

CHAPTER - 12

HYDROCARBON

Organic compounds which contains both Carbon and Hydrogen.

Classification

On the basis of carbon skelton, hydrocarbon are mainly two type

- 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 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

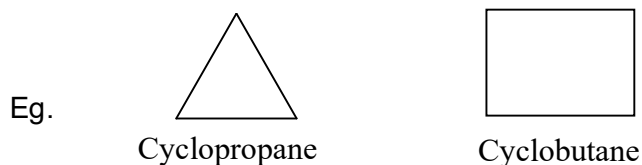
- 1) Homocyclic
- 2) Hetero cyclic

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

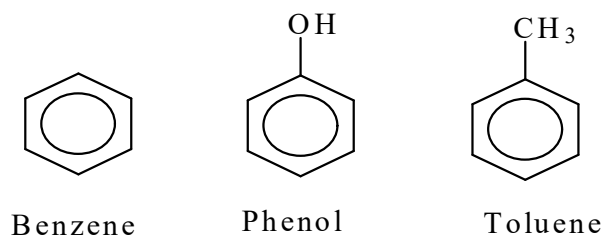
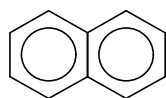
**b) Aromatic compounds**

From the word Aroma (Fragrant smell)

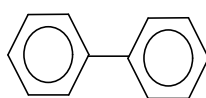
Two types

i) Benzenoid compound

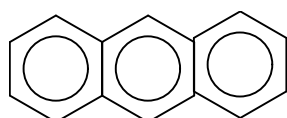
Compounds containing one or more fused or isolated benzene rings.

Fused

Naphthalene

Isolated

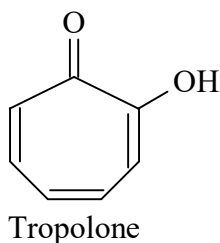
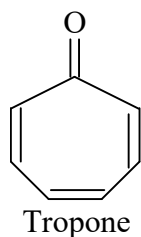
Biphenyl



Anthracene

ii) **Non Benzenoid aromatic compounds**

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

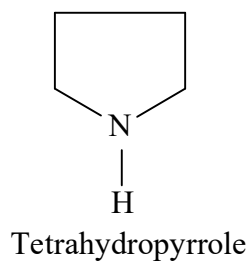
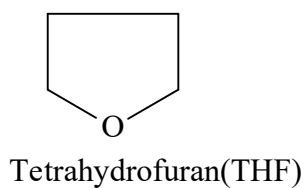


2. Heterocyclic compounds

Rings contains carbon and hetero atoms

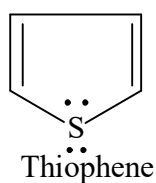
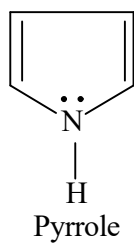
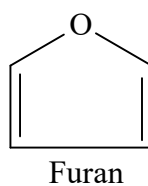
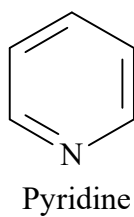
a) Alicyclic heterocyclic

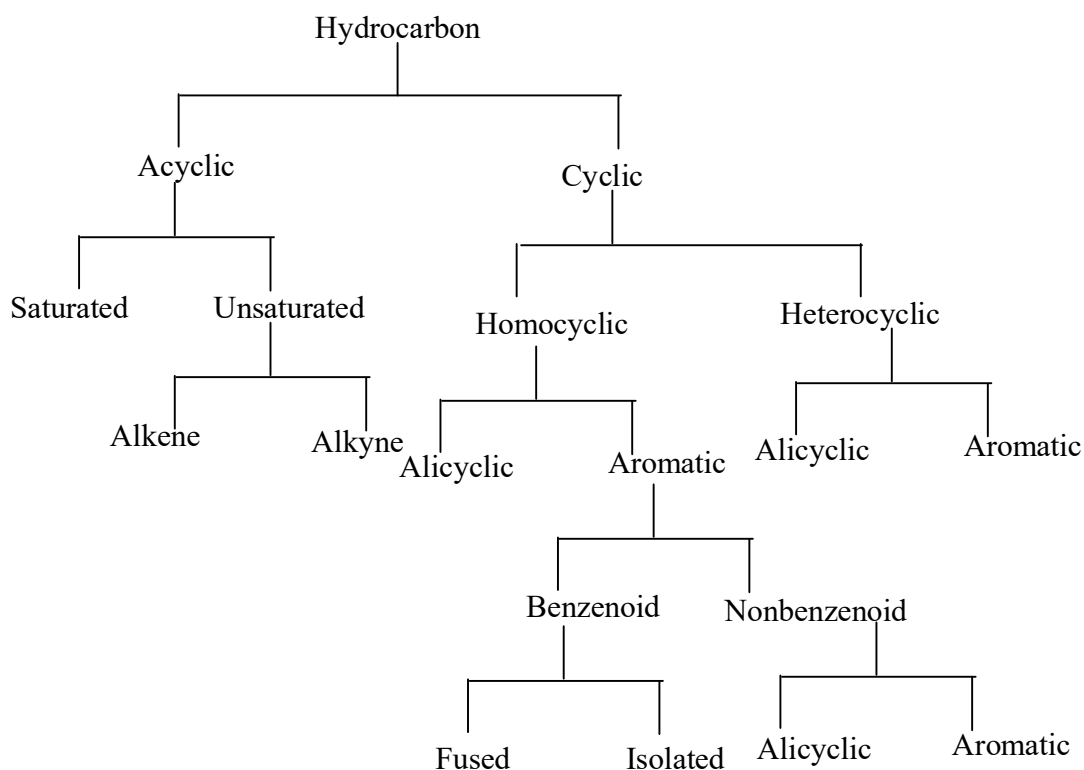
Alicyclic compounds contains hetero atoms



b) Aromatic hetero cyclic

Aromatic compounds containing heteroatoms





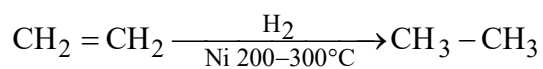
I. Alkanes / Paraffins

General formula C_nH_{2n+2}

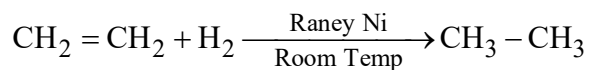
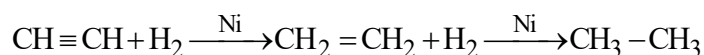
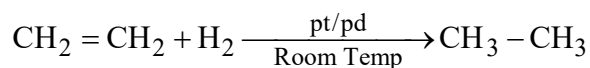
Preparation

1) From unsaturated hydrocarbon

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



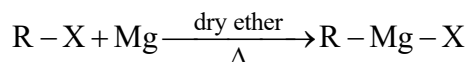
Reaction known as sabatier & senderen reaction



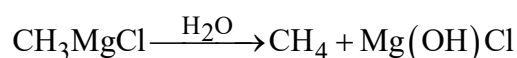
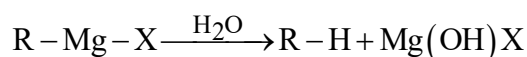
2) From alkyl halide

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 presence of dry ether.

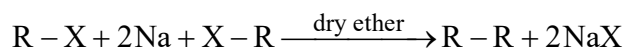


$R-Mg-X$ is a source of carbanion so reacts with any H^+ medium to form Hydrocarbon

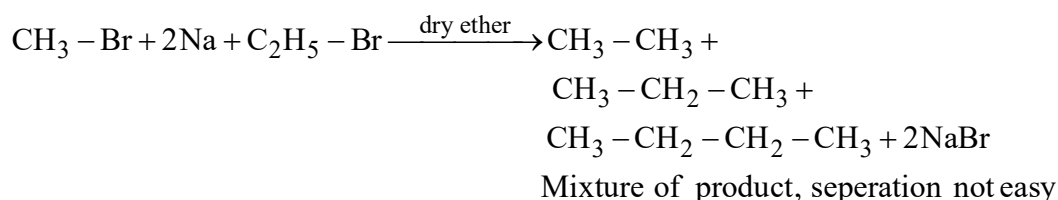


b) Wurtz reaction

An ether solution of alkylhalide is treated with sodium to 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



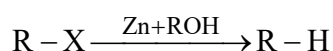
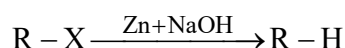
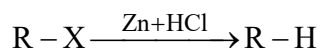
Limitation : 1) Methane cannot be obtained

2) Tertiary alkylhalide does not give the reaction

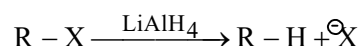
3) Only for the preparation of symmetrical alkanes.

e) Reduction of alkyl halide

Haloalkane reacts with metals dissolving in acid / base / alcohol

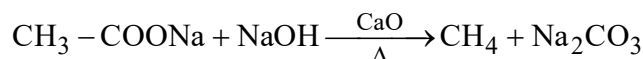
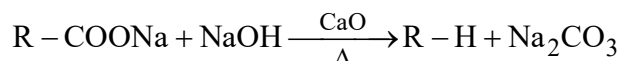


Haloalkane reduces with strong reducing agent $LiAlH_4$, R-H is formed



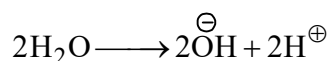
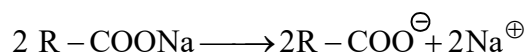
- 3) From carboxylic acid
a) using sodalime

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

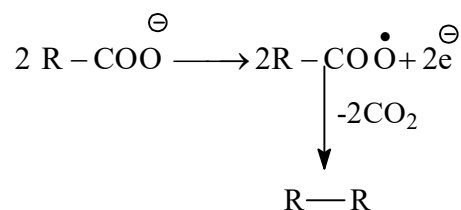


- b) Kolbe's electrolytic decarboxylation

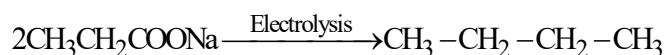
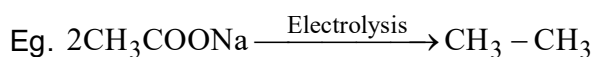
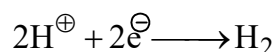
Aqueous sodium / potassium salt of mono carboxylic acid electrolysis, hydrocarbons are formed having twice the number of carbon atom in the parent alkyl group



At Anode



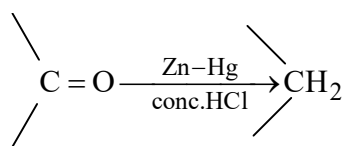
At Cathode



- 4) Reduction of carbonyl compounds

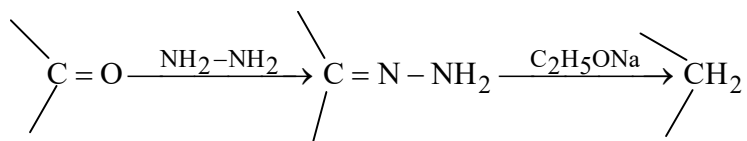
- a) Clemmensen reduction

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



Properties

1) Physical properties

1st four members (C₁-C₄) - colourless, odourless, gases

Next 13 (C₅-C₁₇) - colourless, odourless, liquids

From C₁₇ - colourless, odourless, solids

• **Boiling points :**

Bp of n - alkanes increases regularly with increasing number of carbon atoms.

In case of isomeric alkanes branching increases bp decreases

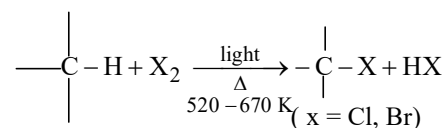
Chemical Reactions

I. Substitution reaction

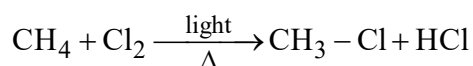
Replacement of H by another atoms / group

i) Halogenation

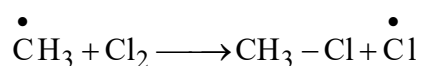
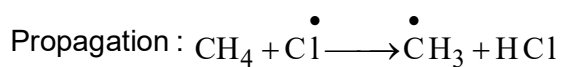
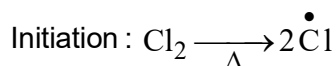
Replacement of H by halogen

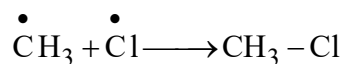
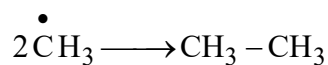
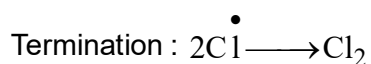


Halogenation reaction depends on nature halogen and type of H

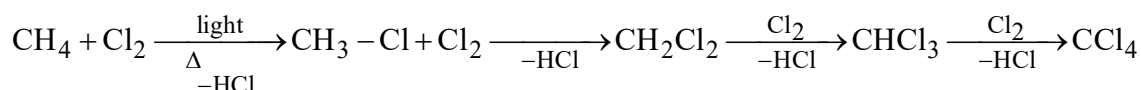


Mechanism



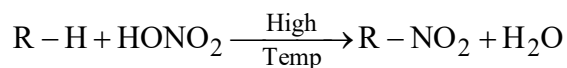


In presence of excess Cl_2 all hydrogens are replaced by Cl,

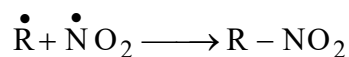
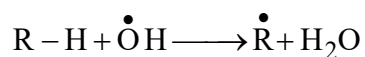
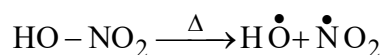


ii) Nitration

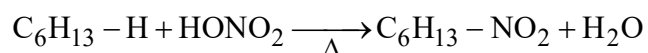
H atom replaced by nitro group



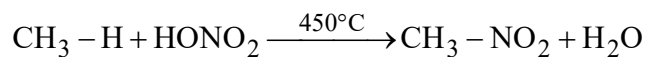
Mechanism



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



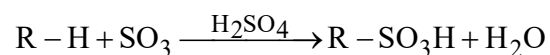
Mixture of vapour of an alkane and nitric acid is heated at $400^\circ - 500^\circ\text{C}$ nitro alkane is formed. This method is known as vapour phase nitration.

