

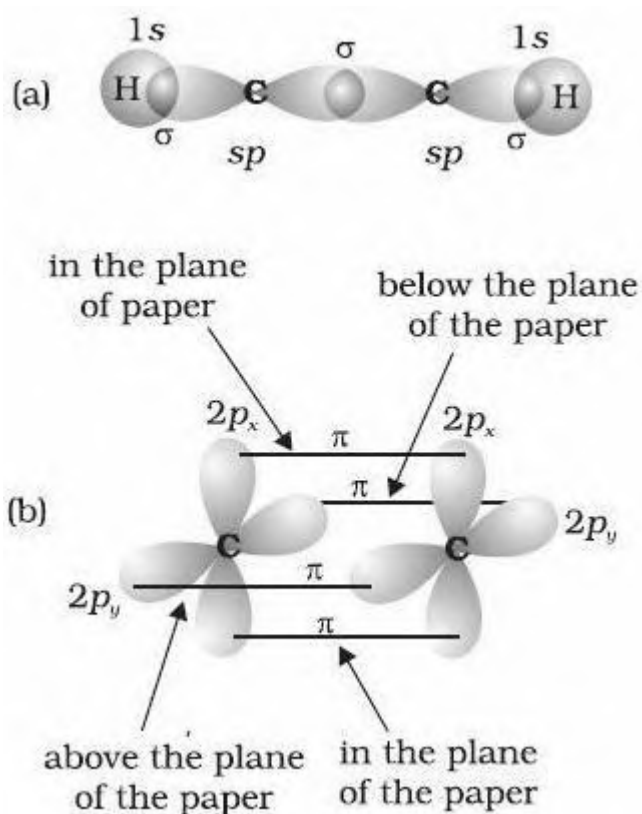
ALKYNES

Alkynes are unsaturated hydrocarbon with at least one triple bond between two carbon atoms ($C \equiv C$)

Their general formula is $C_n H_{2n-2}$

They are also called as acetylenes

STRUCTURE OF ALKYNES



Each carbon atom of ethyne has two sp hybridised orbitals.

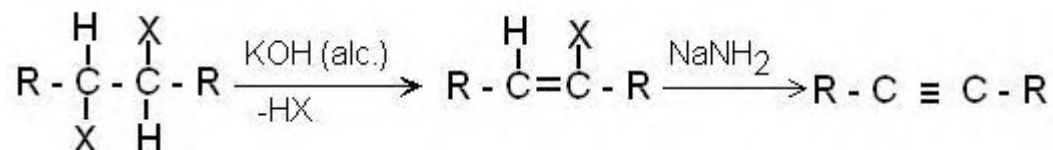
Carbon – carbon sigma (σ) is obtained by the head – on overlapping of the two sp hybridized orbitals of the two carbon atoms

The remaining sp hybridized orbital of each carbon atom undergoes overlapping along the internuclear axis with $1s$ orbital of each of the two hydrogen atom forming two sigma bond ($C-H$ bond) $H-C-C$ bond angle is of 180°

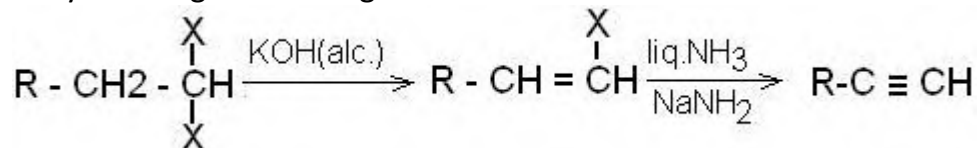
Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the $C-C$ sigma bond. The $2p$ orbitals of one carbon atom are parallel to the $2p$ orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi(π) bonds between two carbon atoms.

