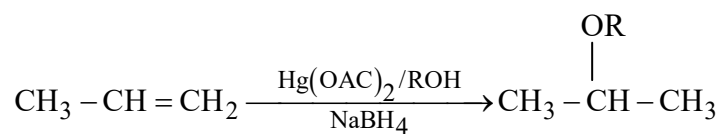
2. Hydroboration - Oxidation

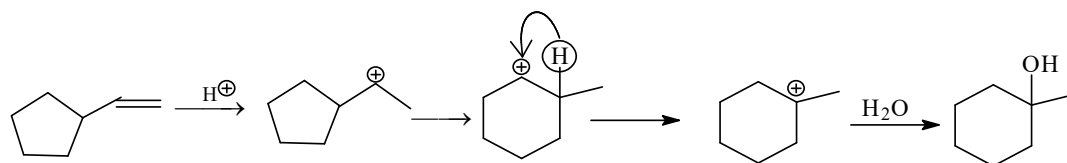
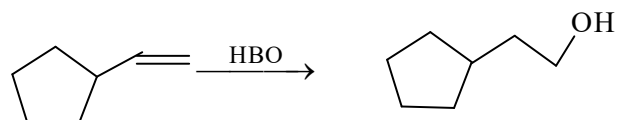
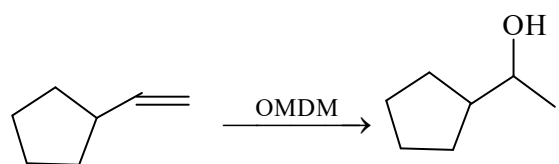
When alkenes react with borane form trialkyl borane which on oxidised with H_2O_2 in aqueous alkaline medium alcohols are formed Anti Markovnikov alcohol.



**Syn addition****3. Oxymercuration - Demercuration**

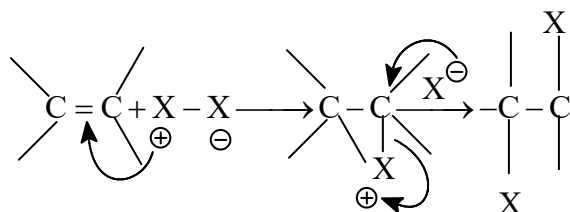
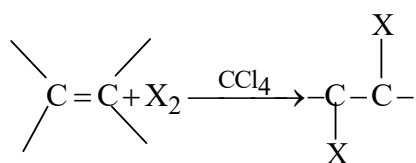
It is hydration of an alkene to form Markovnikov alcohol, there is no intermediate forming.

**Alkoxy Mercuration – Demercuration**

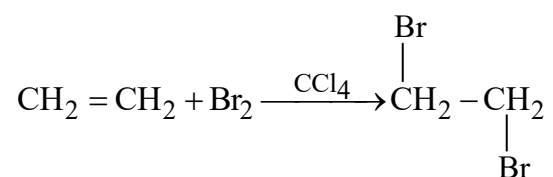


Addition of Halogen

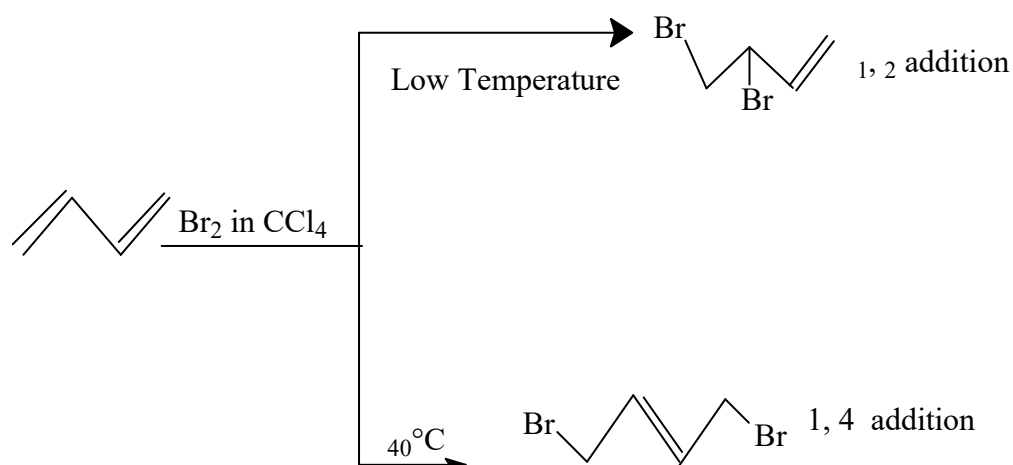
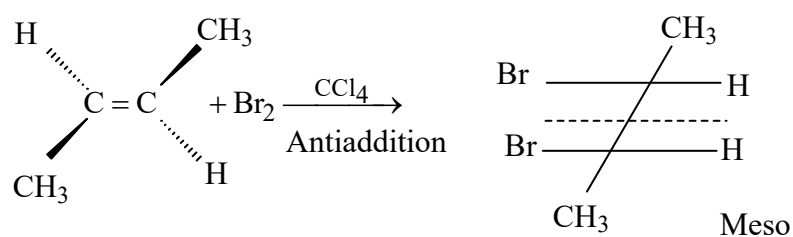
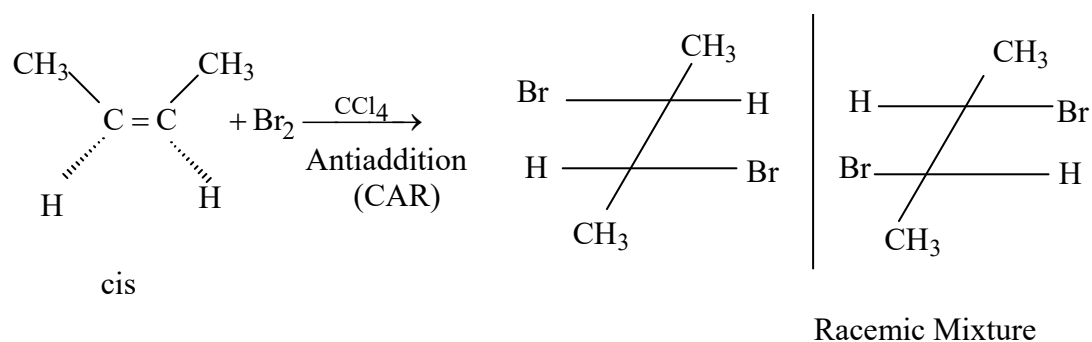
Formation of vicinal halide



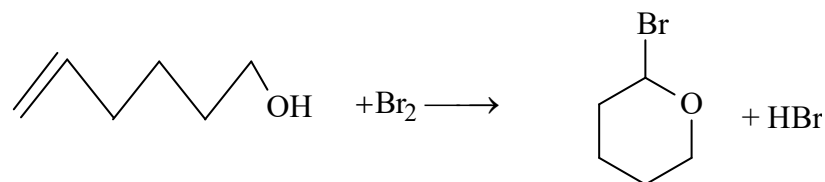
These are antiaddition reaction



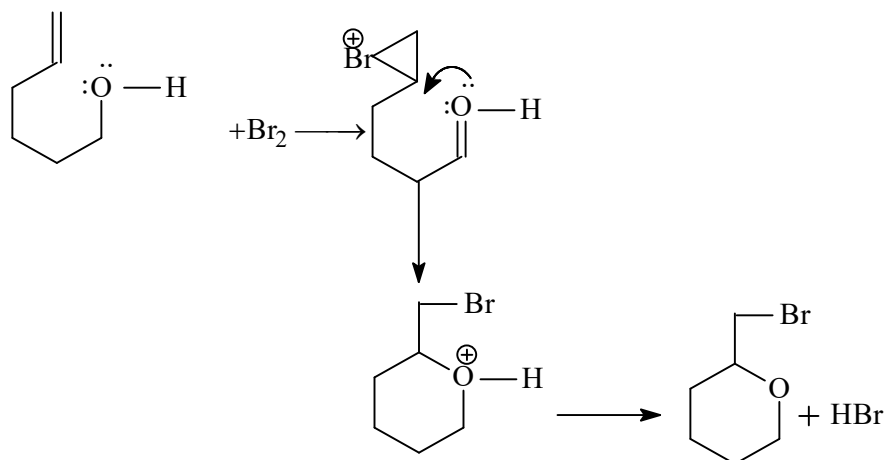
The reddish brown colour of bromine is discharged and colourless vicinal dibromide is formed, this reaction is used for test for unsaturation.



If alkenes containing nucleophilic center cyclisation takes place

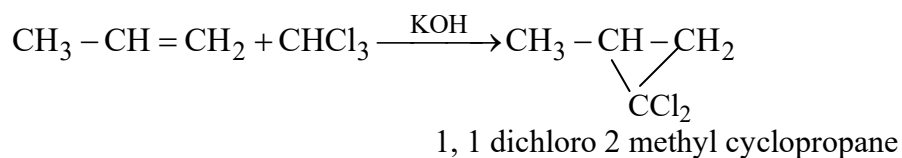
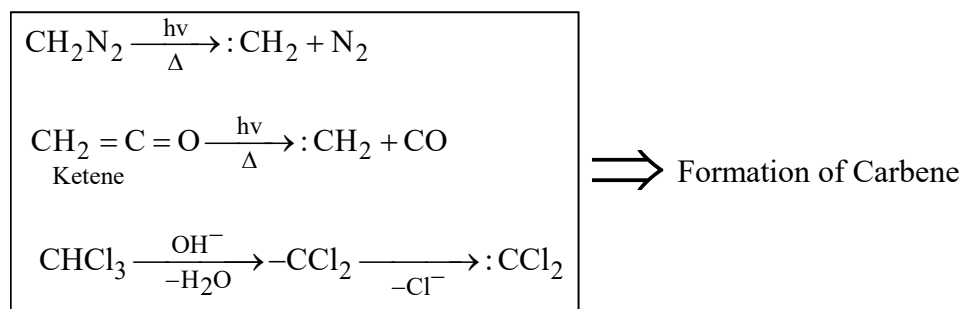
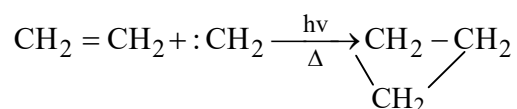


Mechanism



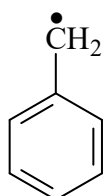
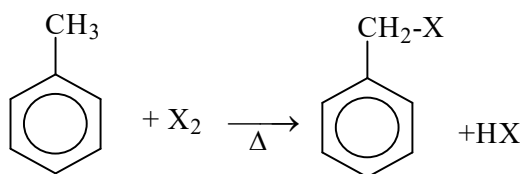
Addition of Carbene

Formation of cycloalkane

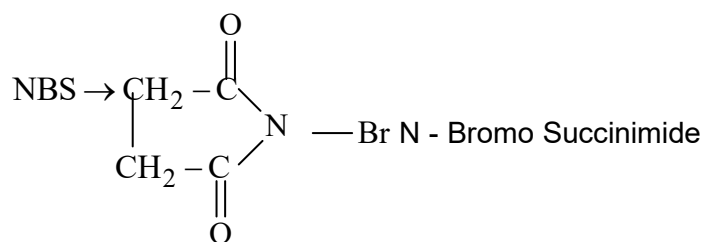
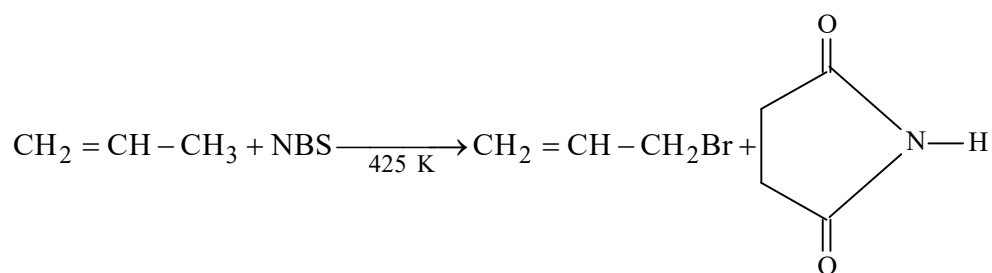
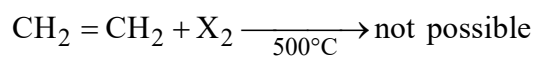


Addition of Hypohalous Acid

Formation of halohydrin

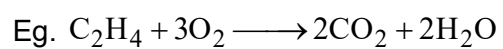
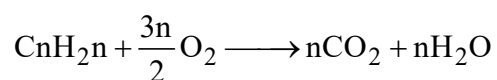


Allyl and benzyl radicals are resonance stabilised.