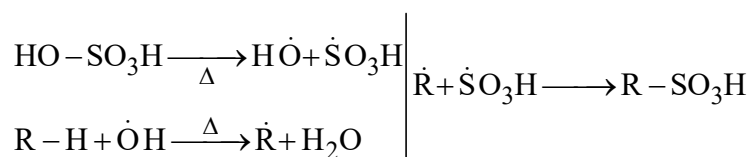


iii) Sulphonation

H atom replaced by SO_3H group

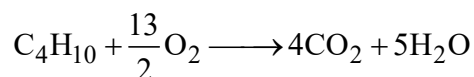
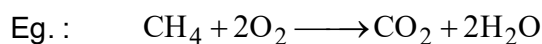
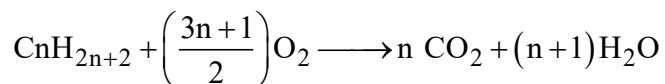
Higher alkanes contains six or more carbon atom heated with fuming H_2SO_4 at about 400°C





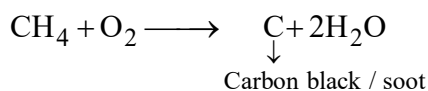
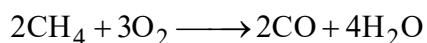
II. Oxidation reaction

a) Complete oxidation / combustion reaction

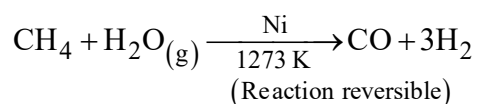


b) Incomplete oxidation

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

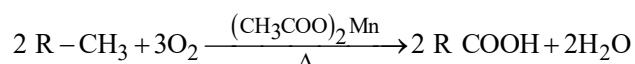
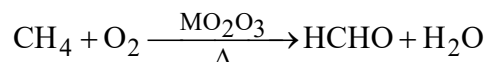
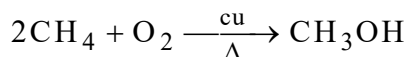


Carbon black is used for the preparation of black ink, paint etc. When methane is react with super-heated steam in presence of Ni at high temp, water gas is formed

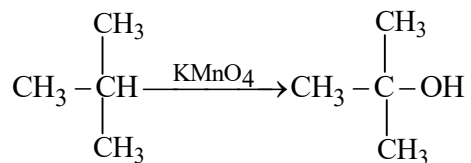


c) Catalytic oxidation

Different catalyst give different product

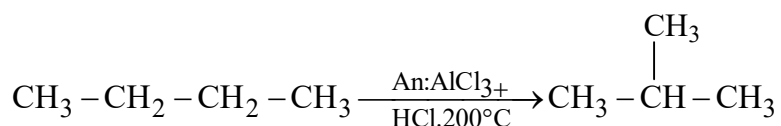


Alkanes having 3°H are oxidised by oxidising agents to corresponding alcohol.



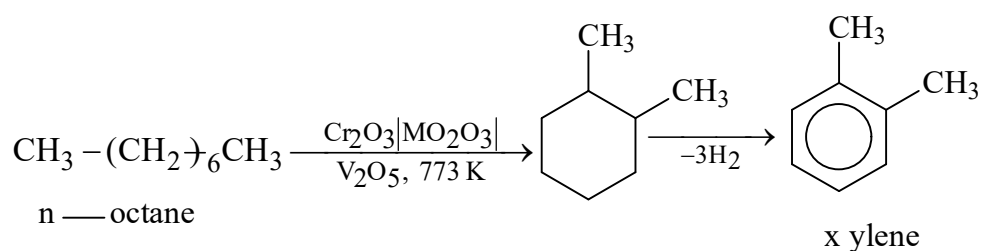
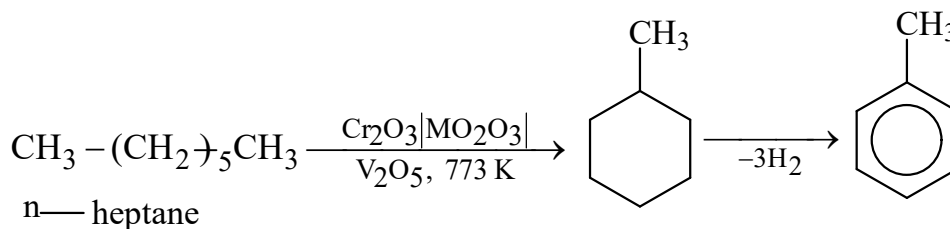
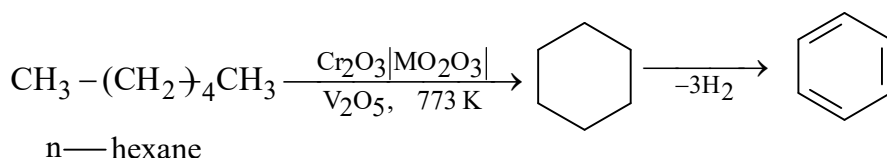
III. Isomerisation

Alkanes when heated in presence of an : AlCl_3 and HCl at about 200°C and 35 atm



IV. Aromatisation

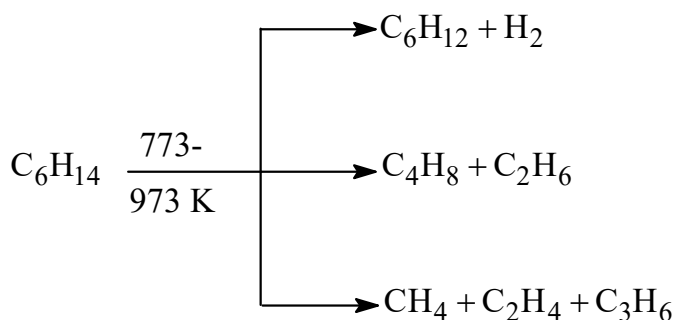
Alkanes contain 6 - 10 carbon atom are heated with metallic oxides and followed by dehydrogenation to form aromatic compounds



V. Pyrolysis

Decomposition of a compound by applying heat is known as pyrolysis

Pyrolysis of alkane to lower members is known as thermal cracking

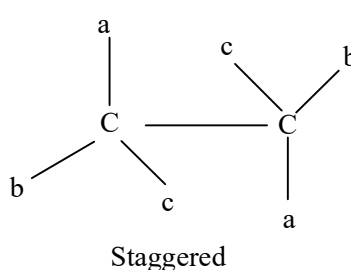
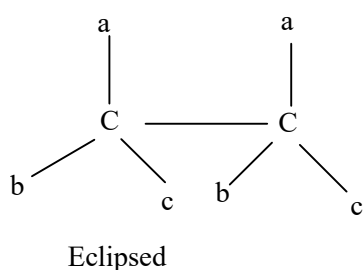


Isomerism in alkanes

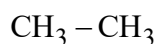
Conformational isomerism

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

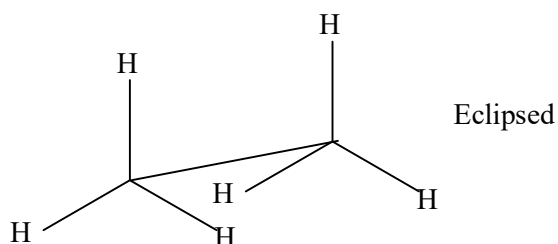
- It arises due to the free rotation around a C-C
- The energy of arrangement is max when bond pairs are very close to each other, such forms are called eclipsed conformation (Least stable)
- The energy of arrangement is min when bond pairs are far apart, such forms are called staggered conformation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



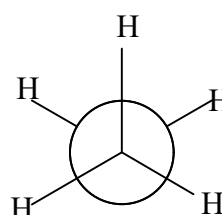
Conformations of ethane

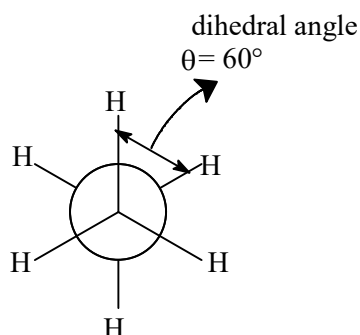
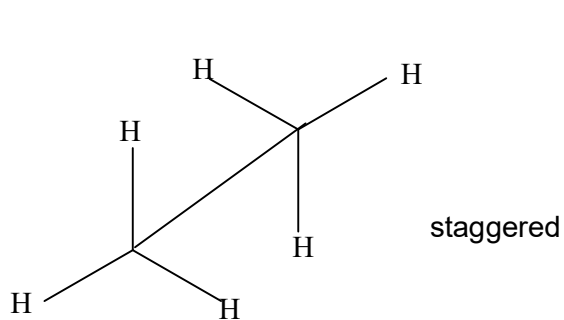


1) Saw - House projection

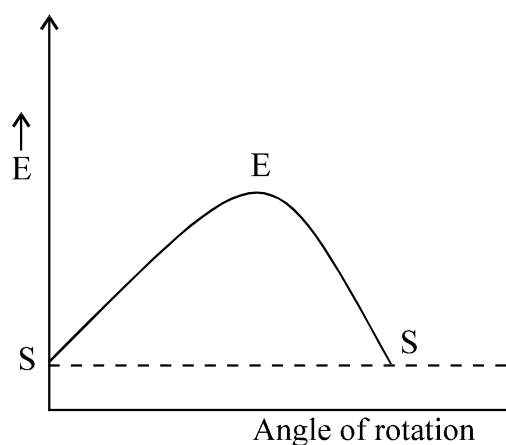


2) New - man projection





Energy level diagram



Conformations of butane

Alkene

General formula C_nH_{2n}

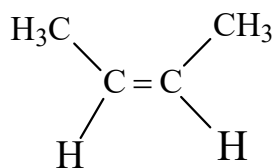
Isomerism in alkene

Geometrical isomerism

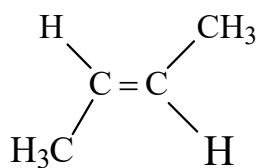
Two compounds having same molecular formula but different spatial arrangement around a carbon - carbon double bond. Such isomers are called geometrical isomers and the phenomenon is known as geometrical isomerism.

- 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

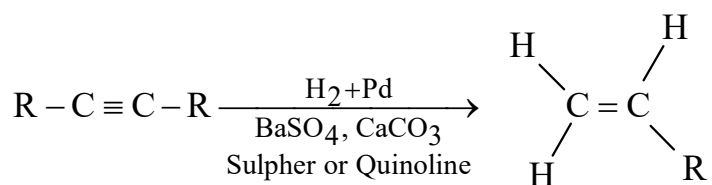
Conditions :

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

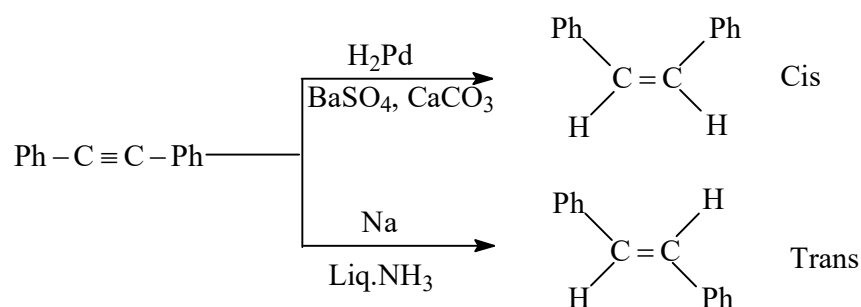
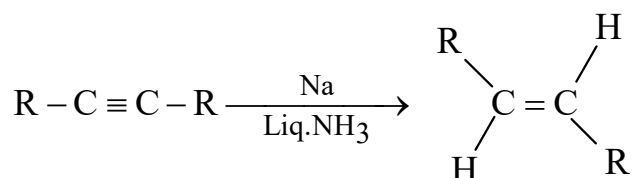
Preparation

I. From alkynes

Alkynes undergo partial reduction to form alkenes, Alkynes reduced with H_2 in presence of Pd over CaCO_3 or BaSO_4 with added lead acetate and quinoline - is known as Lindlar catalyst