METHOD OF PREPARATION OF ALKYNES

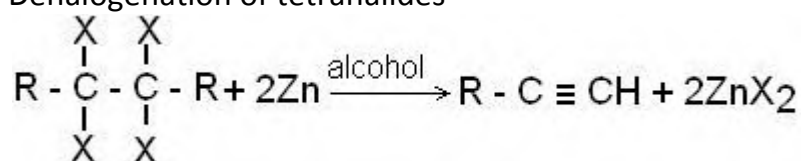
1. Dehydrohalogenation of vicinal dihalides



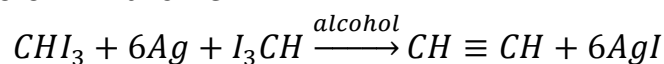
2. Dehydrohalogenation of geminal dihalides



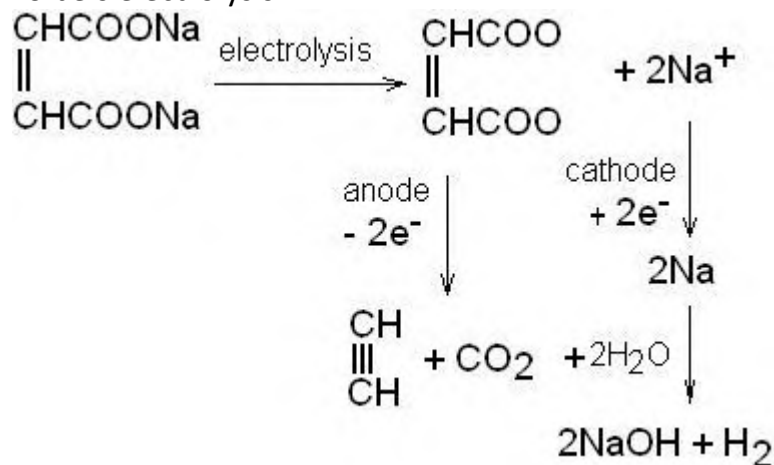
3. Dehalogenation of tetrahalides



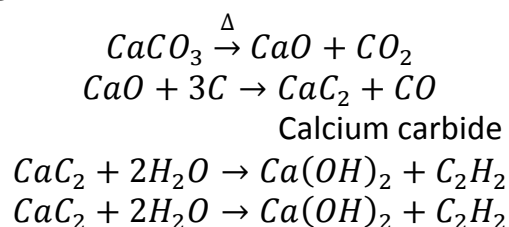
4. Reaction of iodoform with silver



5. Kolbe's electrolysis



6. From calcium carbide



PHYSICAL PROPERTIES OF ALKYNES

- Physical state
 - Alkynes are colourless and odourless with the exception of acetylene which has a characteristic odour.
 - (C₂ to C₄) members are colourless gas, next eight are liquids and higher ones are solids
- Melting and boiling point

Melting and boiling point of simple alkynes are slightly higher than corresponding alkenes and alkenes. This can be attributed to their symmetrical linear shape, so that molecules can pack closely in the crystal lattice
- Solubility

Alkynes are insoluble in water but readily soluble in non-polar solvents like benzene, ether etc
- Density : Alkyene are lighter than water.
- Polarity

Alkynes are slightly more polar than alkenes because sp hybridized carbon is more electronegative in comparison of sp² hybridized carbon atom of alkenes

CHEMICAL PROPERTIES OF ALKYNES

- Reactivity of alkynes

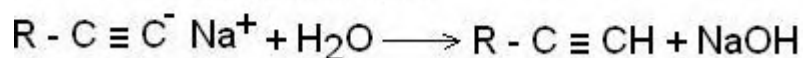
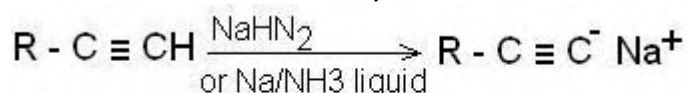
Alkynes are less reactive than alkene towards electrophilic addition reactions. This is due to following reasons

 - Sp – hybridized carbon atom of triple bond is more electronegative hence π – electrons of alkynes are more tightly held and thus less readily available for reaction with electrophile
 - Π – electron cloud of alkynes is more delocalized in cylindrical form and thus less readily available for addition reactions
- Acidic character of alkynes
 - Acetylene is weaker acid than water or alcohol but stronger than ammonia
 - Acidic character of alkynes can be explained on the basis of percentage of s-character of the hybrid orbital.