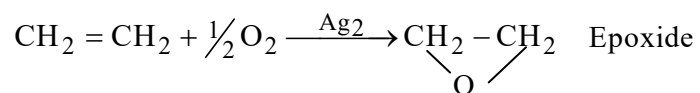


OXIDATION REACTION

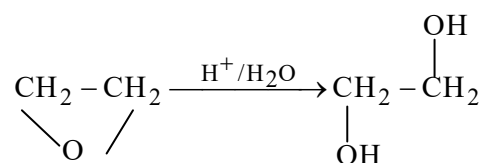
1. Complete oxidation



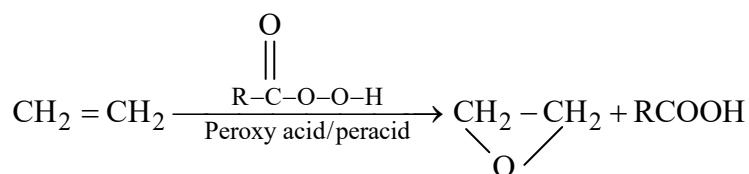
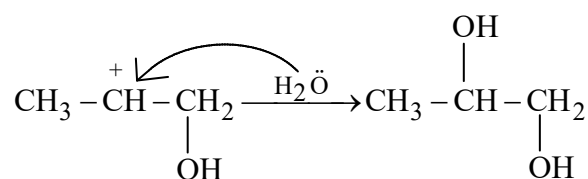
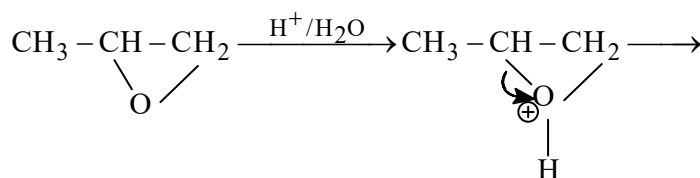
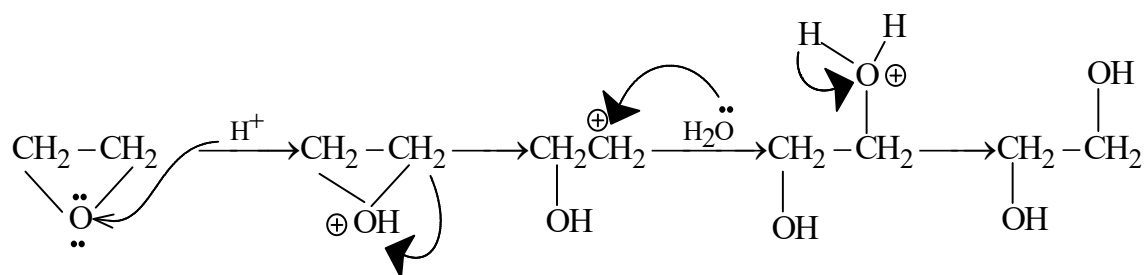
2. Incomplete / partial oxidation

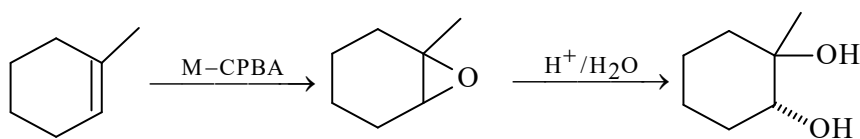
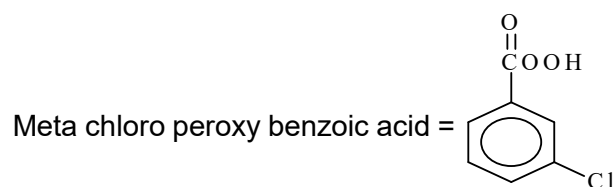
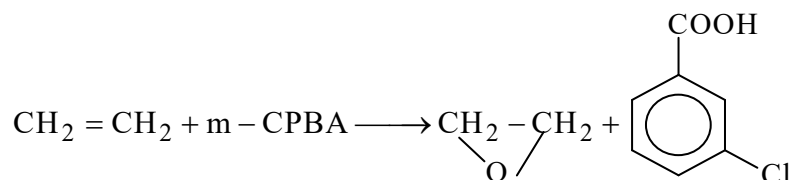
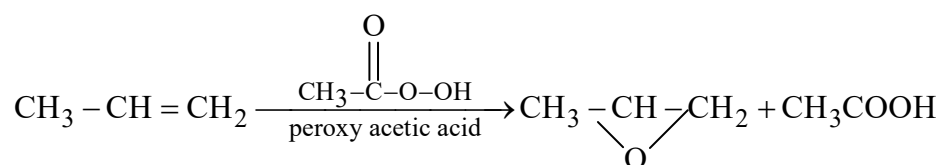


Epoxide undergo acidic hydrolysis give vicinal diol and reaction is known as hydroxylation. It is anti hydroxylation reaction

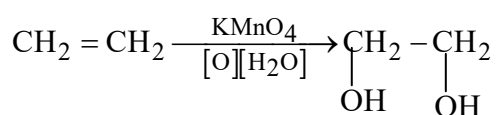
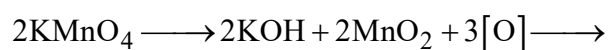


Mechanism



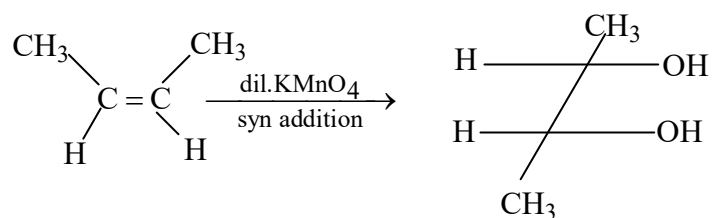


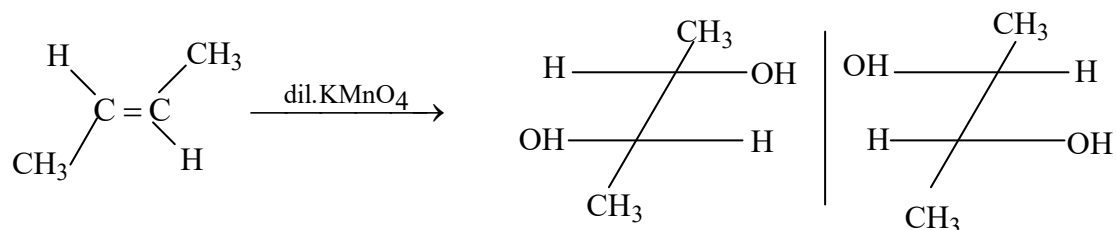
Oxidation using Dil. /cold KMnO_4



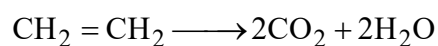
syn addition and vicinal diol

The purple colour / KMnO_4 is discharged and colourless, Vicinal diol is formed is known as

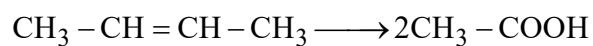




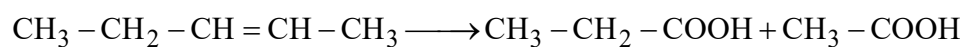
Oxidation using Acidified or Alkaline hot $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$



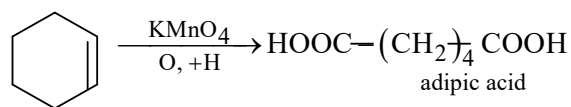
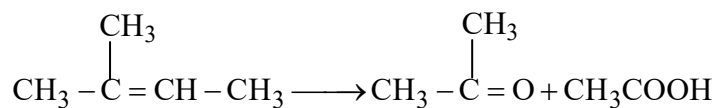
Terminal can be converted into CO_2 and H_2O



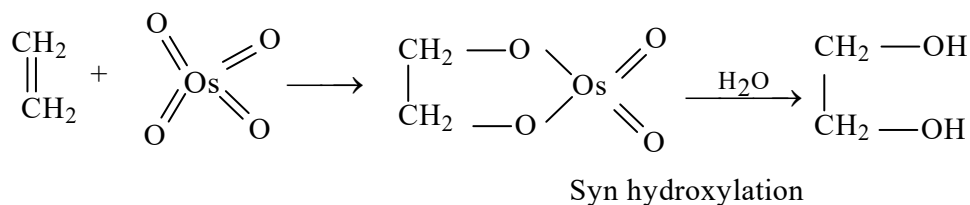
Without terminal the respective acids will be formed

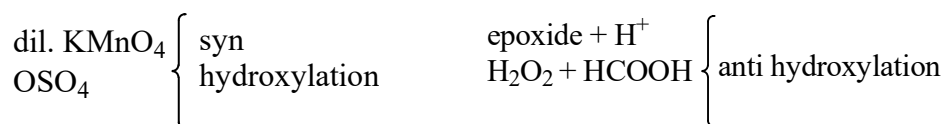
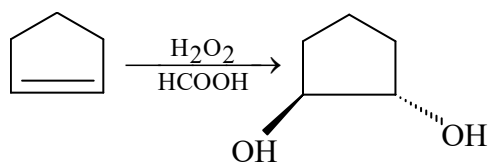


If no H is present on C then it becomes CO (Keto)

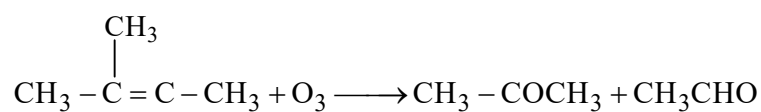
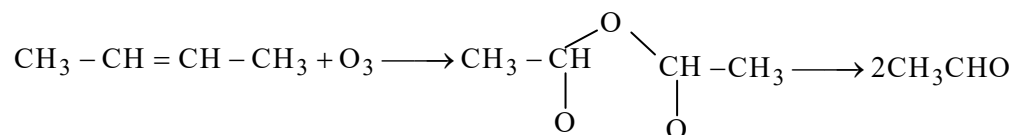
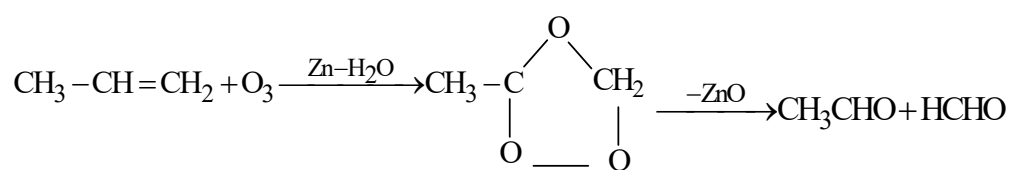
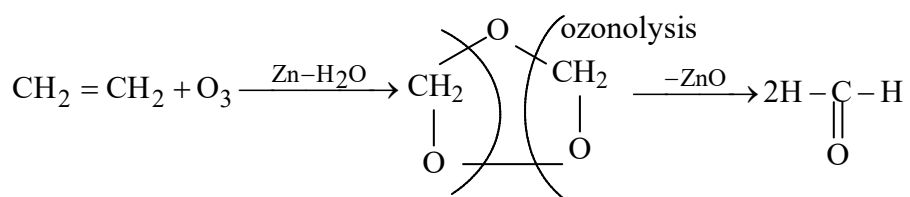
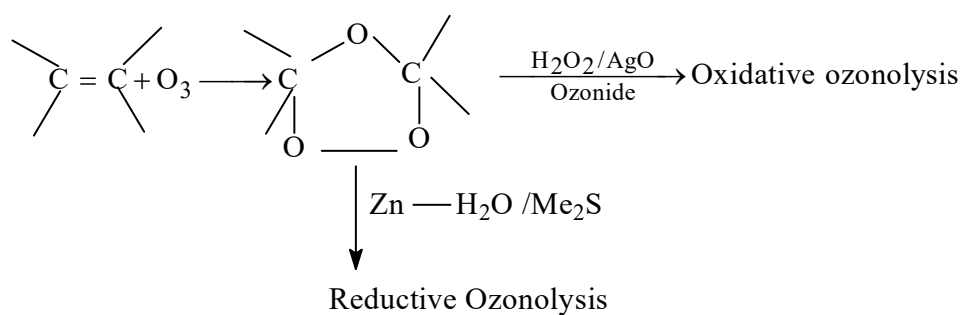