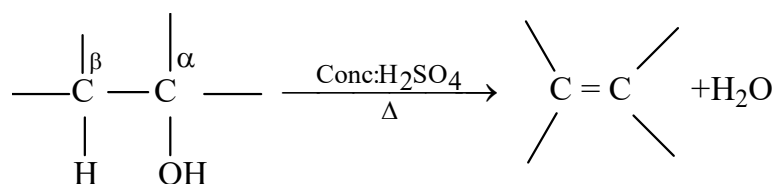


Alkynes on reduced with Li or Na in NH_3 give trans alkene: Birch reduction



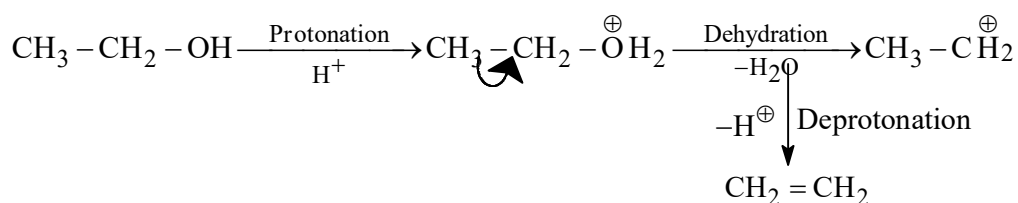
II From monohydric alcohols

Alcohols undergo dehydration in presence of protonic acid (conc. H_2SO_4 /Conc : H_3PO_4) or heated with catalyst such as alumina or an. ZnCl_2 give alkenes

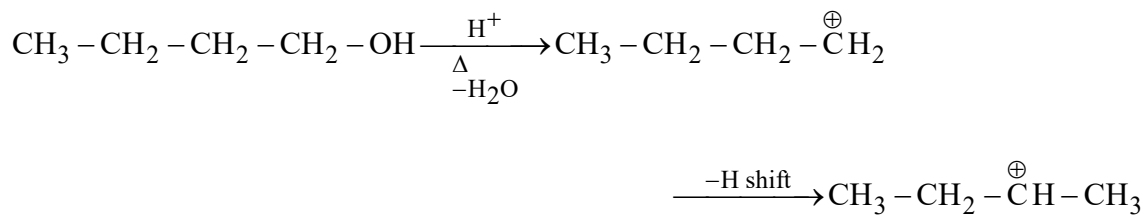
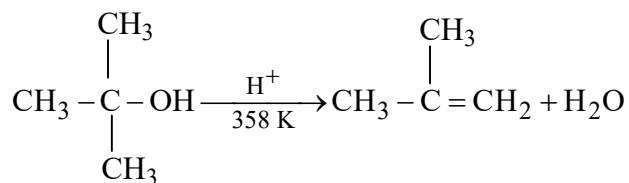
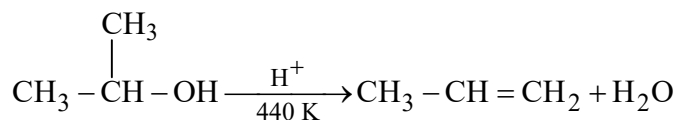
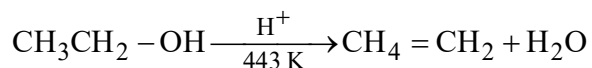


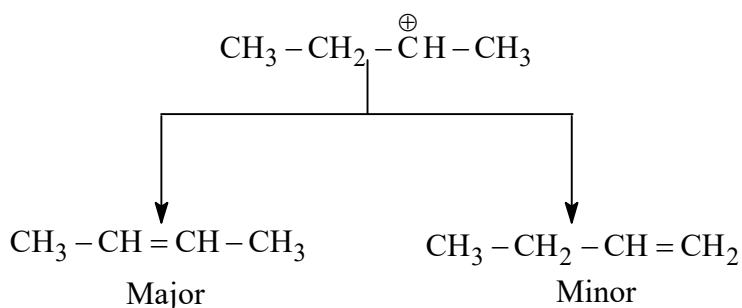
β - Elimination

Mechanism



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

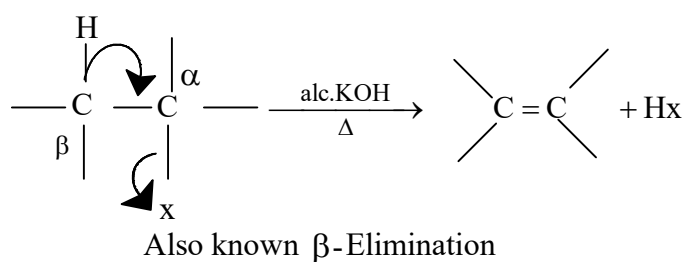




In this case more than one product is formed, major product is determined by Saytzeff's rule i.e. more substituted alkenes are the major product.

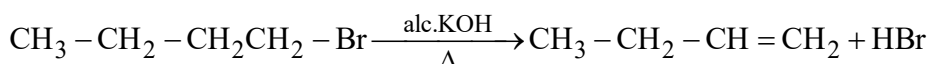
III. From alkylhalide

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

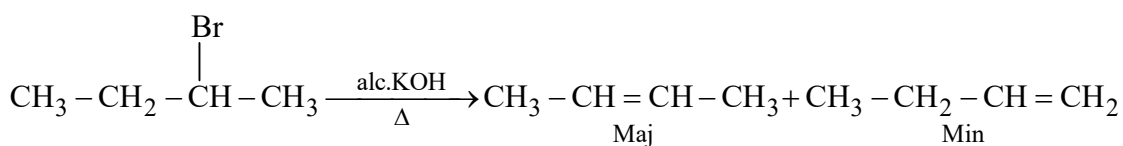


The leaving nature of halogens $\text{F} < \text{Cl} < \text{Br} < \text{I}$ order of reactivity of R-X $3^\circ > 2^\circ > 1^\circ$

Reaction follows E^2 Mechanism.

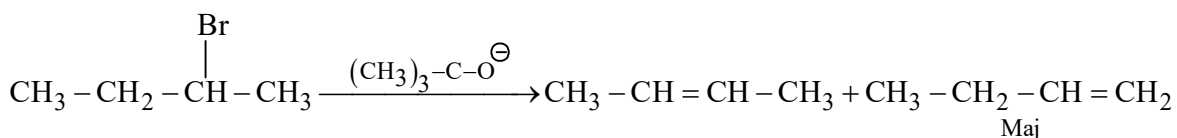


In case of terminal halide, terminal alkenes are formed



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

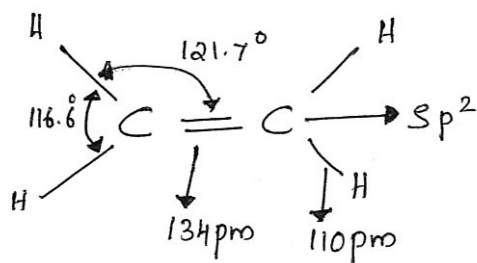
If the elimination is carried out in the presence of bulky bases, Hoffmann's elimination follows



E^2 elimination depends on periplanar geometry two types of periplanar

Properties

Physical properties



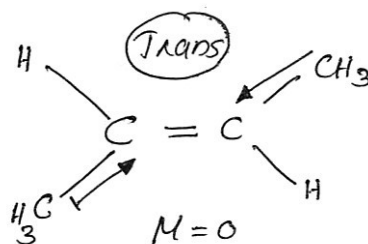
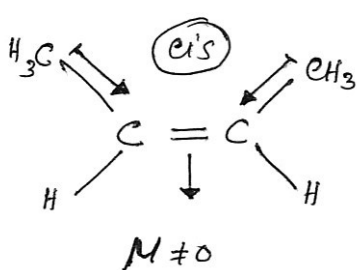
First 3 members are gases

Next 14 members are liquids

Others are solids

Melting and Boiling points

Molecular mass increases mp and bp increases



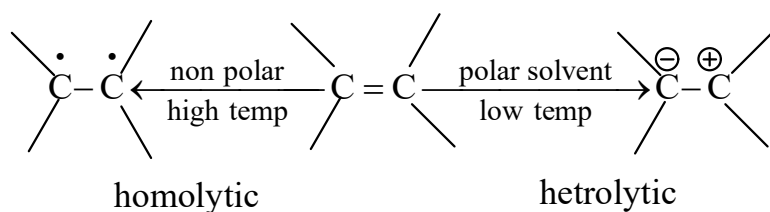
Cis isomer having more bp than trans due to more polar nature

Trans isomer having higher mp than cis due to more symmetry.

CHEMICAL REACTIONS

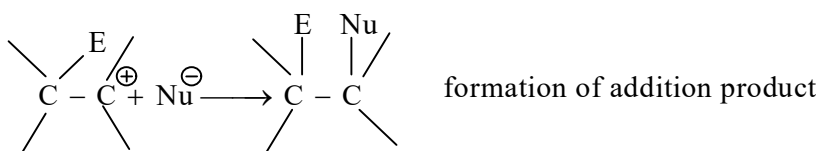
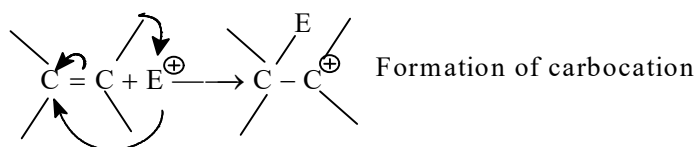
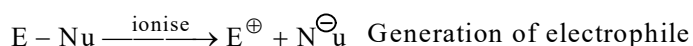
The π electrons in alkenes are loosely held and easily polarisable in presence of a polar solvent at low temperature heterolytic cleavage take place and favour ionic mechanism.

In presence of a non polar solvents at high tempetrature homolytic cleavage takes place and favour free radical mechanism



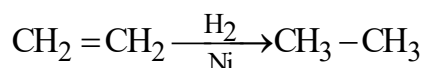
IONIC MECHANISM

Alkenes show electrophilic addition reaction through 3 steps

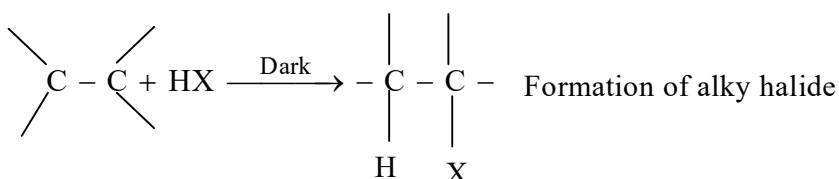


IMPORTANT ADDITION REACTION

1) Addition of Hydrogen



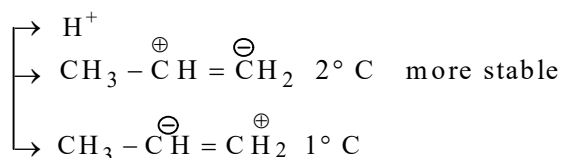
2) Addition of hydrogen halide



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"

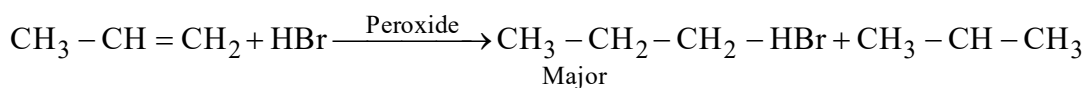
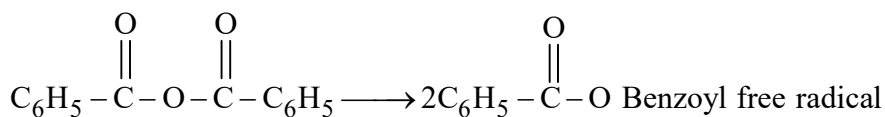
The rule states that addition of unsymmetrical reagent to an unsymmetrical alkene the negative part of the adding molecule attached to the carbon containing lesser number of H-atom

Proof for Markovnikov rule:

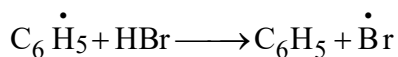
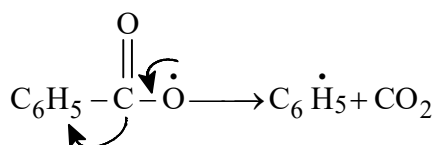
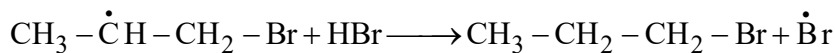
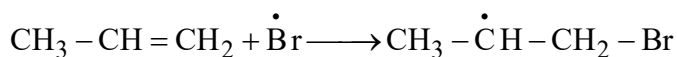
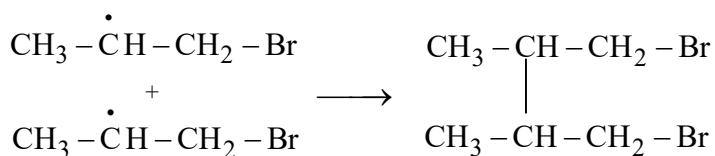
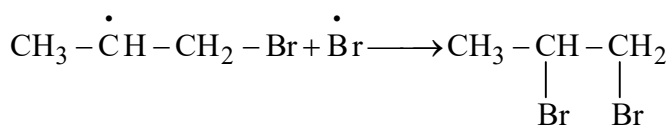
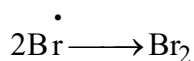


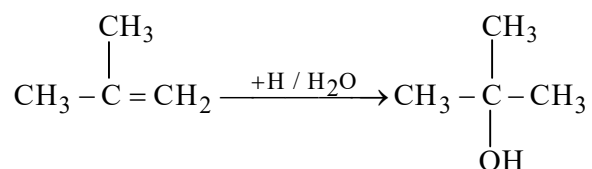
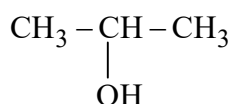
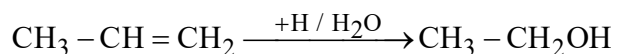
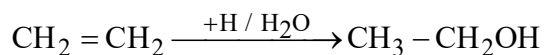
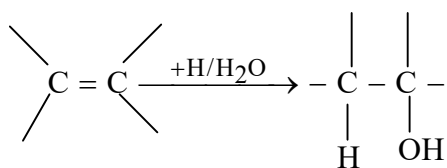
$2^\circ C$ is more stable hence it forms the major one. This reaction occurs due to electromeric shift. The reason for the repulsion of electrons to the next is due to +I effect of methyl thus providing a pushing force.