Hydrocarbon	Hybrid orbital	%of s-character
Alkanes	sp ³	25%
Alkenes	sp ²	33.33%
Alkynes	Sp	50%

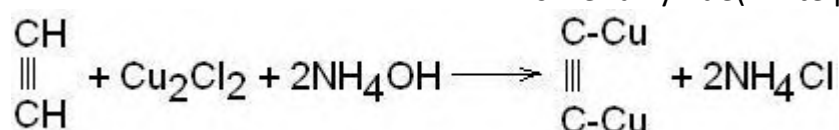
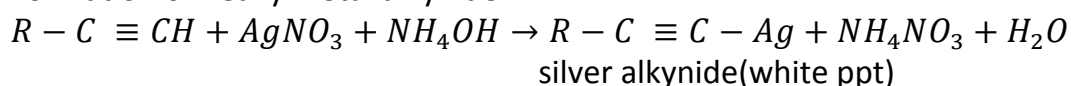
- More s-character, more is electronegativity. Therefore C-H bond in acetylene are strongly held by carbon nuclei which facilitates the removal of hydrogen.
- Order of acidic character can be given as
H₂O > ROH > CH≡CH > NH₃ > CH₂ = CH₂ > CH₃ – CH₃

- (i) Formation of sodium acetylides.



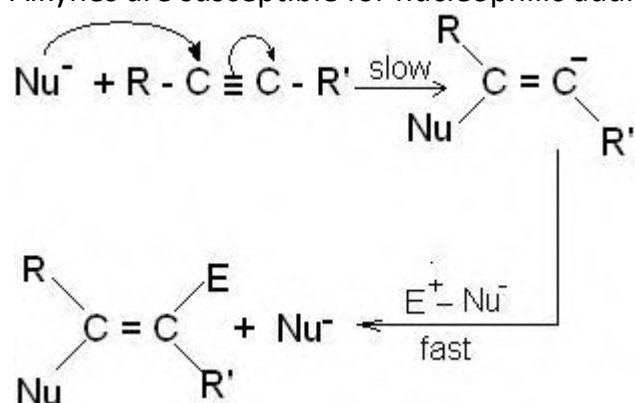
Sodium alkynides are stable when dry but readily hydrolysed by water, regenerating the alkyne.

- (ii) Formation of heavy metal alkynide

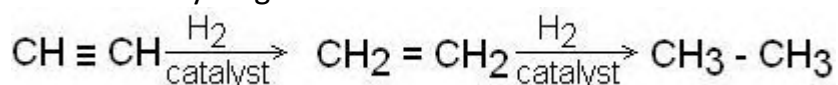


3. Addition reaction

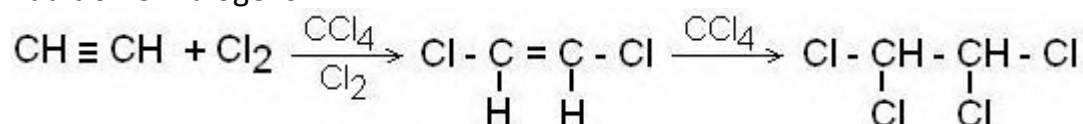
Alkynes are susceptible for nucleophilic addition reaction.