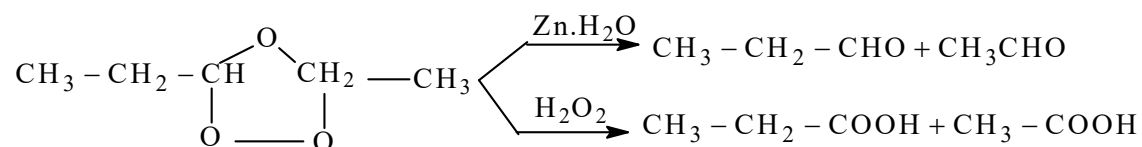
Oxidation using OsO_4





OZONOLYSIS REACTION

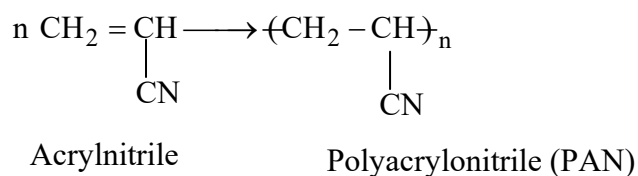
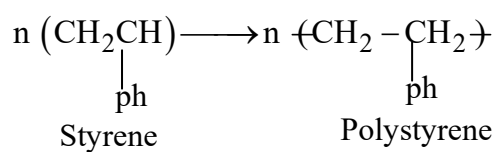
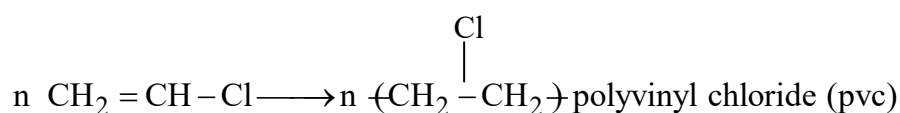
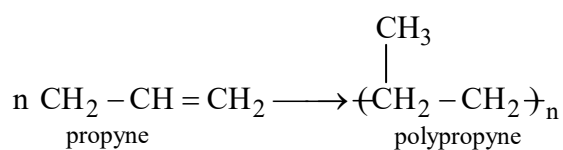
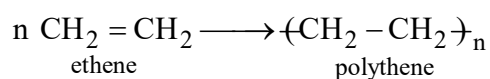


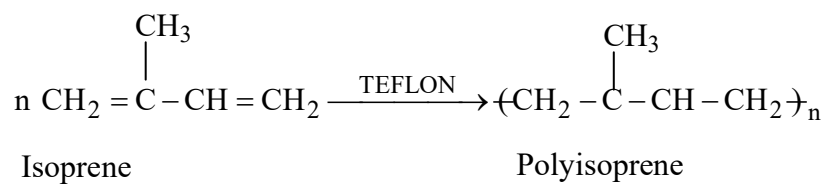
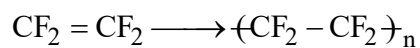
Oxidative ozonolysis**Polymerisation reaction**

Polymerisation is a process by which a large number of simple molecules combine to form a large molecule. The simple molecules are called monomers while the large molecule is called a polymer

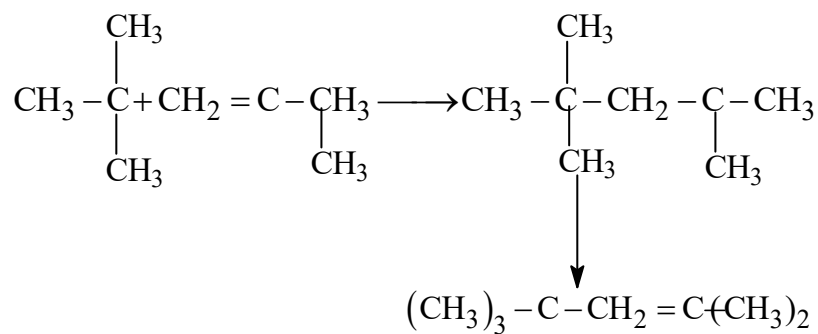
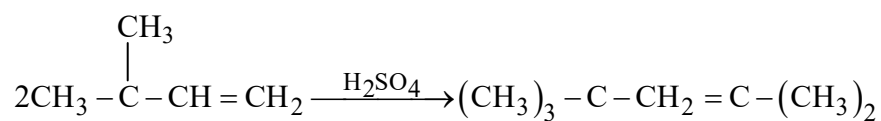
Conversion of monomer \rightarrow polymer

- At 473 k and 1500 atm



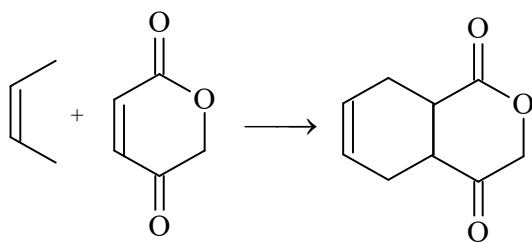
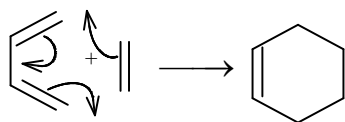


Dimerisation reaction



Diels Alder Reaction

(4 + 2) Cycloaddition of conjugated alkene with an enophile ($= / \equiv$)



ALKYNES

- General formula : C_nH_{2n-2}
- Less than 4 H atom corresponding paraffins
- Known as acetylene
- First member is acetylene others are derivatives of acetylene

Eg. $CH \equiv CH$ methylene $CH_3 - C \equiv C - CH_3$ $CH_3 - C \equiv C - CH_2 - CH_3$ $CH_3 - C \equiv C - CH_3$

Dimethyl acetylene

Methyl acetylene

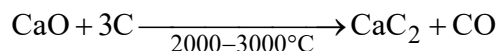
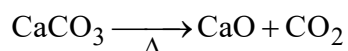
 $CH_2 = CH - C \equiv C - CH_2 - CH = CH_2$

Allyl vinyl acetylene

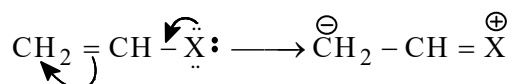
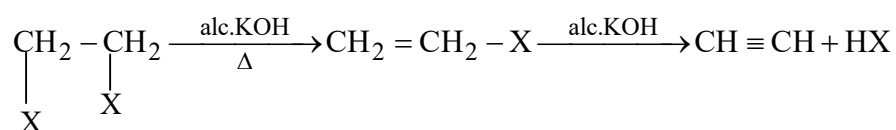
The four half filled orbitals on each C atom merge together to form a single electron cloud in a cylindrical cloud. The C - H bond is passing through the center of the cylinder its bond angle always remains 180° and linear geometry.

Alkynes are less reactive than alkenes due to

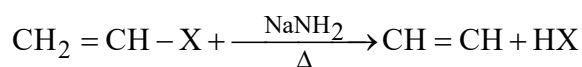
1. the cylindrucal geometry πe^- are not readily available for reactions.
2. Due to the sp hybridised C - atom π i are tightly held by the nucleus thus π i are not readily available.

PREPARATION**1. addition of H_2O on CaC_2** **2. from alkyl halide**

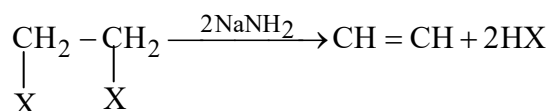
→ from dihalide from vicinal di halides



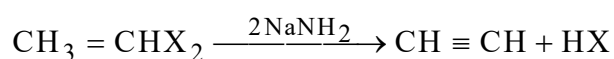
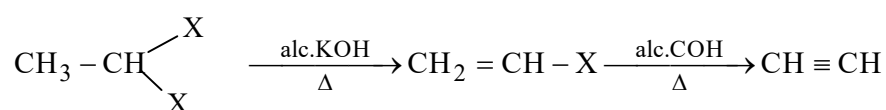
Thus the reaction is very slow hence we can speed up the reaction by using NaNH_2 which is more basic



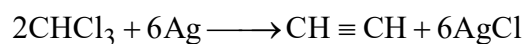
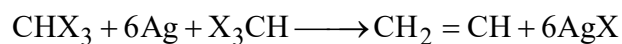
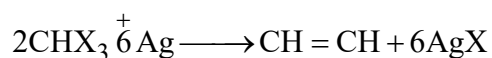
There two step reaction can be concluded into one step using NaNH_2



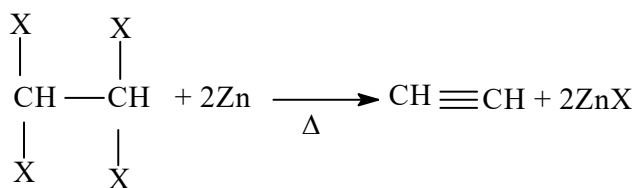
From geminal halide



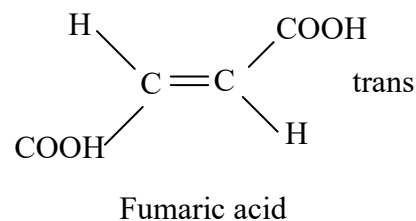
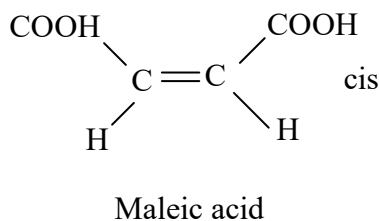
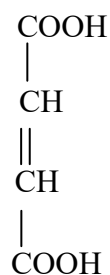
→ From Haloform



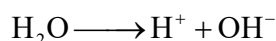
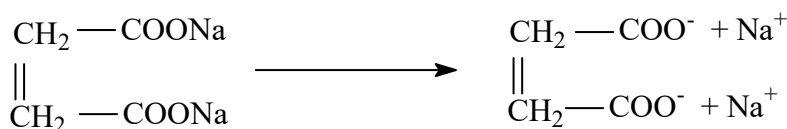
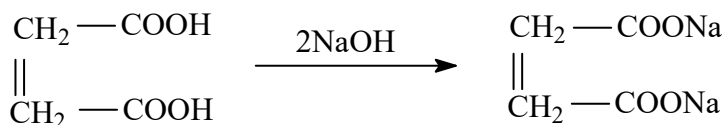
Tetrahalide



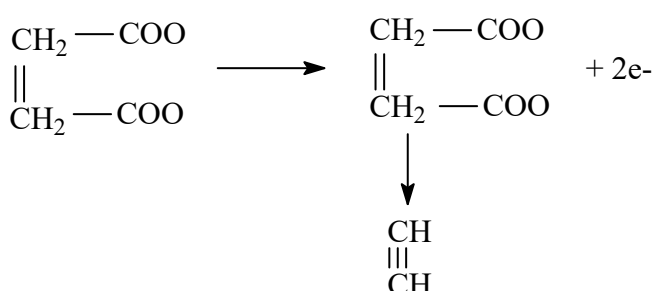
3. From unsaturated dicarboxylic acid



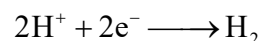
Aqueous Na/K salt of maleic/fumaric acid undergoes Kolbe electrolytic decarboxylation.