• 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 / Peroxide Effect / Kharasch Effect.

**Initiation**

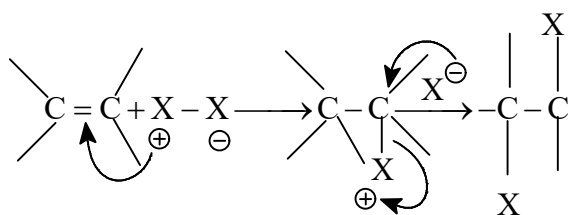
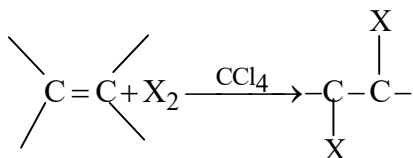
Benzoyl peroxide

**Propagation****Termination****3) Addition of H₂O****1. Acidic Hydration of Alkane**

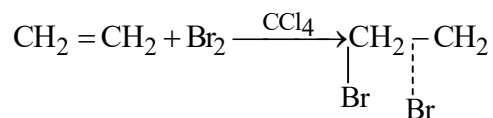


ADDITION OF HALOGEN

Formation of vicinal halide



These are antiaddition so forming vicinal dihalides

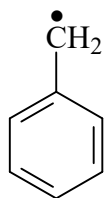
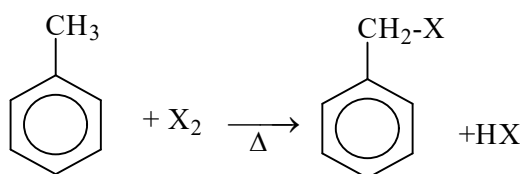
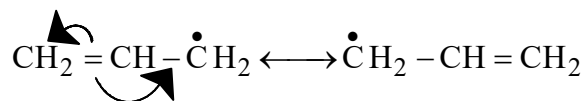
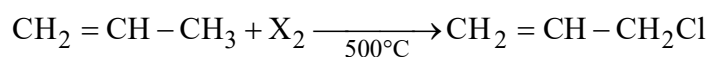


The reddish brown colour of bromine is discharged and colourless vicinal dibromide is formed, this reaction is used for test for unsaturation.

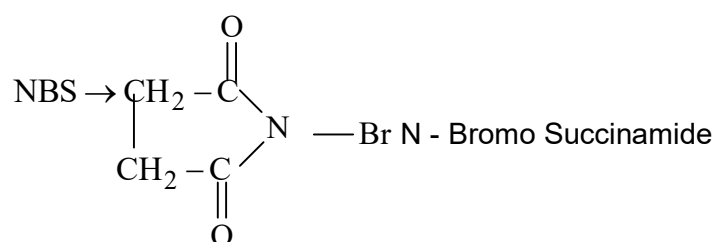
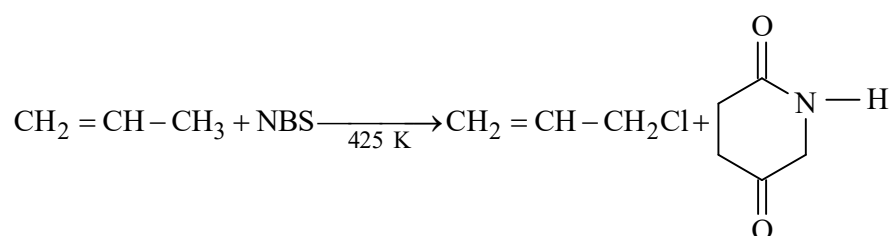
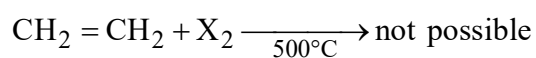
ALKENES SUBSTITUTION REACTION

Higher alkenes are heated with halogen under higher temperature, H atoms from alkyl / benzylic carbon

replaced halogenation taking place and this halogenation is known as Alkyllic / benzylic halogenation

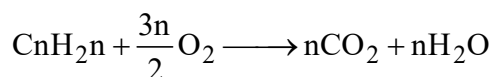


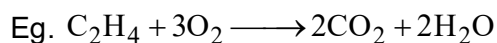
Allyl and benzyl radicals are resonance stabilised.



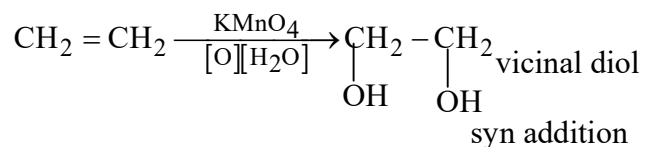
OXIDATION REACTION

1. Complete oxidation



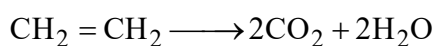


Oxidation using dilute/cold KMnO_4

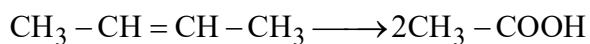


The purple colour / KMnO_4 is discharged and colourless, Vicinal diol is formed is known as Baeyer's test for unsaturation

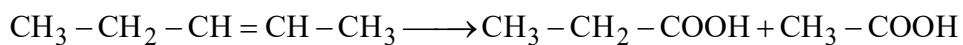
Oxidation using Acidified or Alkaline hot $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$



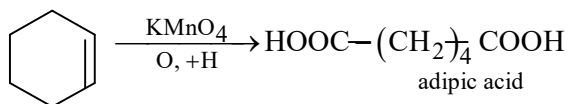
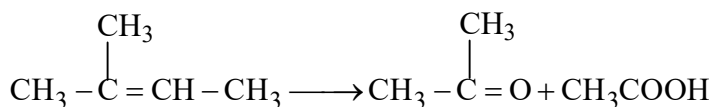
Terminal can be converted into CO_2 and H_2O



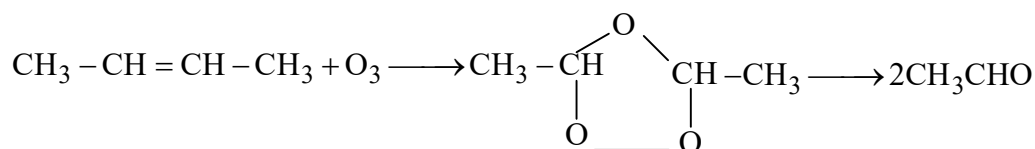
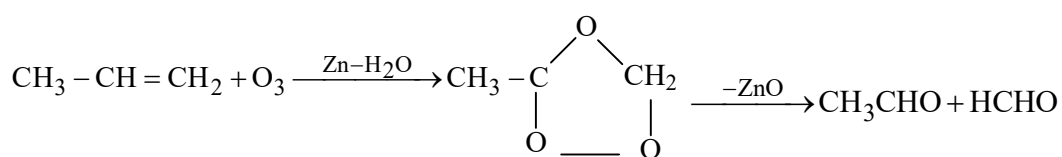
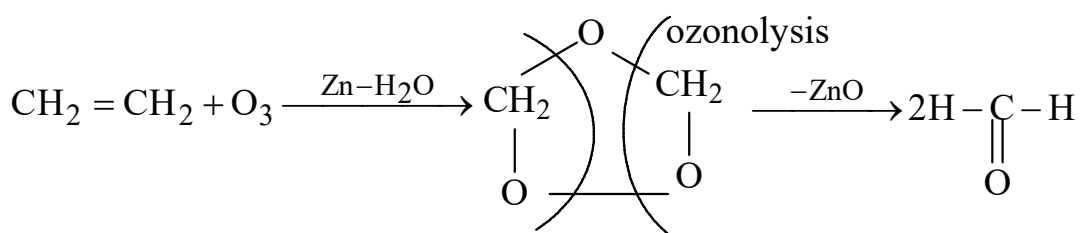
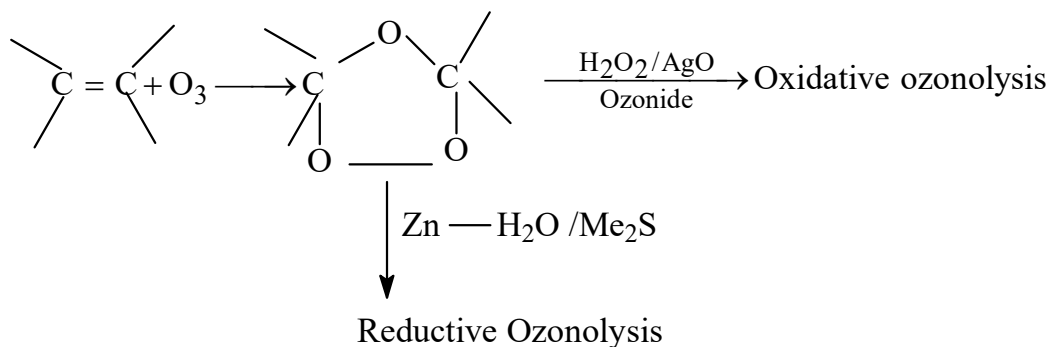
Without terminal the respective acids will be formed



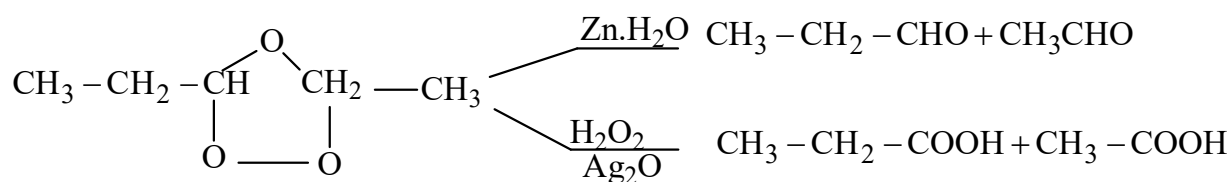
If no H is present on C then ultimately it becomes CO(Keto)



OZONOLYSIS REACTION



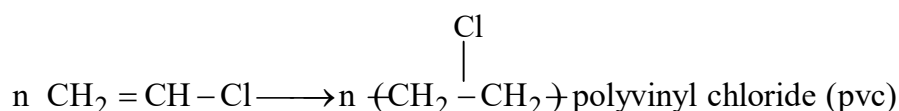
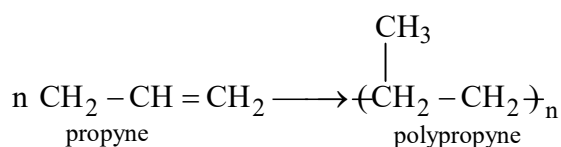
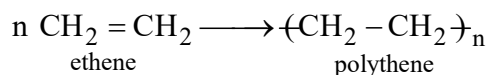
Oxidate ozonolysis



POLYMERISATION REACTION

Conversion of monomer \rightarrow polymer

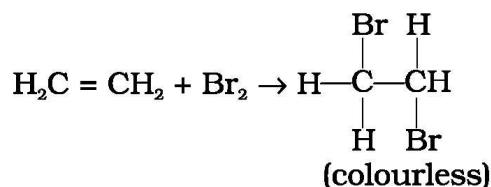
- At 473 k and 1500 atm



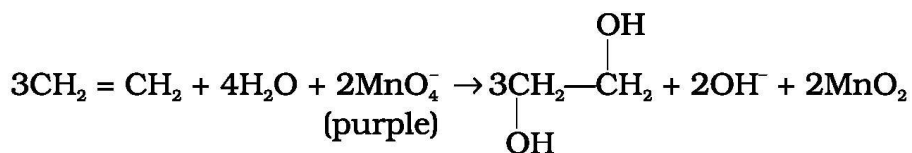
Tests for unsaturation

Theory

Organic compounds containing $> \text{C} = \text{C} <$ and / or $-\text{C} \equiv \text{C}-$ bonds are called unsaturated compounds. These compounds undergo addition reaction with bromine water or the solution of bromine in carbon tetrachloride, chloroform or glacial acetic acid. Addition of bromine to an alkene results in the formation of vicinal dibromide. The reddish orange colour of the solution of bromine in carbon tetrachloride disappears on reaction with an alkene. The reaction is as follows :



Alkenes decolourise the neutral/alkaline KMnO_4 solution and vicinal glycols are formed (**Bayer's test**). Reaction takes place as follows :



Both the above reactions are used as tests for unsaturation.