- (i) Addition of hydrogen



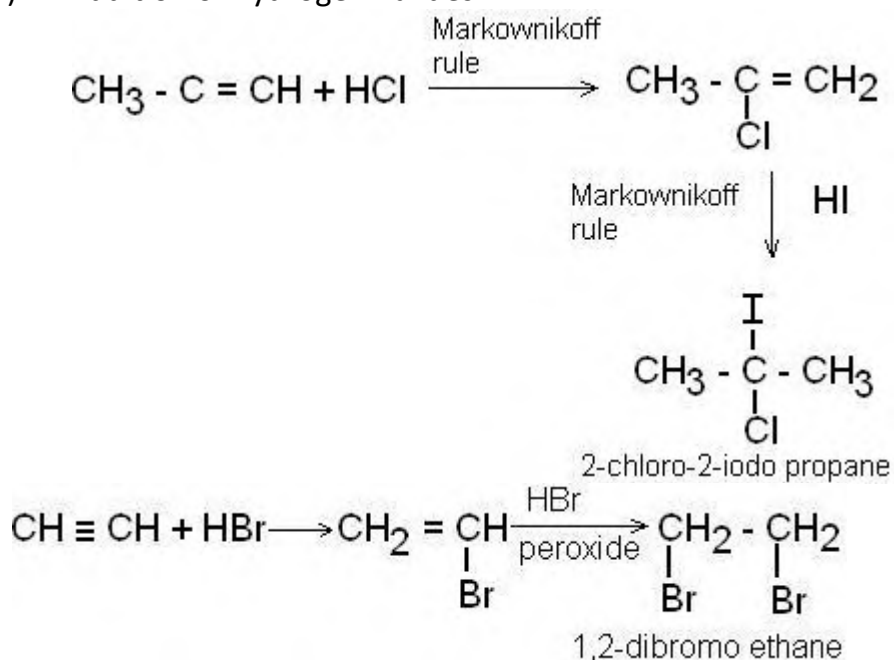
- (ii) Addition of halogens



Order of reactivity of halogens is

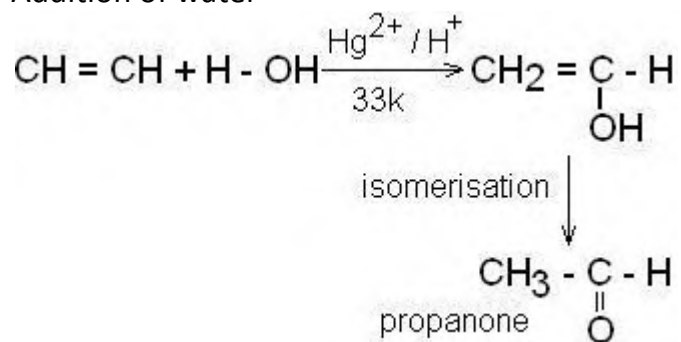


(iii) Addition of hydrogen halides

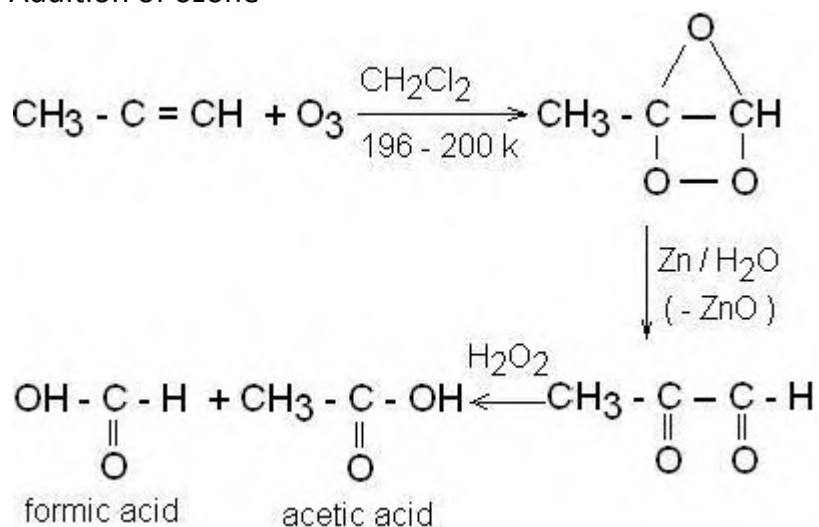


Order of reactivity of halogen acids is
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

(iv) Addition of water

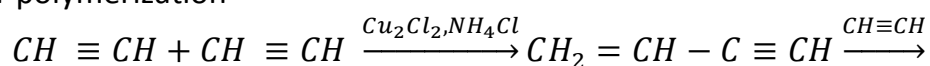


(v) Addition of ozone

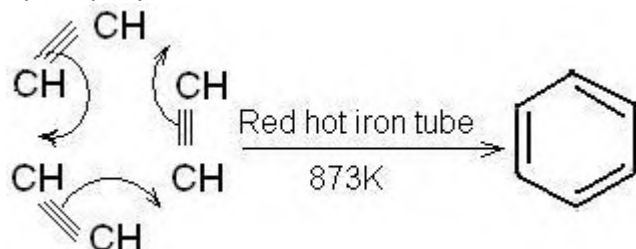


(vi) Polymerisation

(a) Linear polymerization


 $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - \text{CH} = \text{CH}_2$ (divinyl acetylene)

(b) Cyclic polymerization



Uses of alkynes

- (i) Acetylene is used as illuminant
- (ii) It is used for the production of oxy-acetylene flame. The temperature of the flame is above 3000°C. It is employed for cutting and welding of metals
- (iii) It is used as general anesthetic under the name Naracylene.