At anode



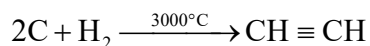
At cathode



4. From C and H

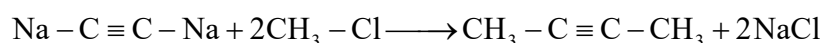
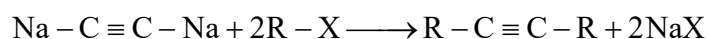
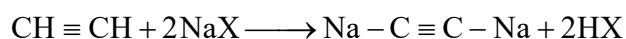
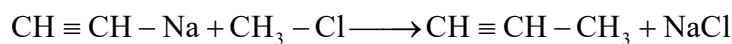
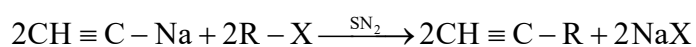
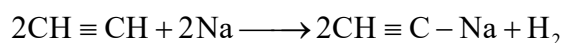
Berthlot method

Passing H_2 gas through an electric arc struck between carbon electrode



5. Preparation of higher alkynes using acetylenes

Acetylene reacts with metals to form metal acetylide. These metal acetylides react with haloalkenes to form higher alkynes.



Physical properties

- Acetylene is a colourless odourless gas.
- First 3 members are gas, next 8 members are liquid, remaining are solids.

Melting and boiling point

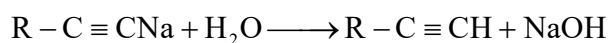
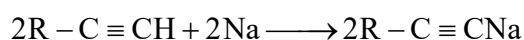
- Melting and boiling points are higher than alkenes due to symmetrical and more polar in nature.
- When size or mol mass is high, boiling point melting point will be high

Solubility

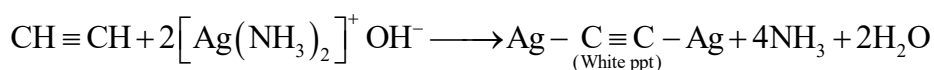
Insoluble in H₂O and soluble in organic solvents

Chemical reactions**1. Acidic character of an alkenes****1. Formation of alkalimetal acetylide**

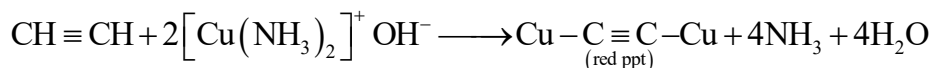
Thermal alkynes react with alkali metals and forms alkali metal acetalides and there acetalides react with H₂O and regenerate acetylene. This shows water is more acidic than acetylene.

**2. Formation of heavy metal acetylide**

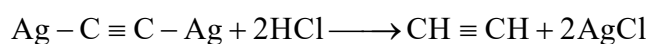
Acetaline react with Tollens reagent $[2Ag(NH_3)_2]^+ OH^-$ ammoniacal silver nitrate form silver acetalide.



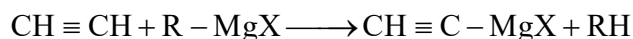
Acetylene reacted with ammoniacal cuprous chloride.



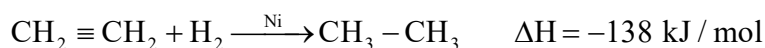
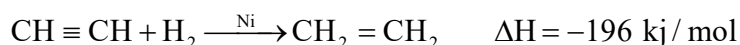
There reagents are used for the detection of terminate alkynes to alkenes.



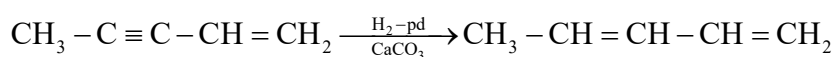
Thus acetylene are weaker than mineral acids

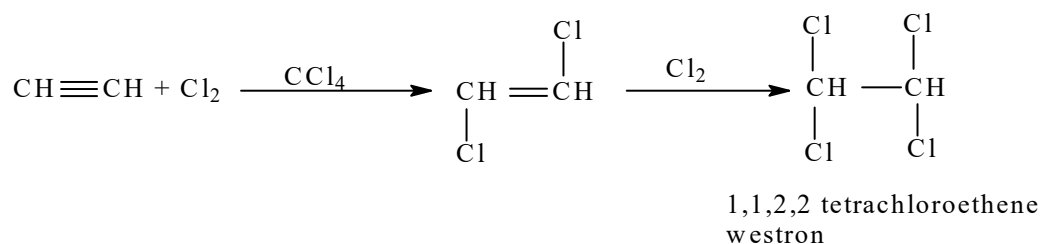
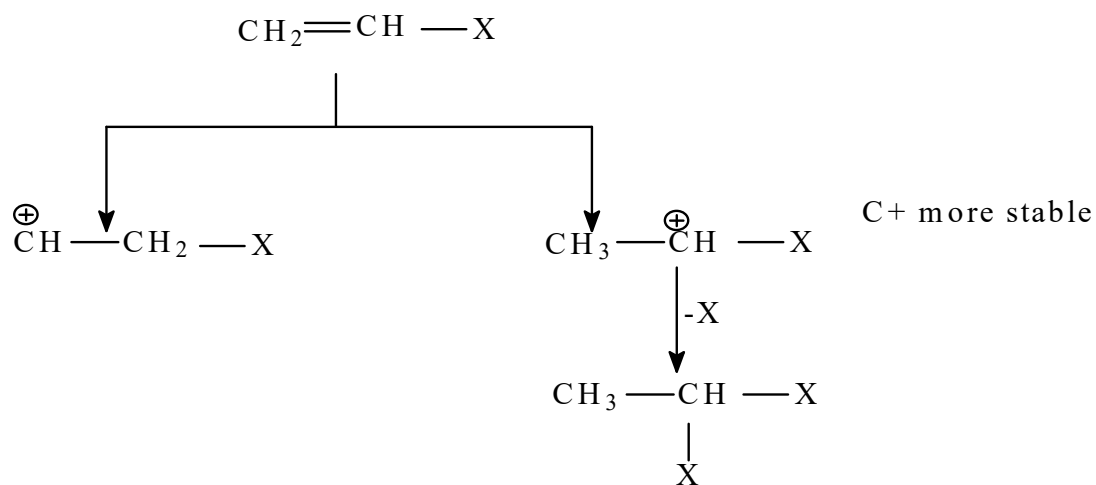
3. Formation of alkynyl grignard reagent**Reason for acidic**

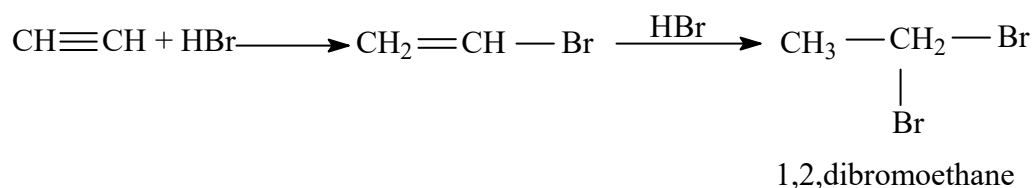
In acetylene C is sp \rightarrow so more s character so highly electronegative. Thus it withdraws electrons from C-H bonds and thus releases H⁺ atom.

Addition reaction**1. Addition of hydrogen**

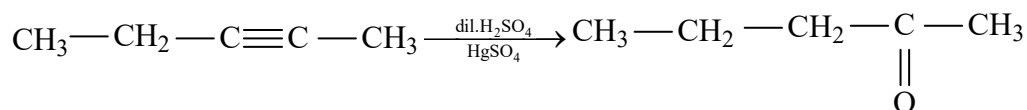
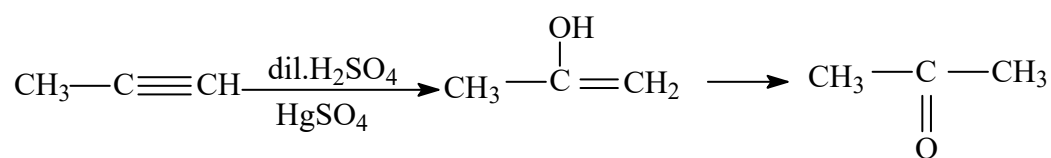
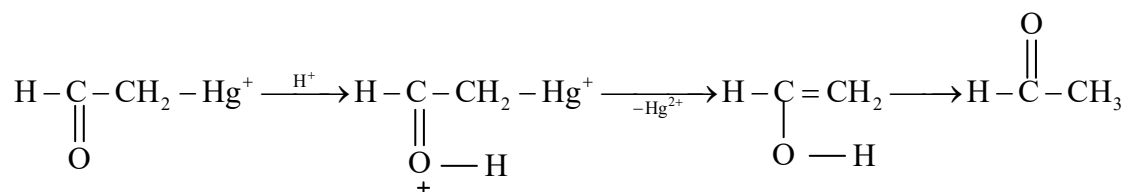
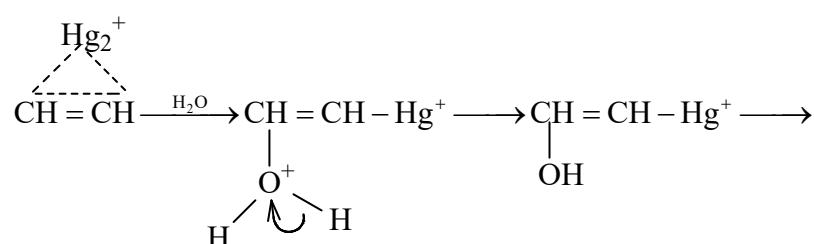
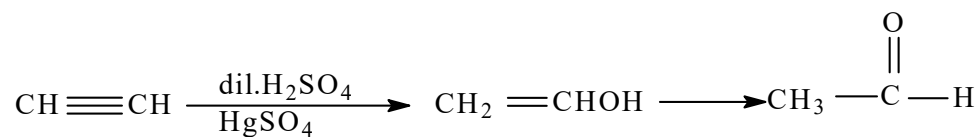
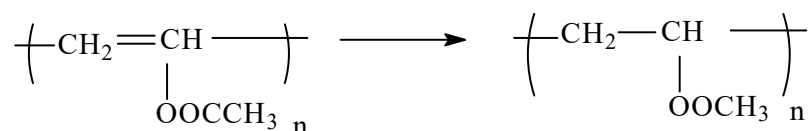
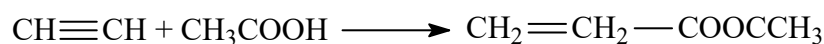
Catalytic hydrogenation of alkynes is more spontaneous then catalytic hydrogenation of alkanes to alkenes.