- Test tubes : Two
- Test tube holder : One



- Potassium hydroxide solution : 1–2 mL
- Carbon tetrachloride/ chloroform : 2 mL
- Bromine water/solution of bromine in CCl_4 or chloroform : 2 mL
- Potassium permanganate solution : As per need
- Compound to be tested : As per need

Procedure

A. Bromine water test

Dissolve 0.1 g or 5 drops of organic compound in 2 mL of carbon tetrachloride in a test tube and add 2% solution of bromine in carbon tetrachloride or bromine water drop by drop with continuous shaking. Decolourization of bromine solution indicates the presence of unsaturation in organic compound.

Potassium hydroxide



Carbon tetrachloride



B. Bayer's test

Dissolve 25-30 mg of organic compound in 2 mL of water or acetone (free of alcohol) and add 1% potassium permanganate solution containing equal volume of 1% sodium carbonate solution. The discharge of the colour of more than one drop of potassium permanganate indicates the presence of unsaturation in the organic compound. Carrying out the reaction under alkaline conditions removes the possibility of confusion due to substitution in aromatic compounds.

Chloroform



Bromine



Potassium permanganate



Note: (i) Unsaturation in an organic compound is confirmed only when both of the above tests are positive.

(ii) In place of CCl_4 any other solvent such as CHCl_3 /dioxan and even water can be used to dissolve the organic compound for carrying out the reaction.

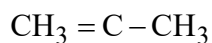
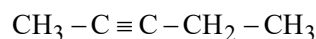
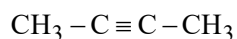
Precautions

- (a) The tests should be performed at room temperature.
- (b) Handle bromine solution carefully. Do not inhale the vapours and also avoid its contact with the skin.

ALKYNES

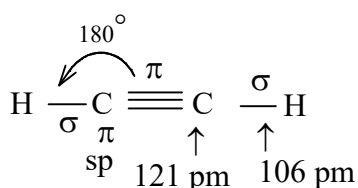
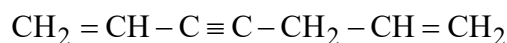
- General formula : $C_n H_{2n-2}$
- Less than 4 H atom corresponding paraffins
- Known as acetylene
- First member is acetylene others are derivatives of acetylene

Eg. $CH \equiv CH$ methylene



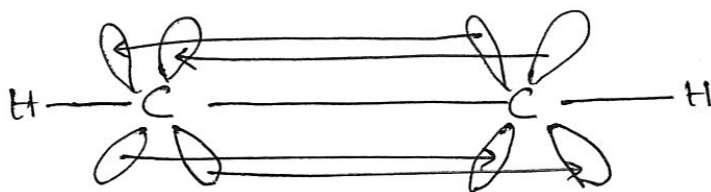
Dimethyl acetylene

Methyl acetylene



Alkyl 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.

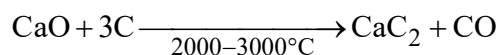
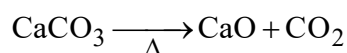


Alkynes are less reactive than alkenes due to

1. the cylindrical 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.

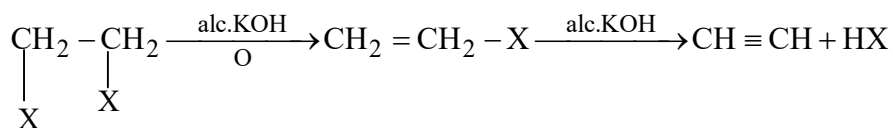
PREPARATION

1. addition of H_2O on CaC_2

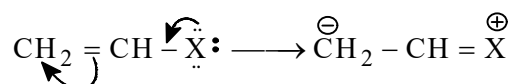


2. from alkyl halide

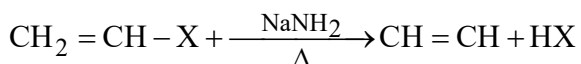
→ from dihalide



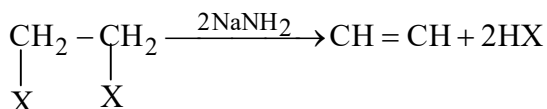
This product formed $\text{CH}_2 = \text{CH}_2 - \text{X}$ is resonance stabilised



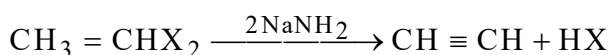
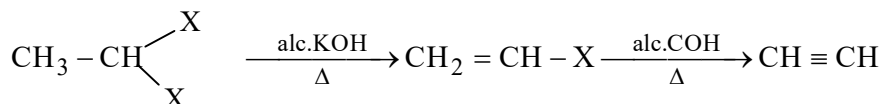
Thus the reaction is very slow hence we can speed up the reaction by using NaNH_2 which is more basic



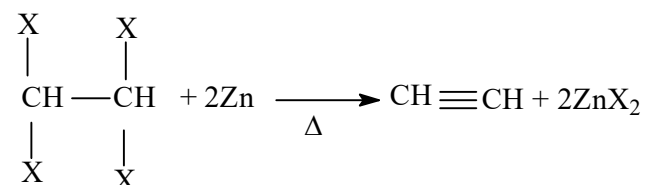
There two step reaction can be concluded into one step using NaNH_2



From geminal halide

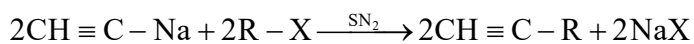
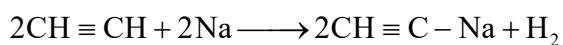


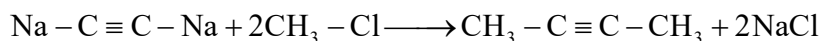
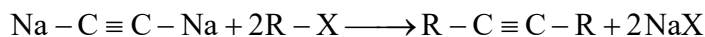
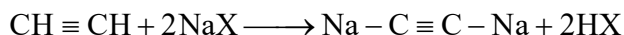
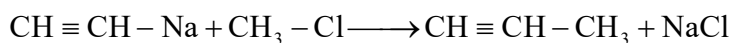
Tetrahalide



5. Preparation of higher alkynes using acetylenes

Acetylene react with metals form metal acetylide. These metal acetylides react with haloalkenes 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 POINT 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

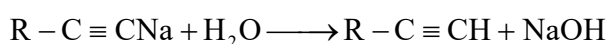
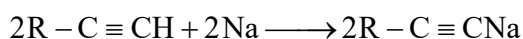
Insoluble in H_2O and soluble in organic solvents

Chemical reactions

1. Acidic character of an alkenes

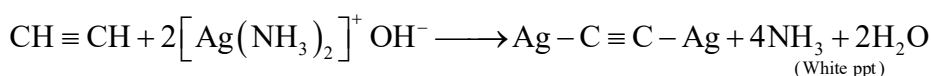
1. Formation of alkalimetal acetalides

Thermal alkynes react with alkali metals and forms alkali metal acetalides and there acetalides react with H_2O and regenerate acetylene. This shows water is more acidic than acetylene.

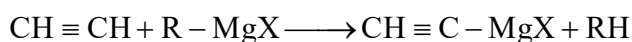


2. Formation of heavy metal acetylides

Acetaline react with Tollens reagent $[2\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ammoniacal silver nitrate from silver acetalide.



3. Formation of alkynyl grignard reagent

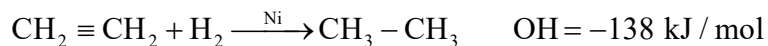
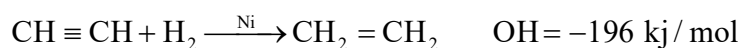


Reason for acidic

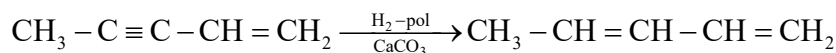
In acetylene C is $\text{sp} \rightarrow$ so more s character so highly electronegativity. Thus it withdraws electrons from C-H bonds and thus releases H^+ atom.

ADDITION REACTION

1. Addition of hydrogen



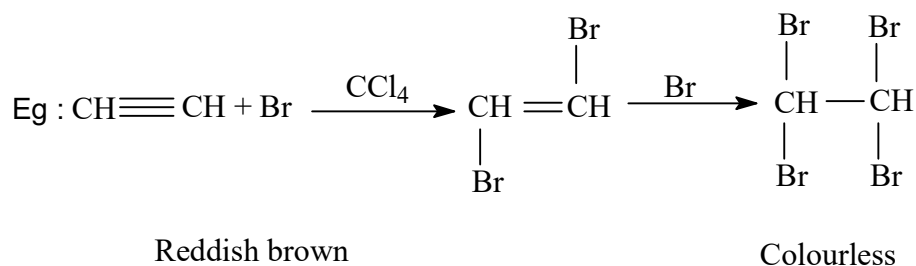
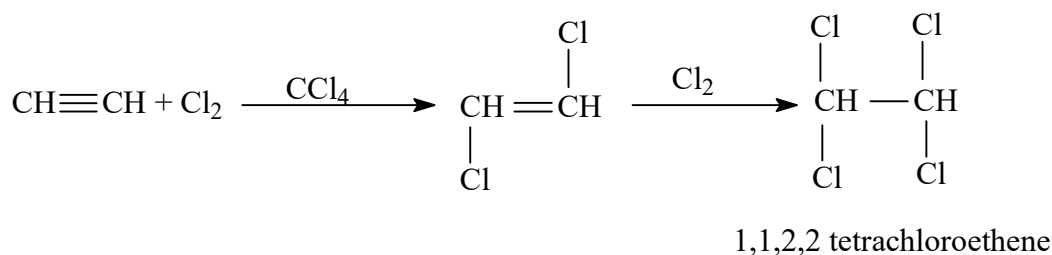
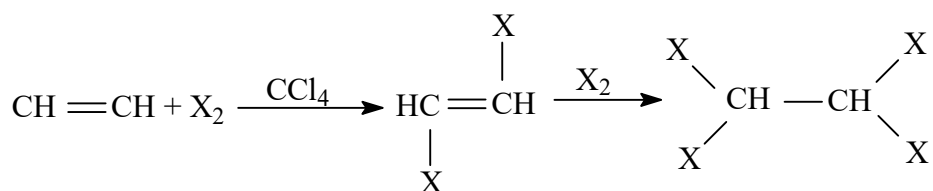
Catalytic hydrogenation of alkynes is more spontaneous than catalytic hydrogenation of alkenes to alkenes.



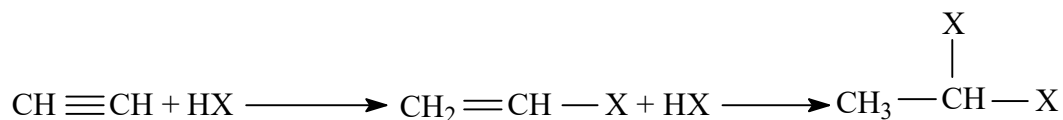
Therefore alkynes are more reactive than alkenes.

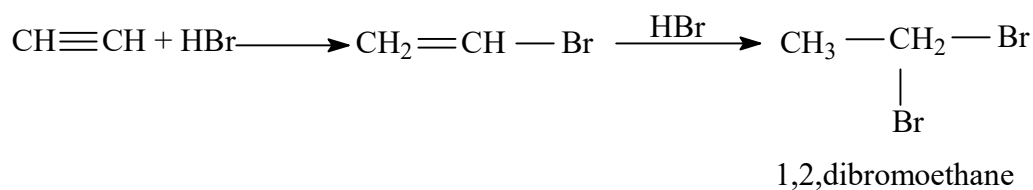
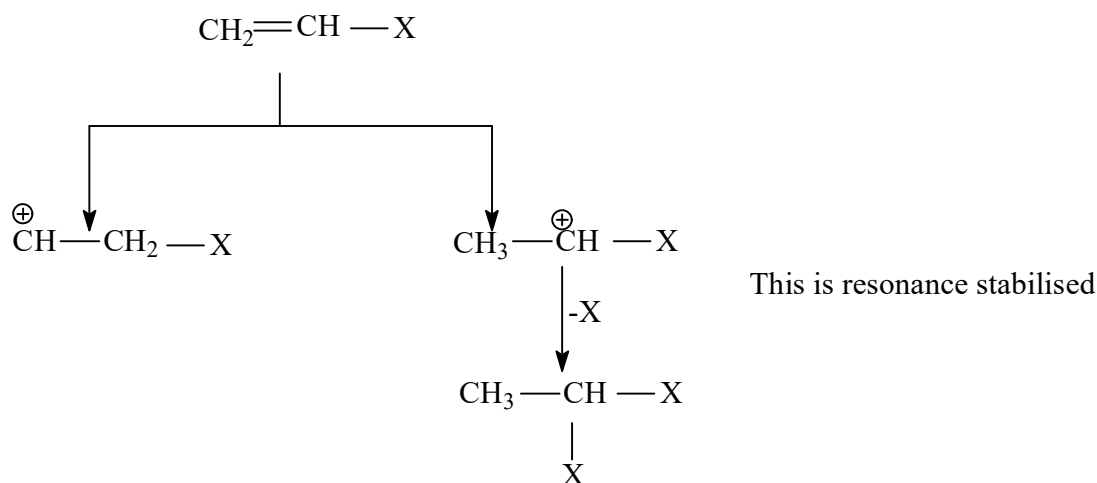
In hydrogenation alkynes are more stable hence whenever add H to \equiv as to form more stable compounds.