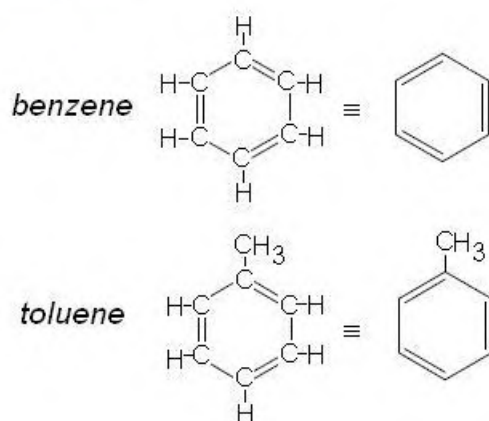
AROMATIC HYDROCARBONS OR ARENES

The term aromatic has been derived from the greek word aroma meaning pleasant odour, but in present form the aromatic compounds are cyclic closed chain) compounds having double bond in alternate positions

Aromatic compound containing benzene ring are known as benzoid and those not containing a benzene ring are known as non-benzoid.

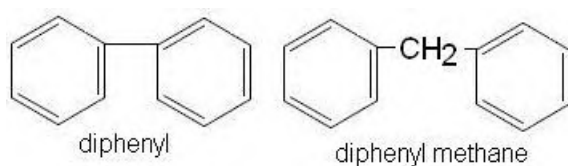
CLASSIFICATION OF ARENES

- (i) **Monocyclic aromatic hydrocarbons:** These consist of only benzene ring, with general formula C_nH_{2n-6} and includes benzene and its homologues



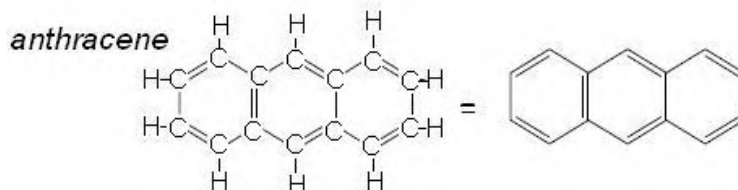
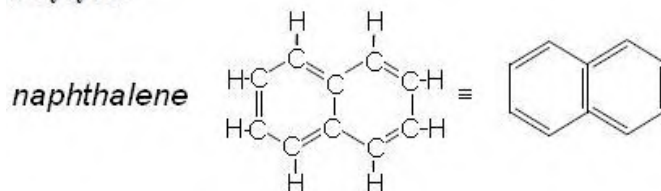
- (ii) **Polycyclic aromatic hydrocarbons:** These consists of more than one benzene ring

(a) **Isolated**



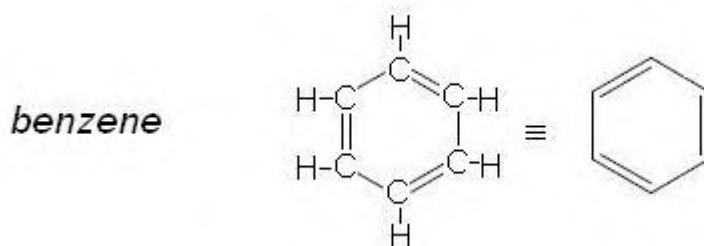
(b) **Fused or condensed**

Polycyclic

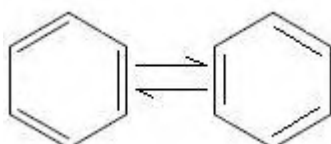


STRUCTURE OF BENZENE

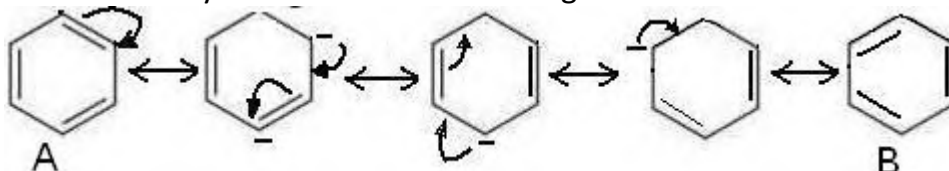
- Benzene was isolated by Michael Faraday in 1825
- The molecular formula of Benzene is C_6H_6 which indicates a high degree of unsaturation
- August Kekule in 1865 proposed a structure of Benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom



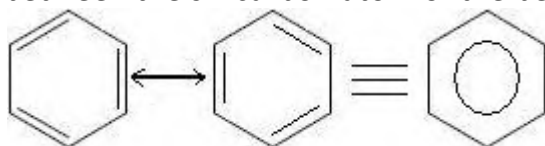
- Kekule suggested the oscillating nature of double bond in benzene as shown



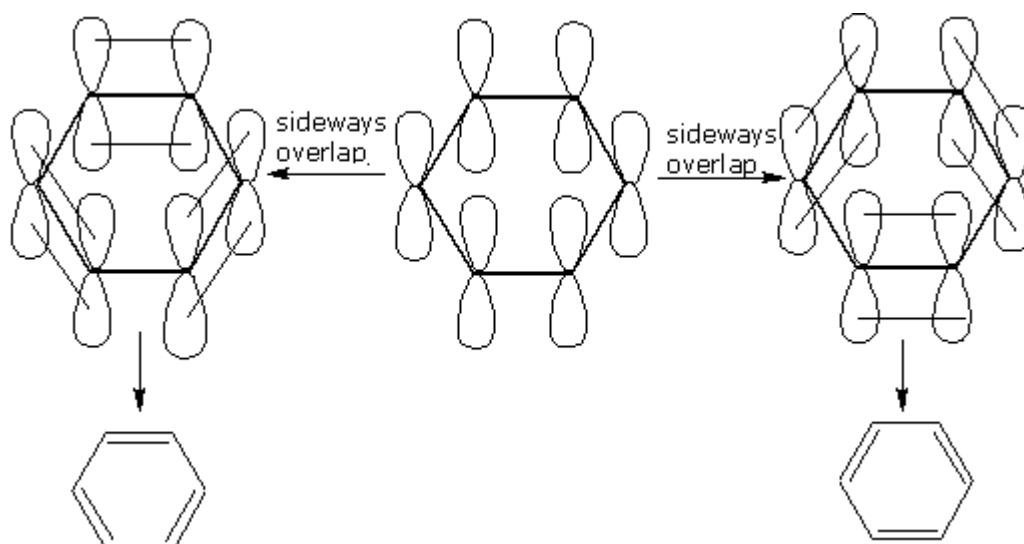
- Benzene is a hybrid of various resonating structure



- A and B are main contributing structures. The hybrid structure is represented by a circle which represents six electrons are delocalized between the six carbon atom of the benzene ring



- Benzene is sp^2 hybridised. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form C-C sigma bonds which are in hexagonal plane. The remaining sp^2 hybrid orbitals of each carbon atom to form six C-H bond. Each carbon atom is now left with one unhybridised p orbital perpendicular to the plane of ring



- All the six C-C bond lengths are of the same order (139pm) which is intermediate between C-C single bond (154pm) and C-C double bond (133pm).
- Thus the absence of pure double bond in benzene accounts for benzene to show addition reactions under normal conditions

AROMATICITY – HUCKEL RULE

Huckel rule states that “ An aromatic compound having a reasonably planar cyclic structure with $(4n+2)\pi$ electron clouds and possessing unusual stability due to delocalization of π – electrons

(a) Benzene

In benzene three double bond i.e. 6π electrons

Now $4n + 2 = 6$ Therefore $n = 1$

Benzene shows aromatic character

(b) Naphthalene

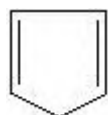
There are five double bonds in naphthalene i.e. 10π electrons