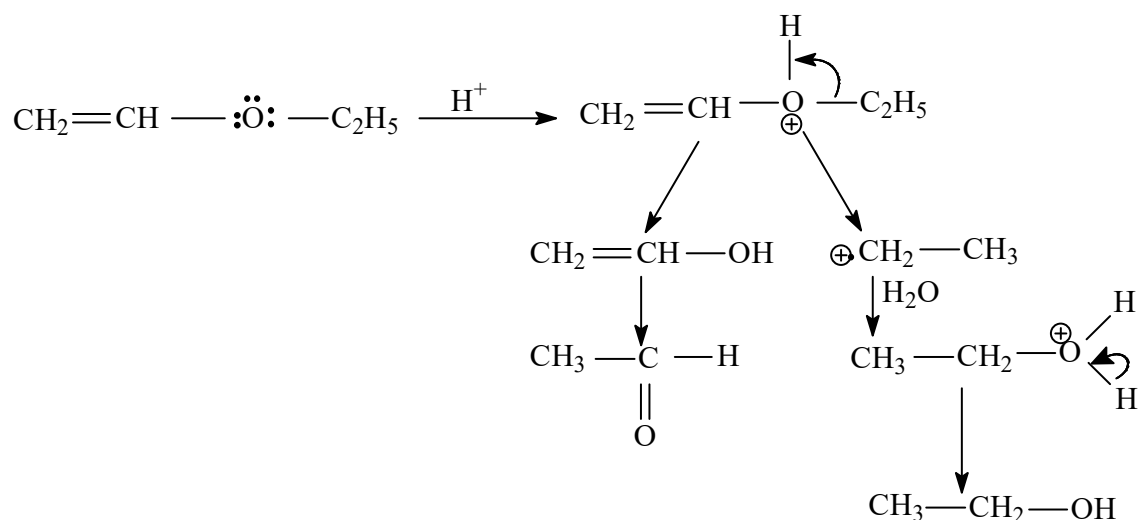
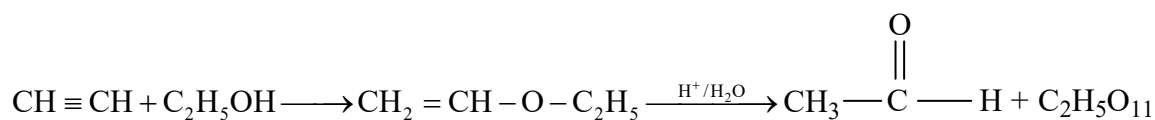


$$\text{CH}=\text{CH} + \text{X}_2 \xrightarrow{\text{CCl}_4} \begin{array}{c} \text{X} \\ | \\ \text{HC}=\text{CH} \\ | \\ \text{X} \end{array} \xrightarrow{\text{X}_2} \begin{array}{c} \text{X} \quad \quad \text{X} \\ \diagdown \quad \diagup \\ \text{CH} - \text{CH} \\ \diagup \quad \diagdown \\ \text{X} \quad \quad \text{X} \end{array}$$

$$\text{CH} \equiv \text{CH} + \text{HX} \longrightarrow \text{CH}_2 = \text{CH} - \text{X} + \text{HX} \longrightarrow \text{CH}_3 - \overset{\text{X}}{\underset{|}{\text{CH}}} - \text{X}$$


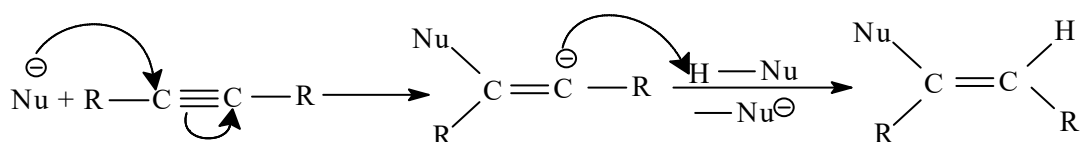
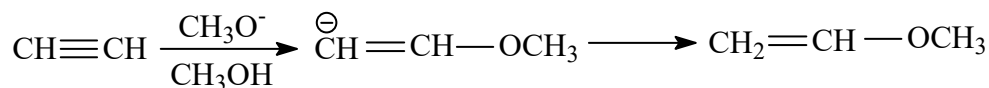
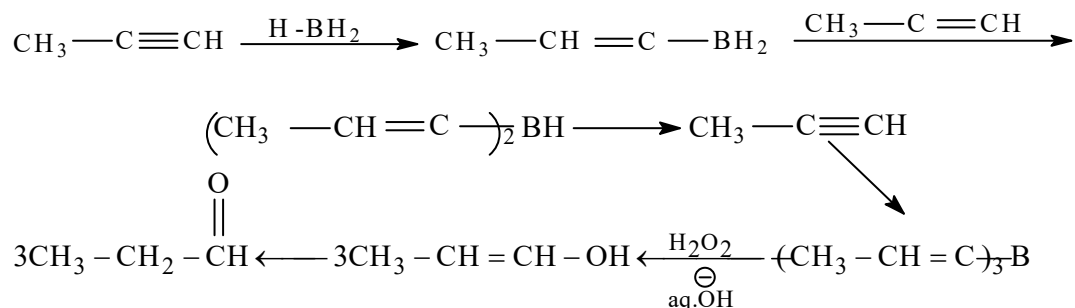
**Addition of H₂O**

Due to low reactivity of alkynes it reacts in presence of mercuric ion.

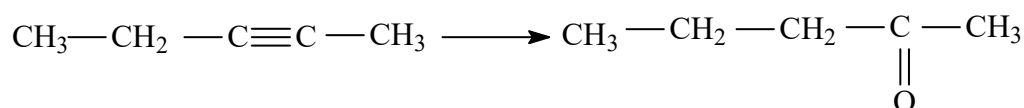
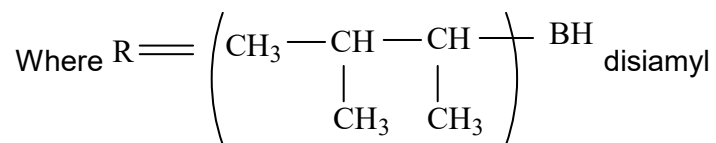
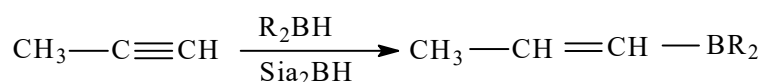
**Addition of acetic acid**

Addition of alcohol**NUCLEOPHILIC ADDITION REACTION**

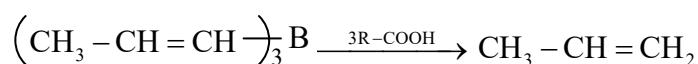
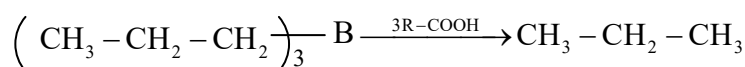
Due to the presence of sp hybridised carbon alkynes can show nucleophilic addition reaction.

**Hydroboration - Oxidation reaction**

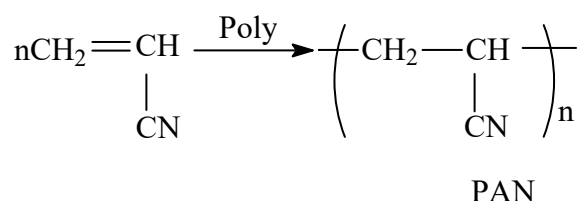
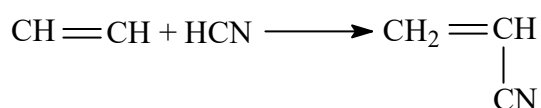
To avoid the multiple addition of alkene bulky boranes like disiamyl borane (1, 2 dimethyl propyl borane) is used



Hydroboration - Alkylation

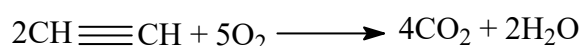


Addition of HCN



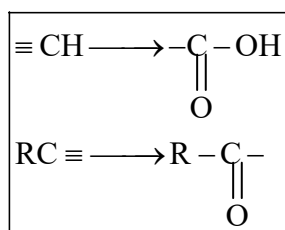
OXIDATION REACTION

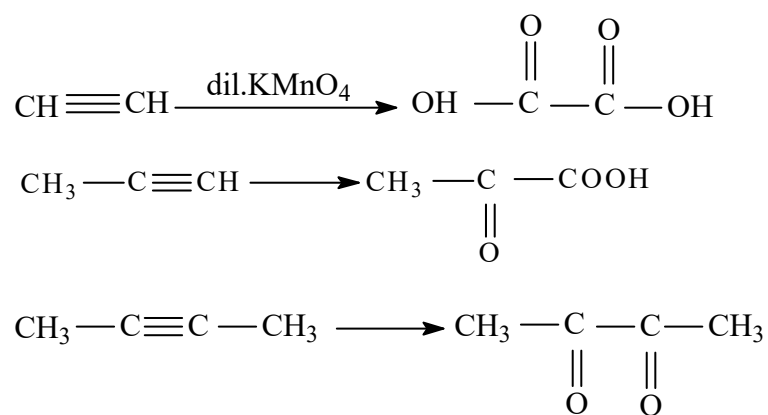
- Complete oxidation



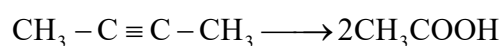
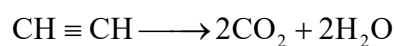
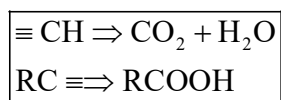
When acetylenes are burnt with air/oxygen under higher pressure they burn to form CO_2 and H_2O atoms with blue flame having higher temperature around 3000°C and this flame is used for cutting and welding metals.

- Oxidation using dilute KMnO_4

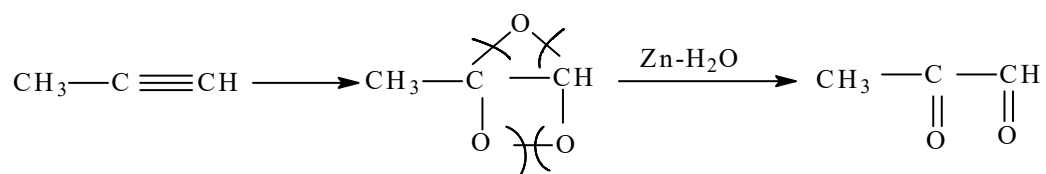
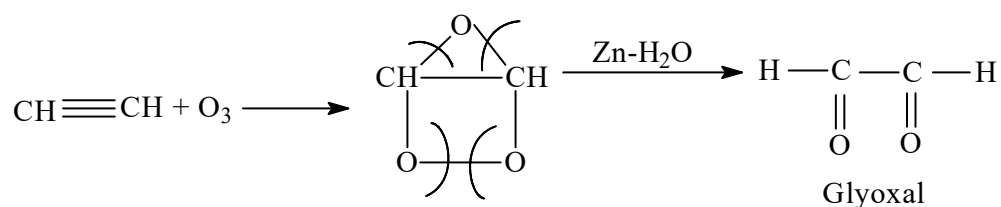




3. Oxidation using acidified alkaline/KMnO₄/K₂Cr₂O₇



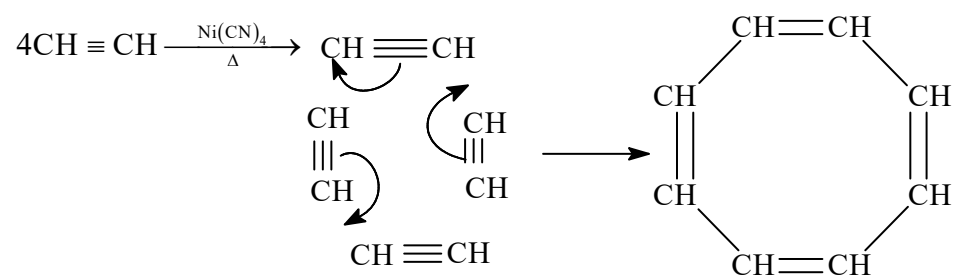
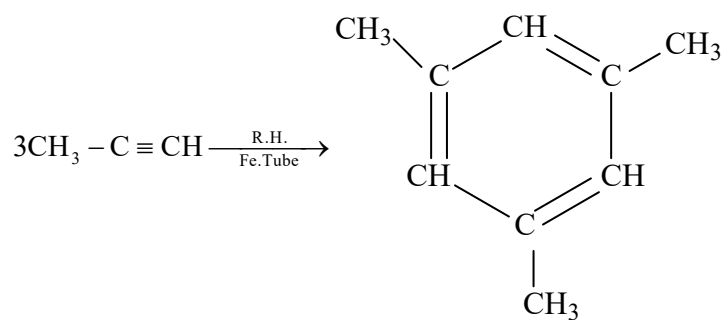
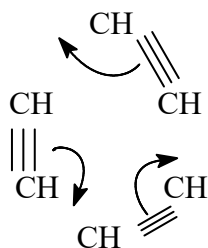
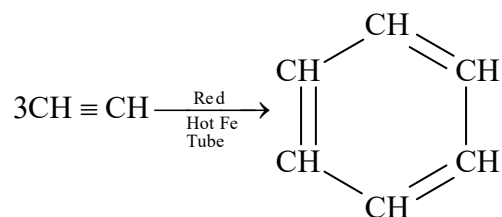
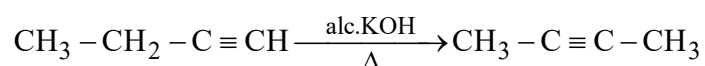
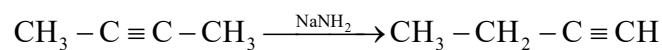
OZONOLYSIS



POLYMERISATION REACTION

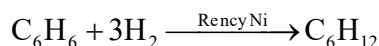
1. Linear polymerisation



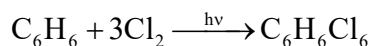
Cyclic polymerisation**ISOMERISATION****BENZENES**

- C_6H_6
- Less than 8H corresponding paraffins

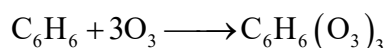
- Highly unsaturated system
 - 8 observations that suggest benzene
1. Benzene and 3 molecules of H on presence of Rency Ni and cyclohexane



2. Benzene add 3 molecule of chlorine and form benzene hexachloride

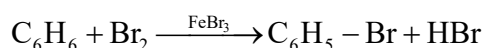


3. Benzene add 3 molecules of ozone and form benzene triozoneide



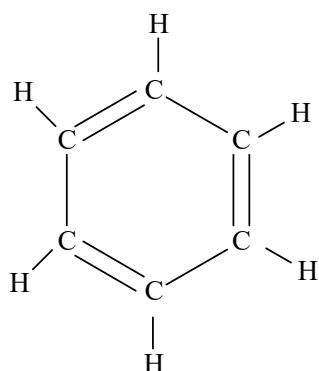
Two observations that suggest benzene shows saturated properties.