2. Addition of halogen

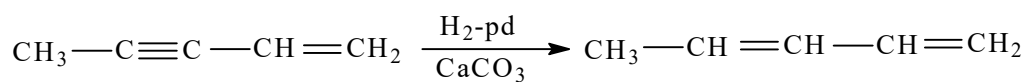


3. Addition of hydrogen halide



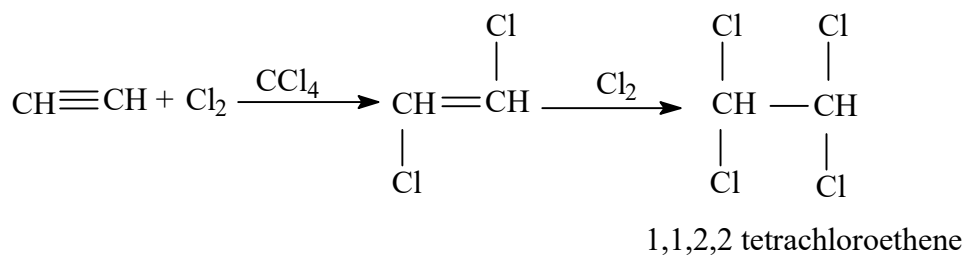
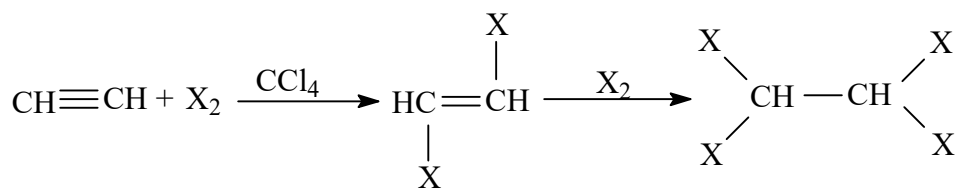


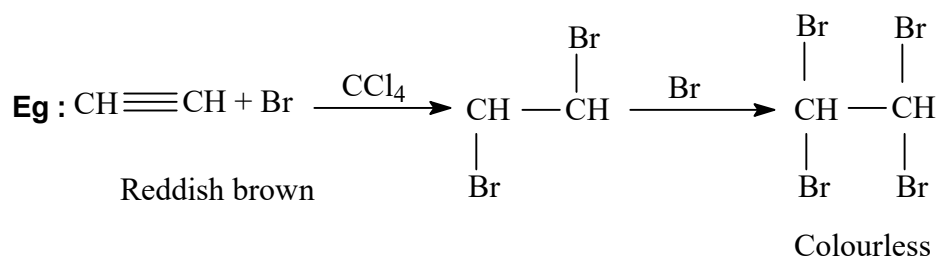
Catalytic hydrogenation of alkynes is more spontaneous than catalytic hydrogenation of alkenes to alkenes.



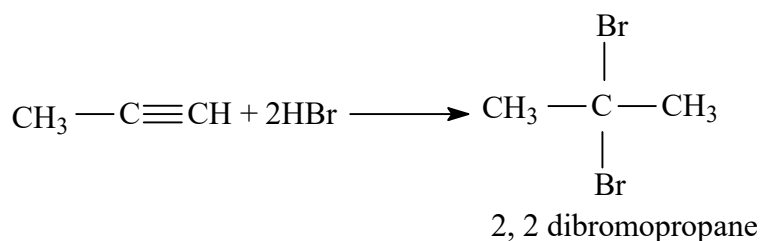
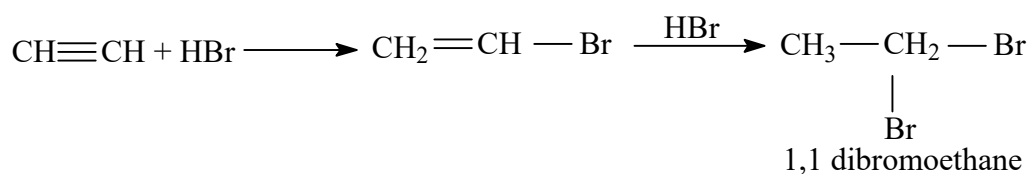
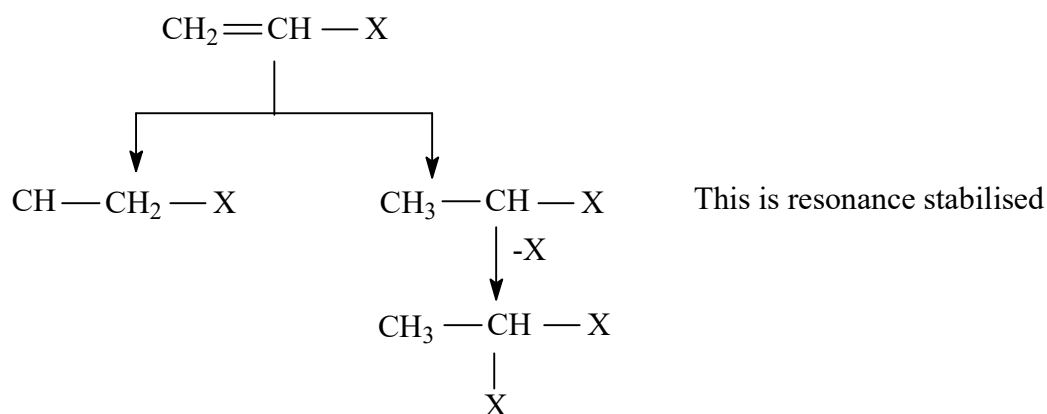
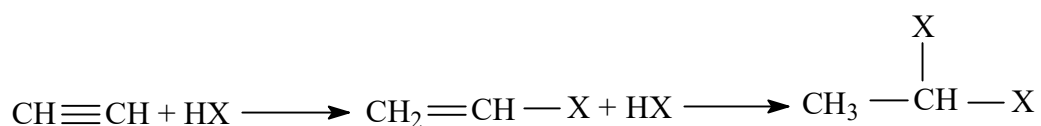
Therefore alkynes are more reactive than alkenes. In hydrogenation alkynes are more stable hence whenever add H to \equiv as to form more stable compounds.

2. Addition of halogen



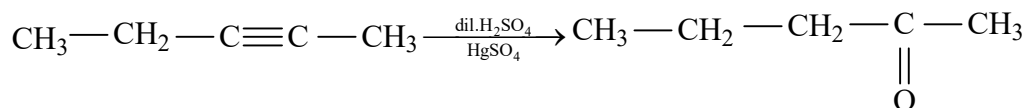
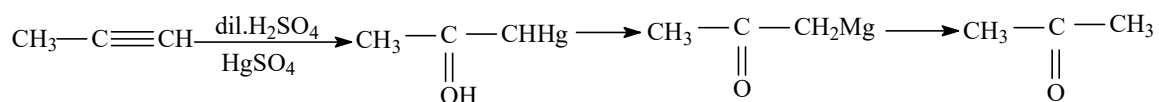
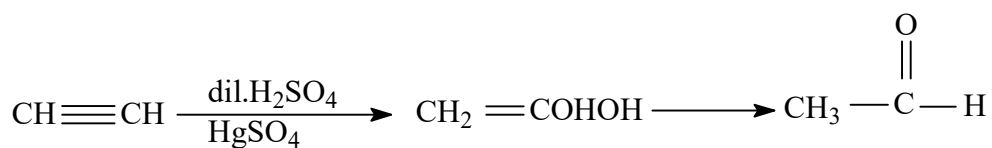


3. Addition of hydrogen halide



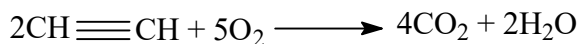
ADDITION OF H₂O

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



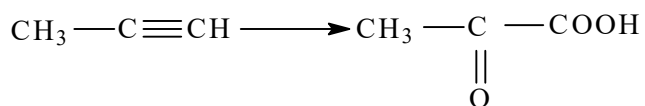
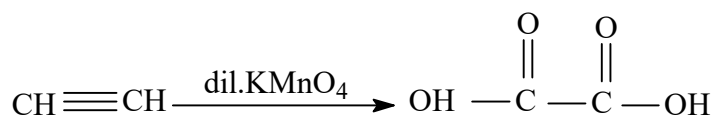
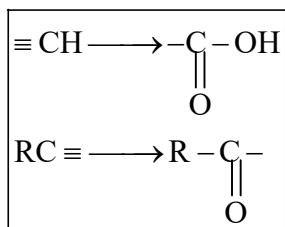
OXIDATION REACTION

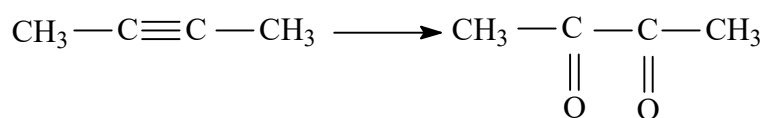
- Complete oxidation



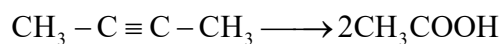
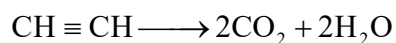
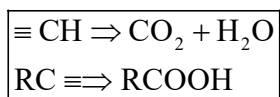
When acetylenes are burnt with air/oxygen under higher pressure they burn to form CO_2 and H_2O atoms with blue flame having higher temperature around 3000°C and this flame is used for cutting and welding metals.

- Oxidation using dilute KMnO_4

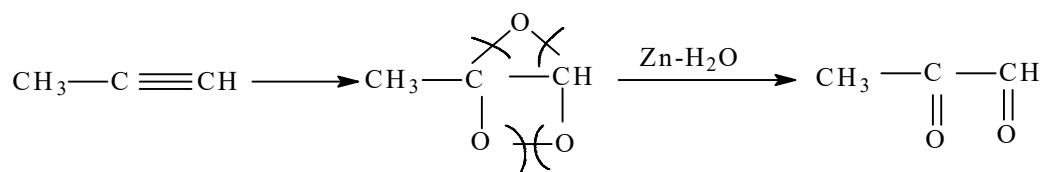
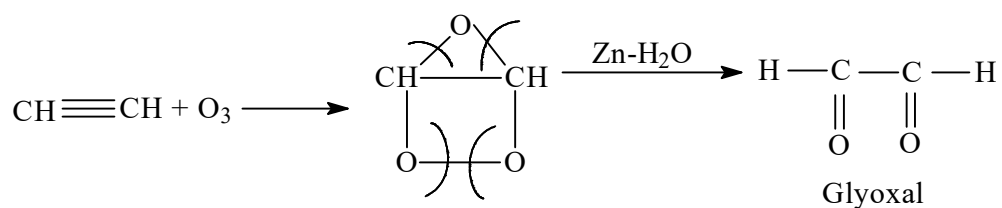




3. Oxidation using acidified alkaline/ $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$



OZONOLYSIS

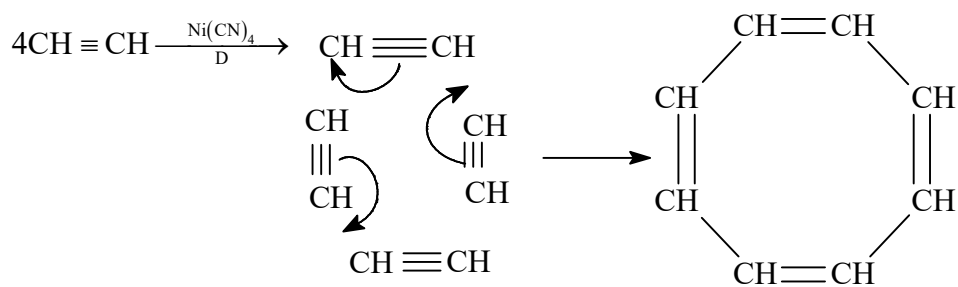
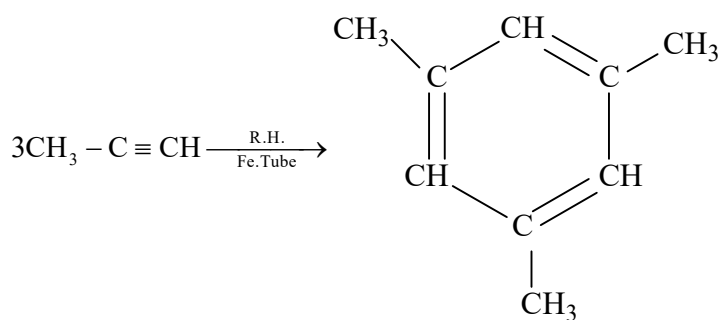
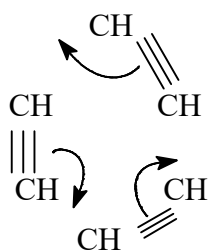
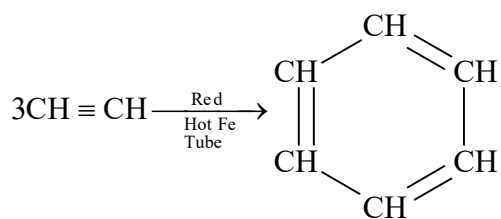


POLYMERISATION REACTION

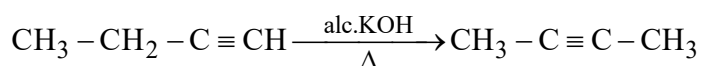
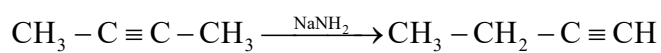
1. Linear polymerisation



CYCLIC POLYMERISATION



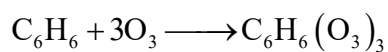
ISOMERISATION



BENZENES

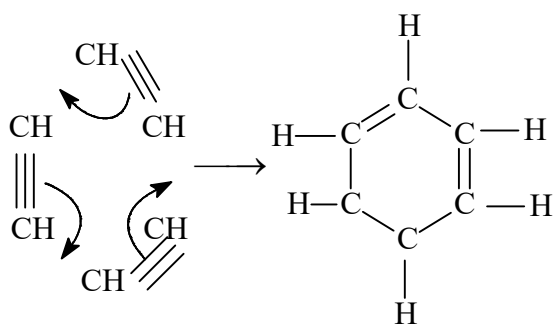
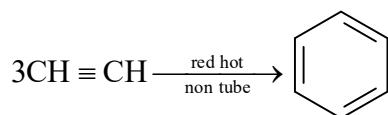
- C_6H_6
- Less than 8H corresponding paraffins

- Highly unsaturated system

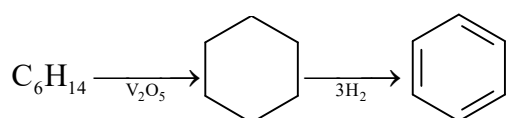


PREPARATION

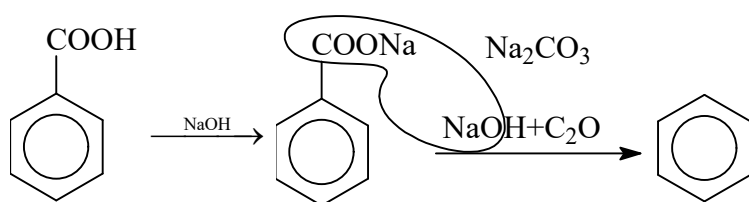
- From acetylene



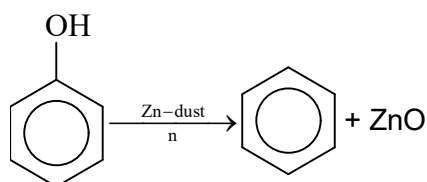
- From normal hexane



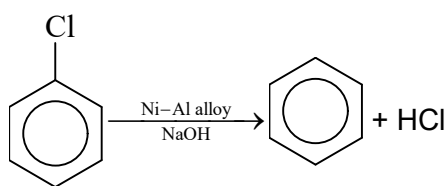
- From sodium benzoate



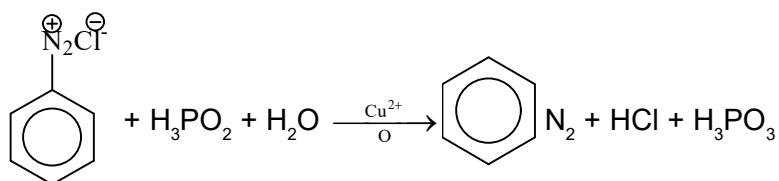
- From phenol



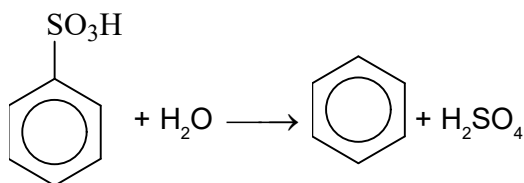
- From chlorobenzene



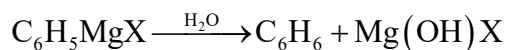
6. From benzene diazonium chloride



7. From benzene sulphonic acid



8. From grignard reagent



PHYSICAL PROPERTIES

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

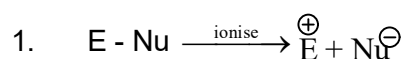
\therefore So boiling point depends only on size.

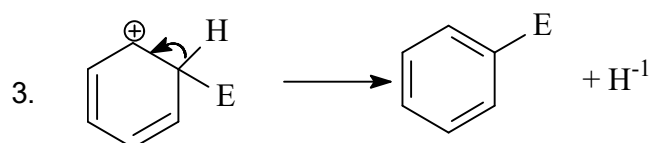
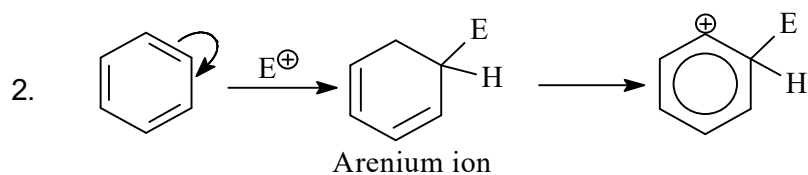
- In case of isomeric, P isomers having high melting point than M and O due to symmetric geometry.
- Benzene insoluble in water but soluble in organic solvent

CHEMICAL REACTIONS

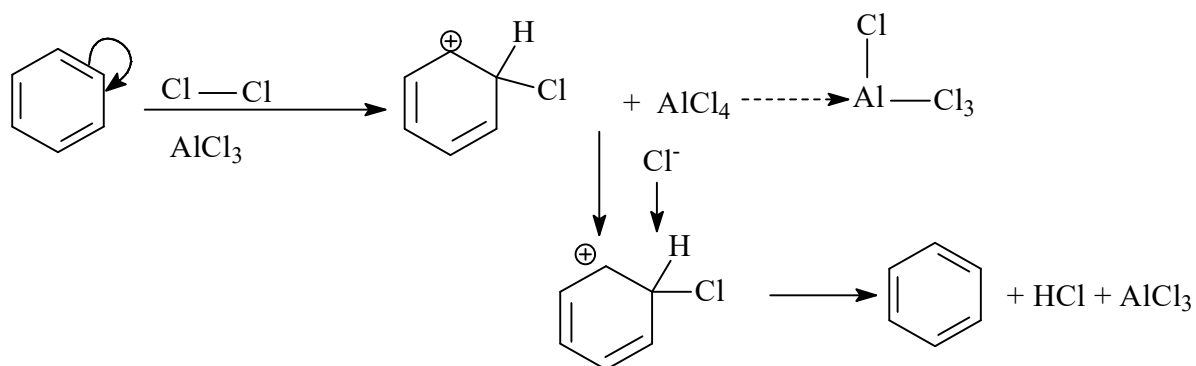
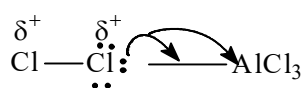
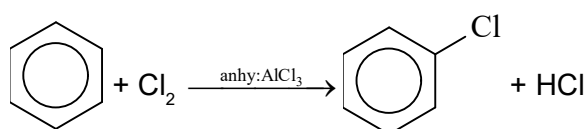
- More reactive than alkanes and less reactive than alkenes and alkynes due to complete delocalisation of electron.

ELECTROPHILIC SUBSTITUTION REACTION

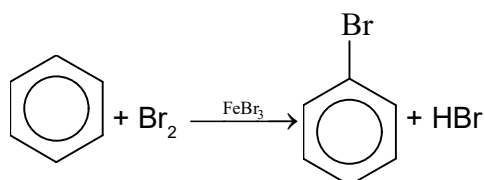


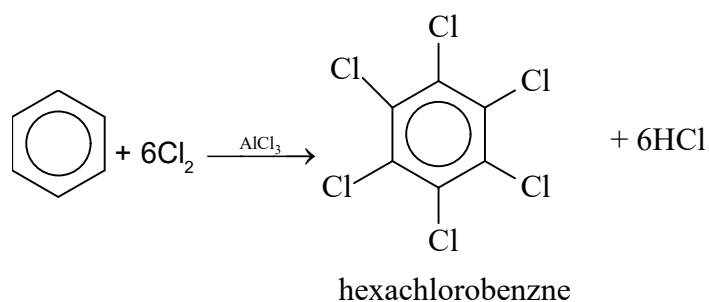
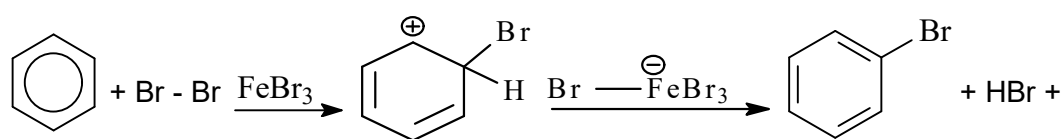


1. Generation of electrophile
 2. Formation of arenium ion
 3. Formation of sub product
1. **HALOGENATION**

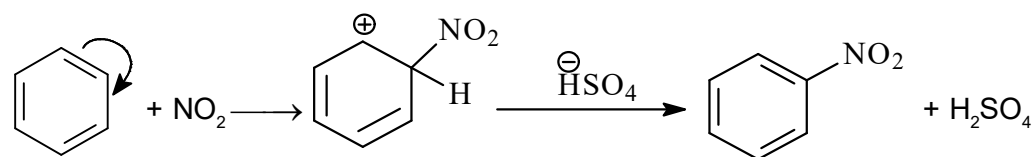
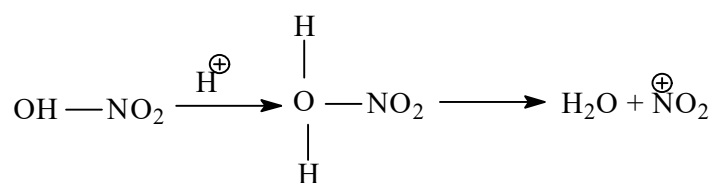
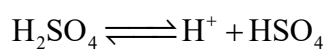
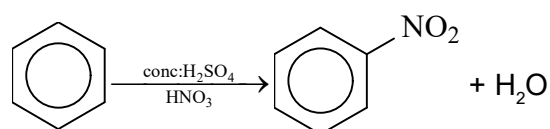


AlCl₃ acts as a halogen carries as well as electrophilic producer. If a halogen carries is present and no light then benzene goes subtraction.

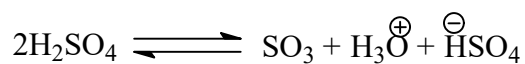
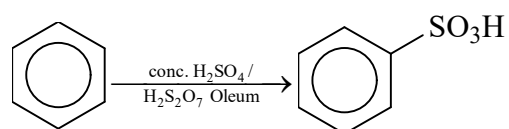


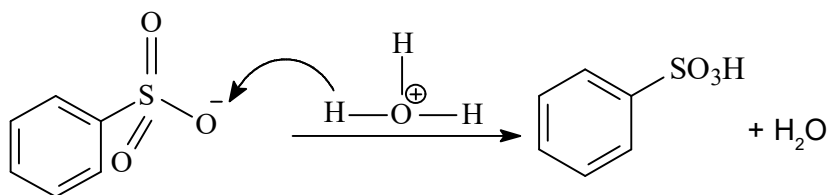
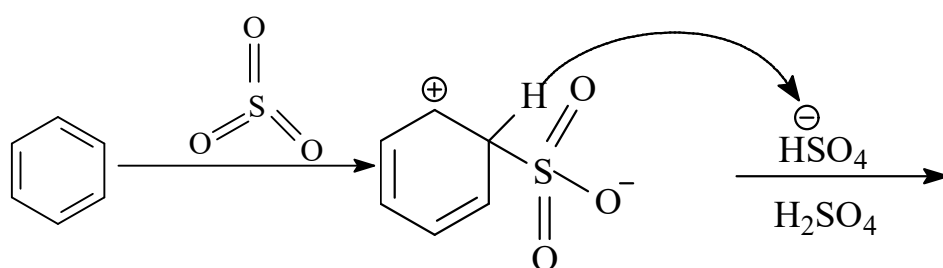


2. Nitration



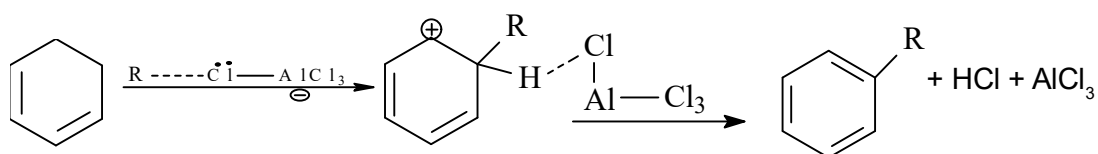
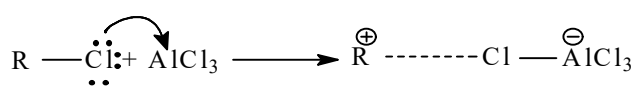
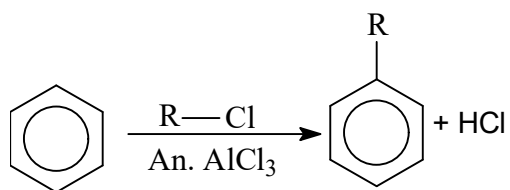
Sulphonation