1. Benzene resist $\equiv \text{KMnO}_4$ oxidation like alkane
2. Benzene does not decolourise Br_2 in CCl_4 but benzene give monosubstitution product with bromine in presence of FeBr_3



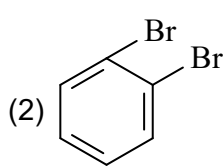
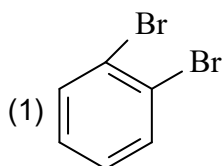
In 1865 Fredrich August Kekule suggest structure of benzene based on his dream

According to Kekule, benzene containing 6C atom join each of alternatively single and double bond and each C atom goin with hydrogen.



Objection against Kekule structure

1. Kekule cannot explain benzene stability against KMnO_4 oxidation
2. Kekule structure explained two type of bond ie single and double bond. But X-ray diffraction shows that benzene have only 1 bond length (ie) 139 pm and is b/w $\text{C}=\text{C}$ and $\text{C}-\text{C}$.
3. Kekule only explained the monosubstitution product but in case of disubstitution product there is two possibilities.



- There is a double bond between C containing two Br

- There is a single bond between C carrying Br

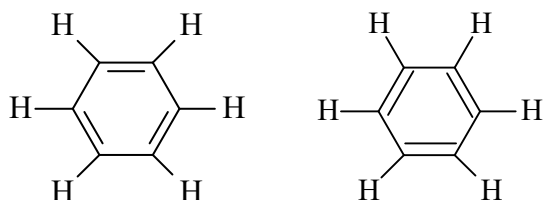
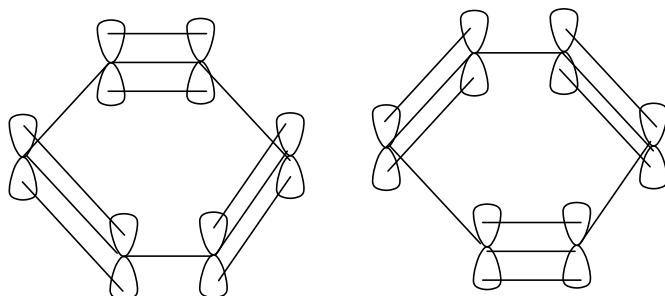
If Kekule's structure was correct there structures exist with two different properties but only one desubstitution product are known. Kekule suggest and equilibrium between there two structures and the position of single and double bond is not fixed

THE STRUCTURE OF BENZENE IS EXPLAINED BY USING

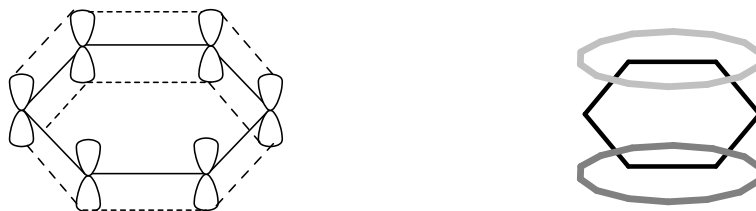
1) MOT

2) Resonance theory

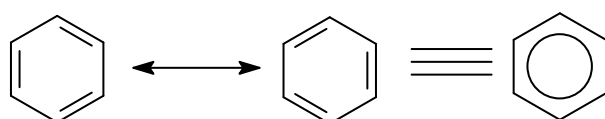
In benzene each C atom form two C–C σ bond with neighbouring two C so there is total 6 C–C σ bond. Each carbon atom forms σ bond with H so there is total 6CH σ bond. The C–C bond angle is 120° so molecule is in planar geometry and each C atom is sp^2 hybridised. Each C atom left on one unhybridised p orbital and there unhybridised p orbitals sidewise overlapping to form there carbon π bond on two ways.

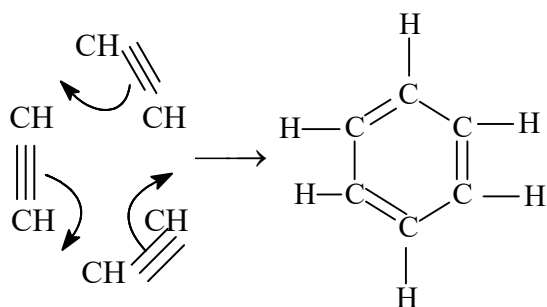
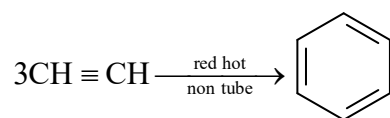
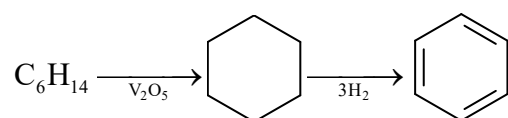
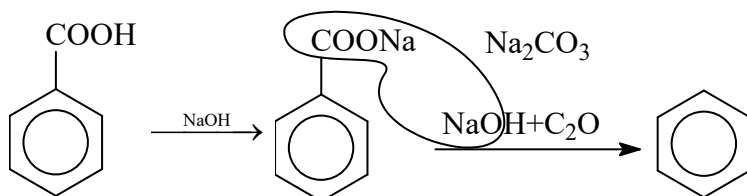
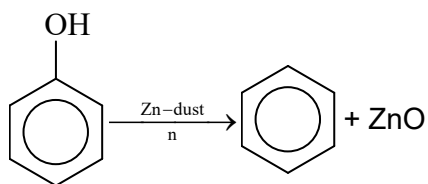
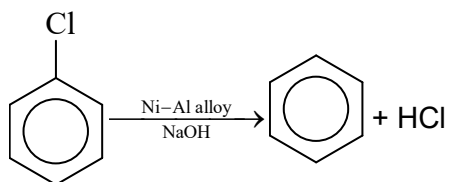


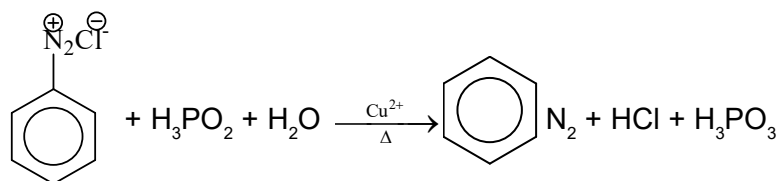
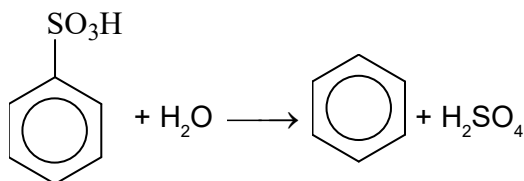
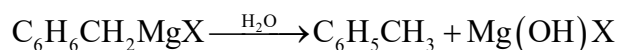
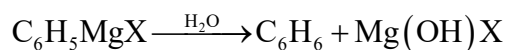
The participation of each π orbitals to form more than one π bond is known as delocalisation and this delocalised π electrons are shown above and below the plane.



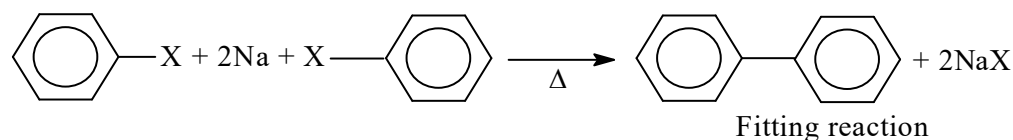
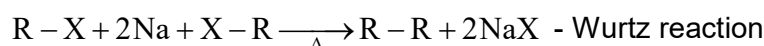
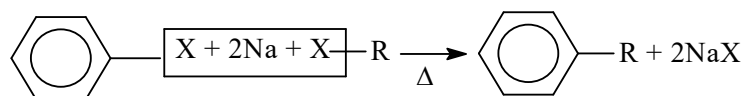
According to resonance theory there π electrons are completely delocalised and there delocalised structures are called canonical structures.



PREPARATION**1. From acetylene****2. From normal hexane****3. From sodium benzoate****4. From phenol****5. From chlorobenzene**

6. From benzene diazonium chloride**7. From benzene sulphonic acid****8. From grignard reagent****9. Wurtz Fittig Reaction**

Haloalkenes react with haloalkenes in presence of disodium in dry ether aralkyl compounds are formed

**PHYSICAL PROPERTIES**

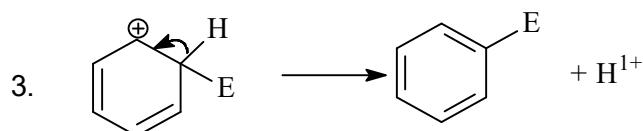
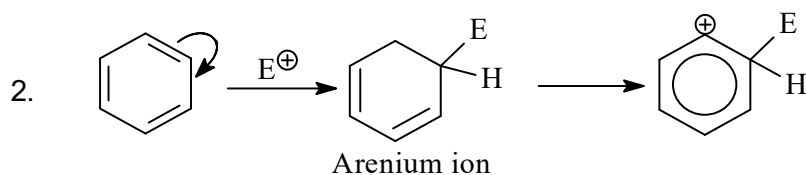
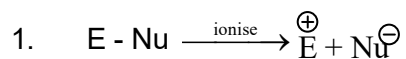
As size increases melting point and boiling point increses. In benzene each π electrons are equally attracted by all carbon atoms so dipole moment is zero.

\therefore So boiling point depends only on size.

- In case of isomeric, P isomers having high melting point than M and O due to symmetric geometry.
- Benzene insoluble in water but soluble in organic solvent

CHEMICAL REACTIONS

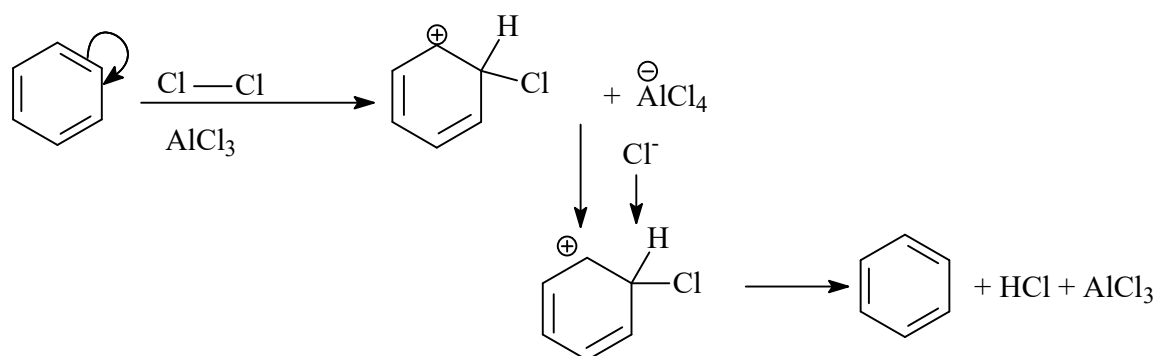
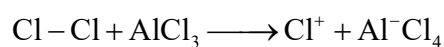
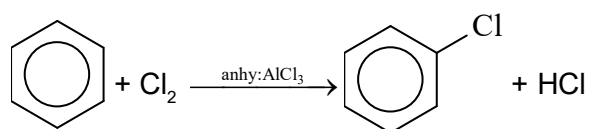
- More reactive than alkanes and less reactive than alkenes and alkynes due to complete delocalisation of electron.