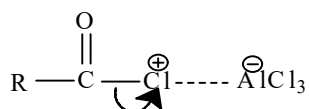
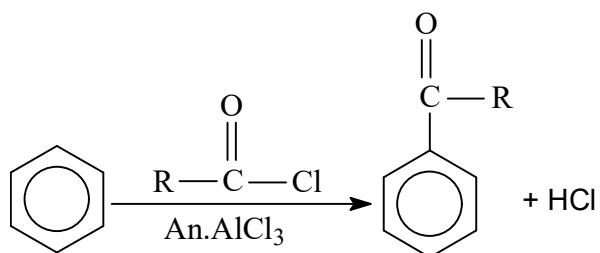


FRIEDEL CRAFT REACTION

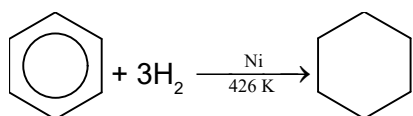
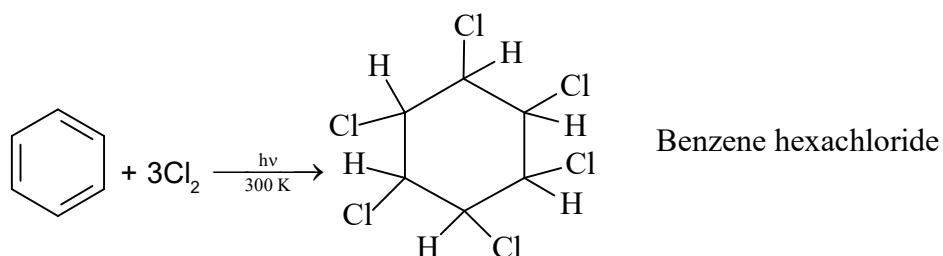
1. ALKYLATION



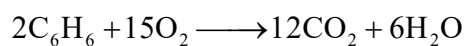
2. ACYLATION



BENZENE ADDITION REACTION

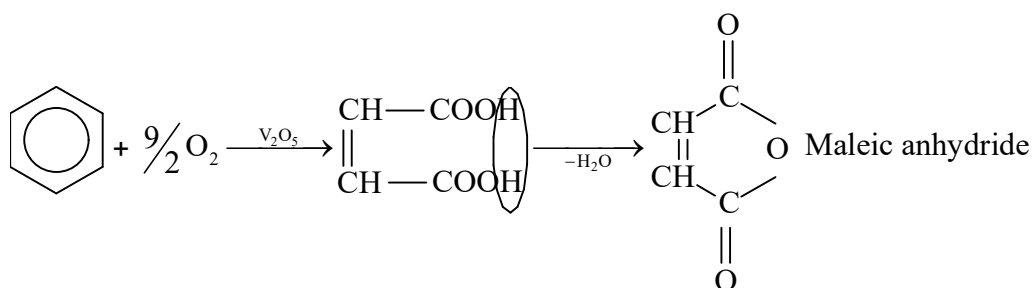


OXIDATION REACTION



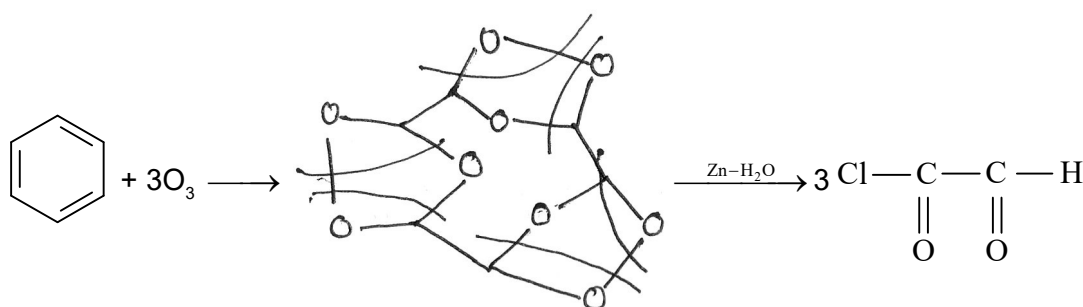
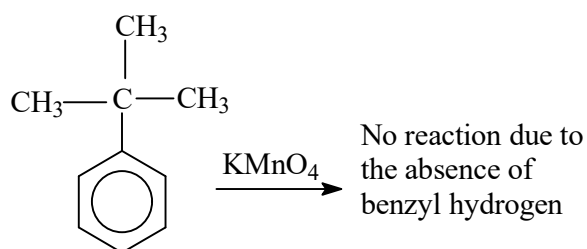
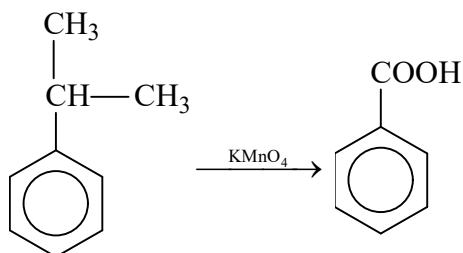
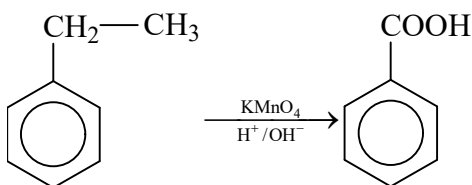
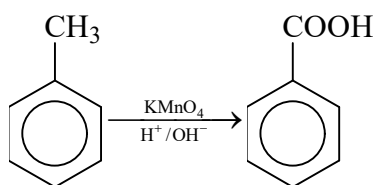
When benzene burns with air/oxygen under pressure, it burns with a yellow sooty flame. This flame indicates the presence of higher carbon content in benzene and is used for distinguishing aliphatic and aromatic compounds.

Incomplete oxidation



Oxidation with KMnO_4

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

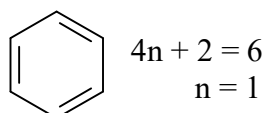


AROMATICITY

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

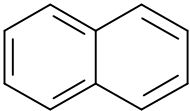


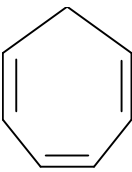
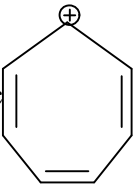

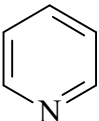
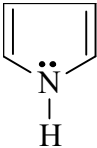

Conditions:

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



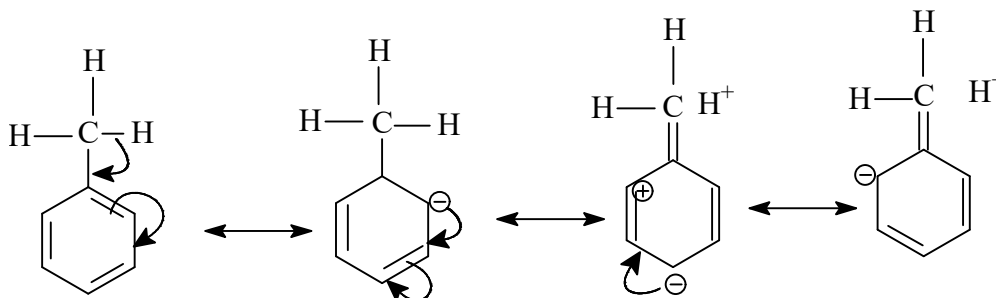
Compounds satisfying $4n\pi e^-$ rule \rightarrow antiaromatic

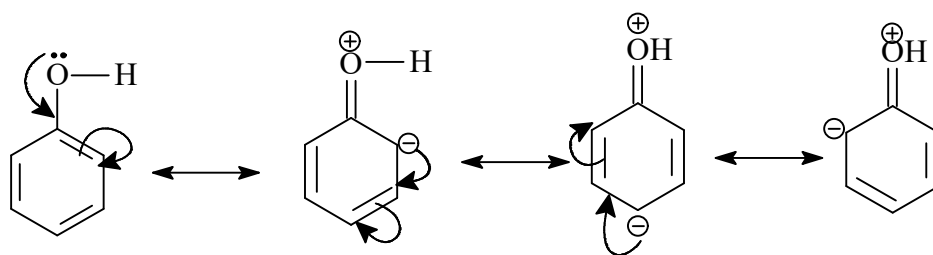
Others are non aromatic

- 
 $4n + 2 = 10$
 $n = 2$ aromatic
- 
 not conjugated \therefore non aromatic
- 
 $4n + 2 = 0$
 $n = 0$ aromatic
- 
 Non aromatic
 
 $n=1$ aromatic
- 
 aromatic $n = 1$
- 
 aromatic
 
 Aromatic $n = 1$
- 
 antiaromatic

Directive Influence of substituents

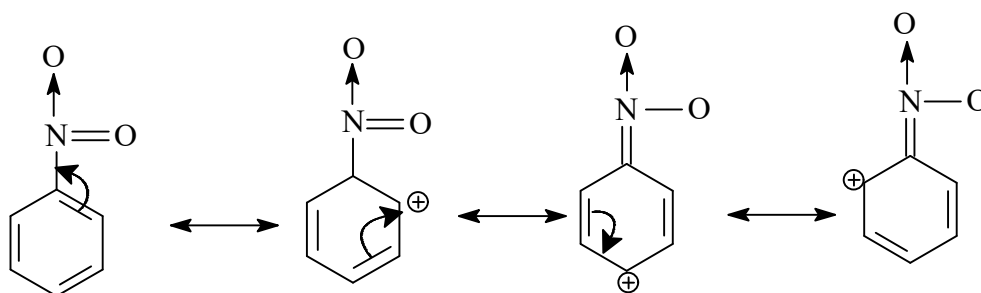
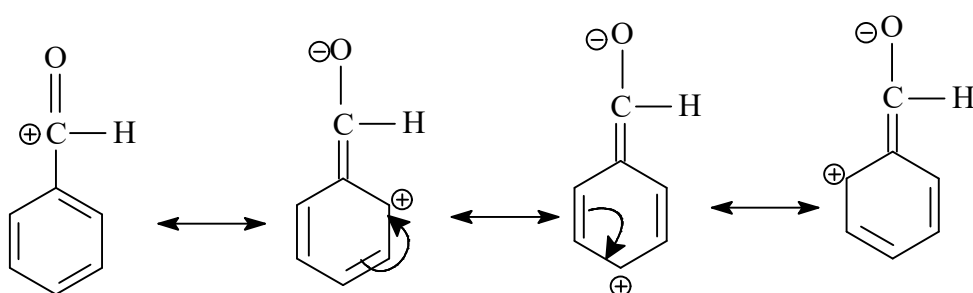
- It is the ability of atoms or group to direct the incoming group to a particular position in benzene ring
 Ortho-para directing group
 Atoms or group which donate electrons towards benzene ring and increases electron density in o and p positions. These groups are ring activating groups.
 All electron donating groups are o and p and ring activators.





META DIRECTING GROUP

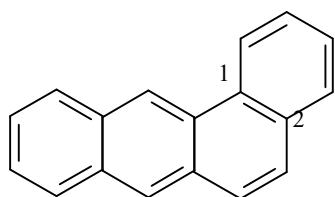
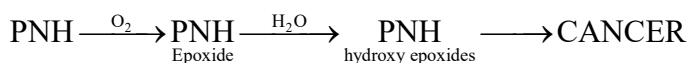
Atoms or group which withdraw electron from benzene rings and decreases electron density at o and p positions. These groups are ring deactivating group. All electron withdrawn groups are meta directing and electron withdrawing.



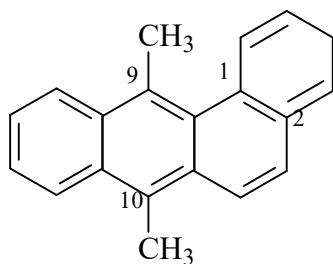
Here N too have / pair but act as M-group because look at the atom near the /-pair if it is high electronegative then it act as M-group.

Polynuclear hydrocarbon

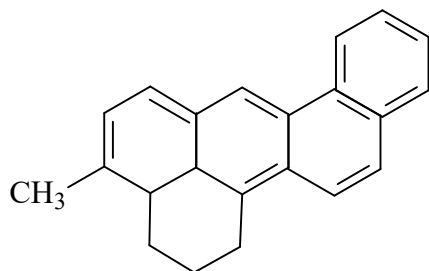
Compounds containing more than one fused benzene ring. These can generate cancer in living tissues so they are known as carcinogenic compound and the nature is called carcinogenicity. The main source of polynuclear hydrocarbon is coal tar.



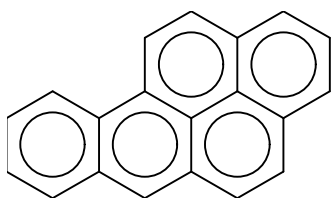
1-2 benzanthracene



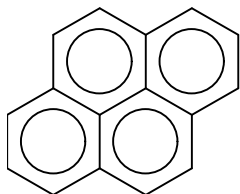
9-10 dimethyl benzanthracene



Methylcholanthrene



Benzpyrene



Pyrene