ELECTROPHILIC SUBSTITUTION REACTION

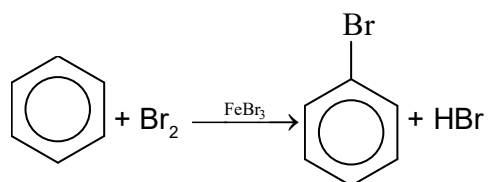
1. Generation of electrophile

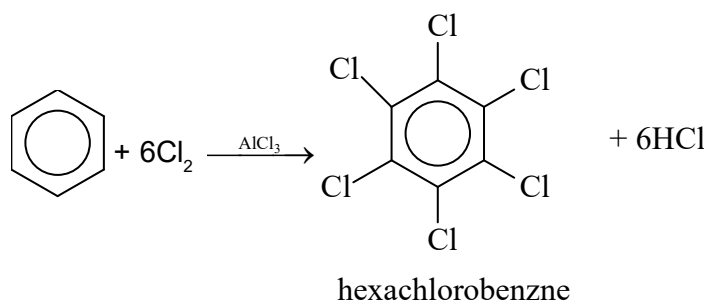
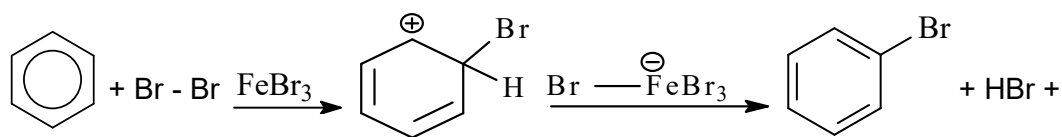
2. Formation of arenium ion

3. Formation of sub product

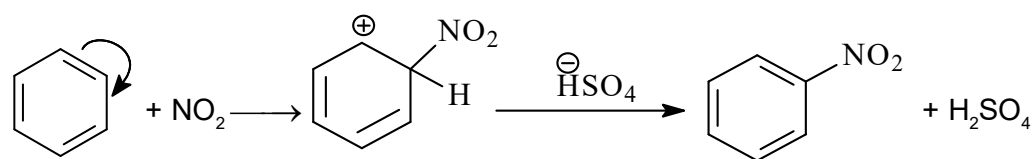
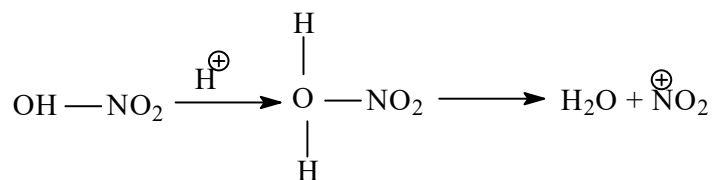
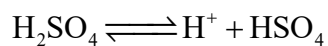
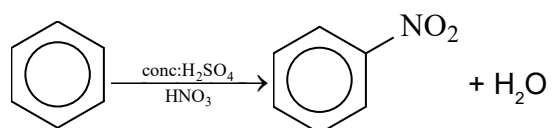
1. HALOGENATION

$AlCl_3$ acts as a halogen carries as well as electrophilic producer. If a halogen carries is present and no light then benzene goes substitution.

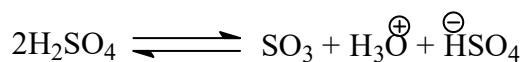
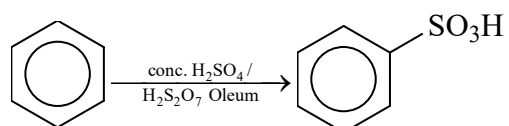


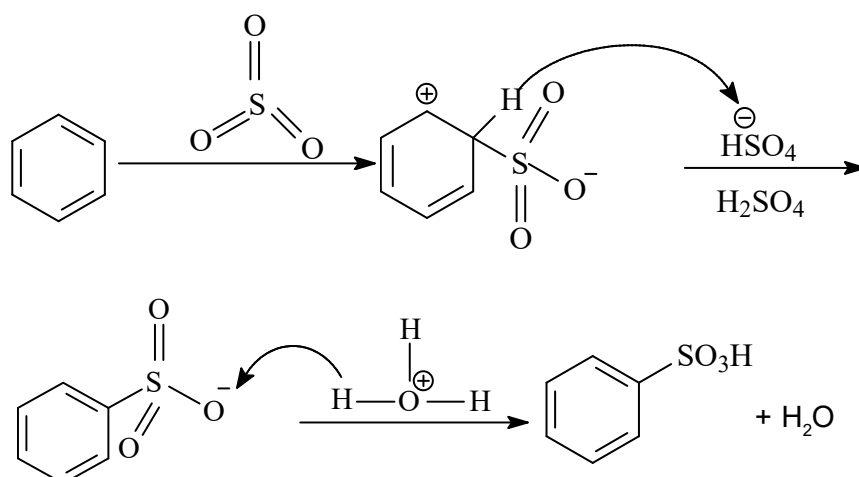


2. Nitration



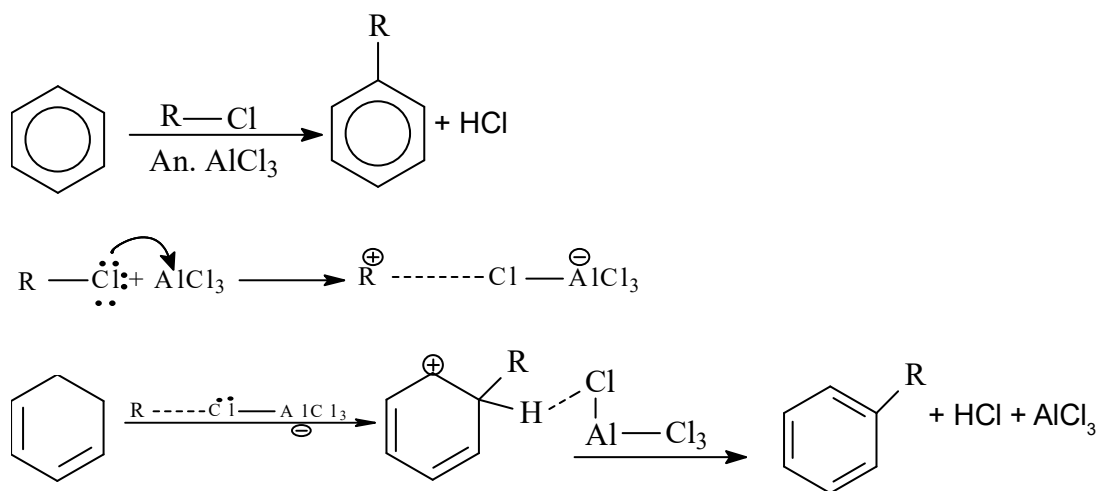
3. Sulphonation



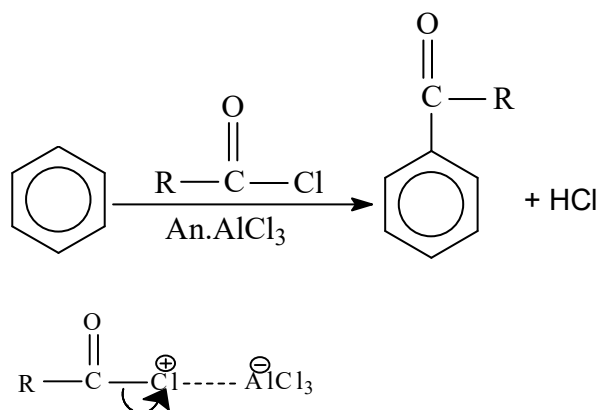


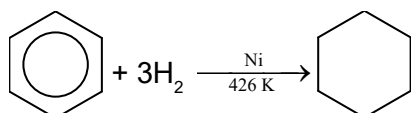
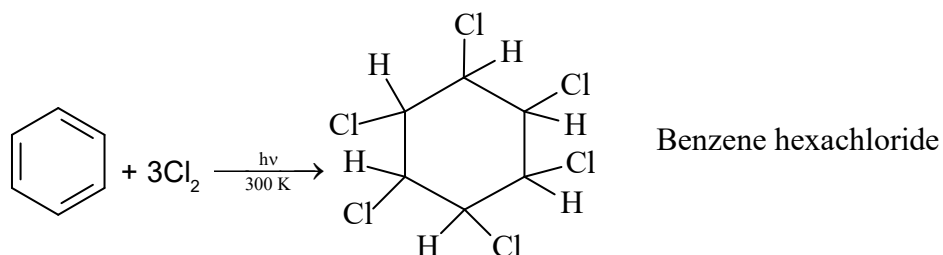
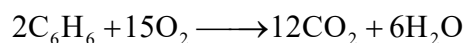
FRIEDEL CRAFT REACTION

1. ALKYLATION

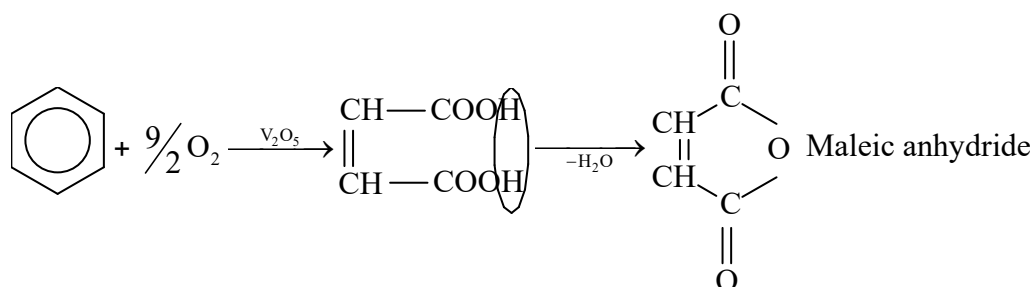


2. ACYLATION

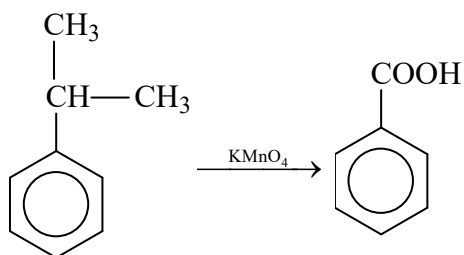
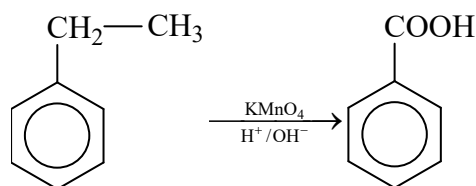
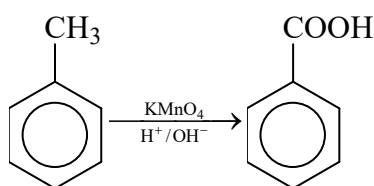


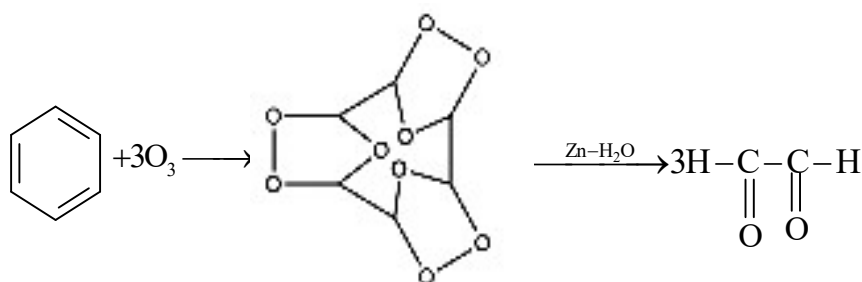
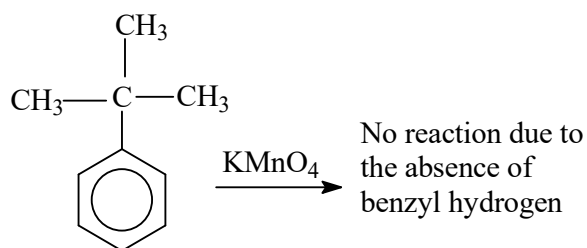
BENZENE ADDITION REACTION**OXIDATION REACTION**

When benzene burn with air/oxygen under pressure, they burn with an yellow sooty flame. This flame indicate presence of higher carbon content in benzene and is used for distinguishing diphetic and aromatic compound.

Incomplete oxidation**Oxidation with KMnO_4**

Benzene resist KMnO_4 oxidation but alkyl benzenes give benzoic acid due to high reactivity of benzylic hydrogen oxidaiton taking place at benzylic carbon.



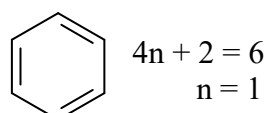


AROMATICITY

According to molecular orbital theory compounds containing $(4n + 2)\pi$ electrons are completely delocalised. Such compounds are called aromatic compounds.

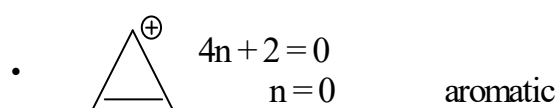
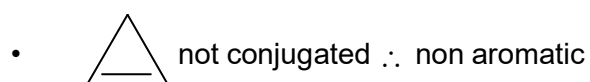
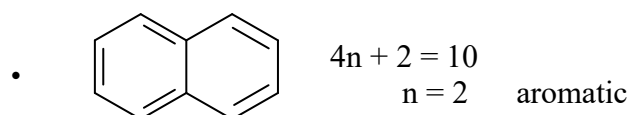
Conditions:

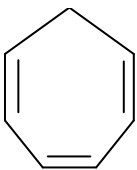
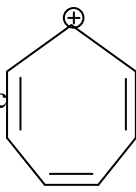
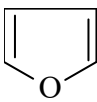
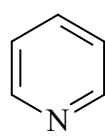
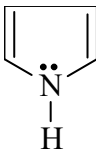

- Cyclic
- Planar
- Conjugated
- Satisfy $(4n + 2)\pi$ rule



Compounds satisfying $4n\pi e^-$ rule \rightarrow antiaromatic

Others are non aromatic



-  Non aromatic
  $n=1$ aromatic
-  aromatic $n = 1$
-  aromatic
  Aromatic $n = 1$
-  antiaromatic

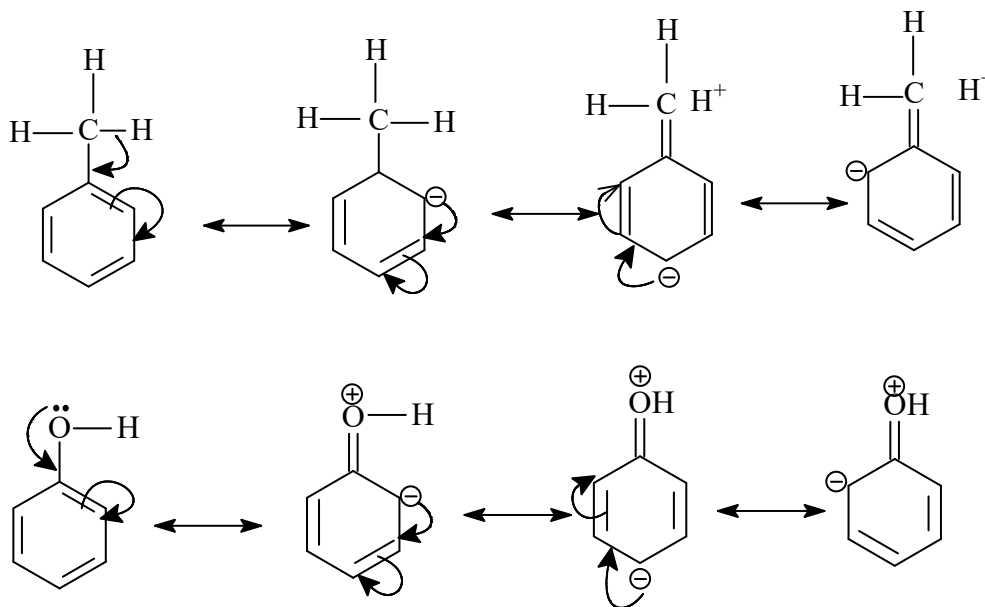
Directive Influence of substituents

It is the ability of atoms ie group to direct the incoming group to a particular position in benzene ring

1. Ortho-para directing group

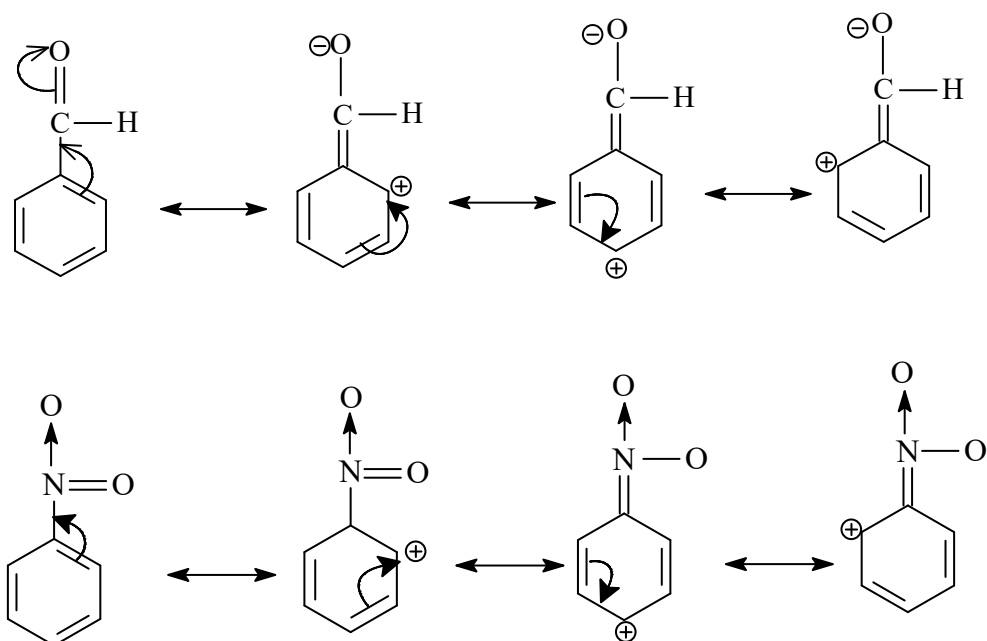
Atoms or group which donate electrons towards benzene ring and increases electron density in o and p positions. These group are ring activating groups.

All electron donating groups are o and p and ring activators.



META DIRECTING GROUP

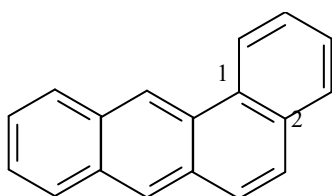
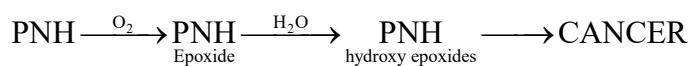
Atoms or group which withdraw electron from benzene rings and decreases electron density at o and p positions. These groups are ring deactivating group. All electron withdrawn groups are meta directing and electron withdrawing.



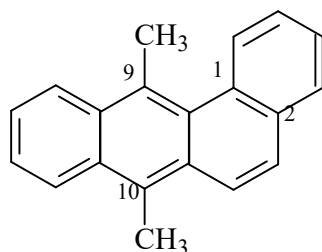
Here N too have / pair but act as M-group because look at the atom near the /-pair if it is high electronegative then it act as M-group.

Polynuclear hydrocarbon

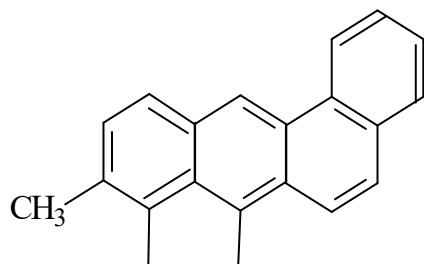
Compounds containing more than one fused benzene ring. These can generate cancer in living tissues so they are known as carcinogenic compound and the nature is called carcinogenicity. The main source of polynuclear hydrocarbon is coal tar.



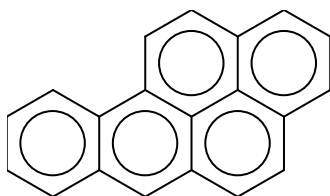
1, 2 benzanthracene



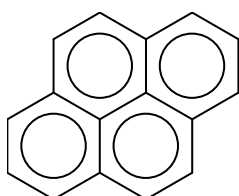
9,10 dimethyl benzanthracene



Methylcholanthrene



Benzpyrene



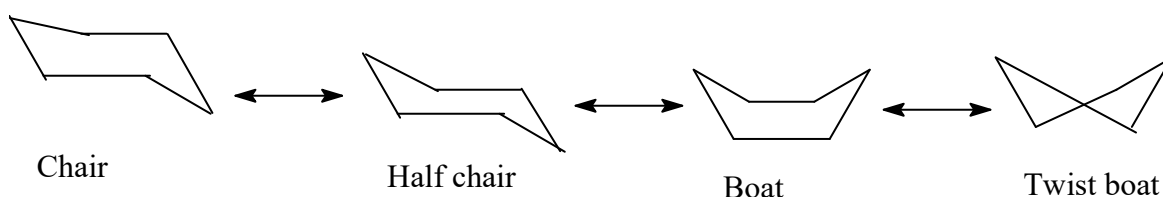
Pyrene

Melting point of alkane

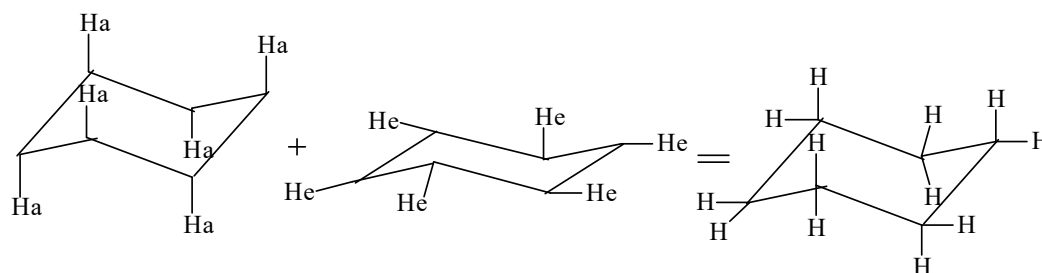
The mp of n - alkanes are not a regular pattern. Alkanes having even number of C atom have higher mp than corresponding alkane with odd no. of carbon ie next & previous. This effect is known as alternating effect / oscillating effect.

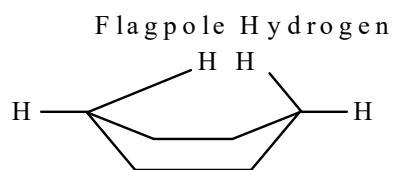
Conformations of cyclohexane

Several 3D shapes that a cyclohexane molecule can assume while maintaining the stability of its chemical bonds cyclohexane ring tend to assume certain non planar conformations and which bond angle closer to $109^\circ.5$ and lower the strain energy.



Two type Hydrogen atoms- Axial and equatorial





Stability order

Chair > Twist boat > Boat > Half Chair

1,2	Cis	1a	2e	
1,2	Trans	1e	2e	MS
		1a	2e	LS
1,3	Cis	1e	3e	MS
		1a	3a	LS
1,3	Trans	1a	3e	
1,4	Cis	1a	He	
1,4	Trans	1e	4e	MS
		1a	4a	LS

- MS– More stable
- LS–Least stable