$4n + 2 = 10$ Therefore $n = 1$

Naphthalene shows aromatic character

(c) Cyclopentadiene

The molecule has two double bonds i.e. 4π electrons



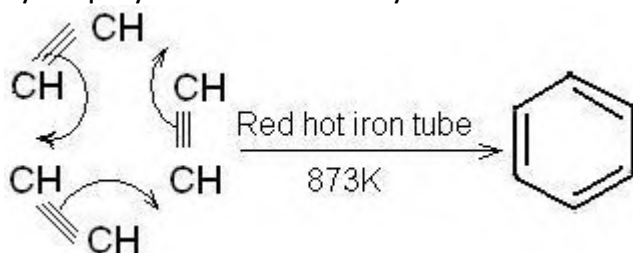
$4n + 2 = 4$ Therefore $n = 0.5$

Cyclopentadiene is non-aromatic

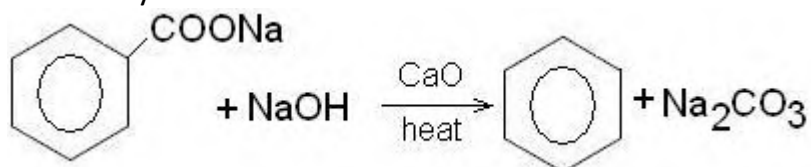
Note: Cyclopentadiene ion is aromatic because it has 6π electrons used in delocalization

METHOD OF PREPARATION OF BENZENE

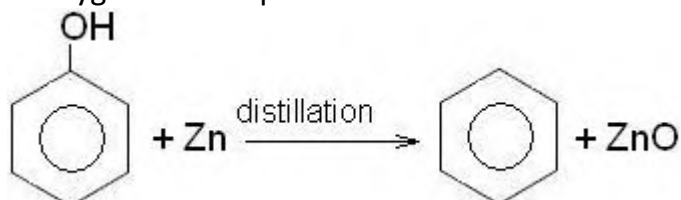
1. Cyclic polymerization of ethyne



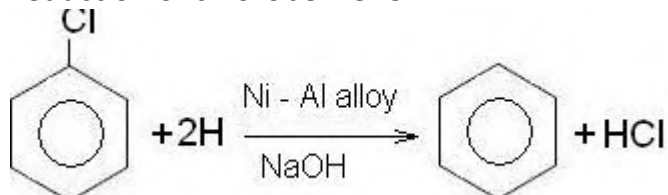
2. Decarboxylation of aromatic acids



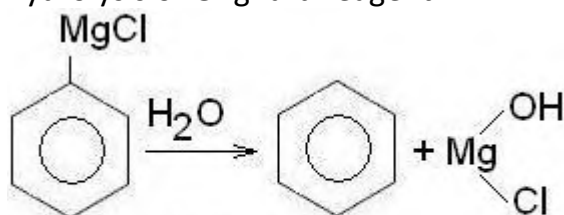
3. Deoxygenation of phenols



4. Reduction of chlorobenzene

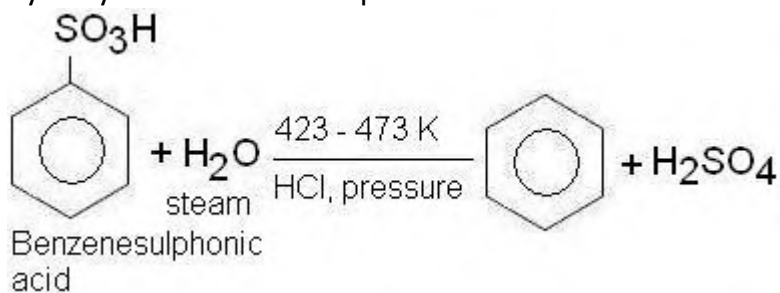


5. Hydrolysis of Grignard reagent



phenyl magnesium
chloride

6. Hydrolysis of benzene sulphonic acid

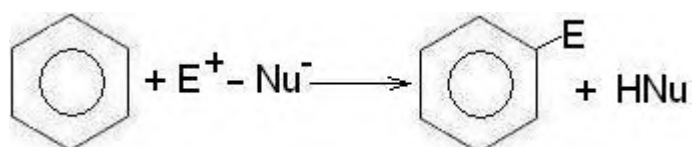


PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS

1. Lower members of aromatic hydrocarbons are colourless liquid while higher ones are solid with characteristic smell
2. These are non-polar compounds insoluble in water but soluble in organic solvent
3. Benzene itself is a good solvent. Fats, resins, rubber etc dissolves in it
4. They are lighter than water
5. They are inflammable and burn with sooty flame because of high carbon contents
6. Their boiling point increases with increase in molecular mass.

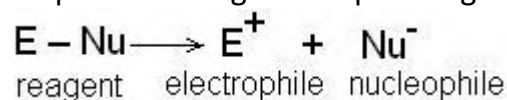
CHEMICAL PROPERTIES OF AROMATIC HYDROCARBONS

I) Electrophilic substitution reactions

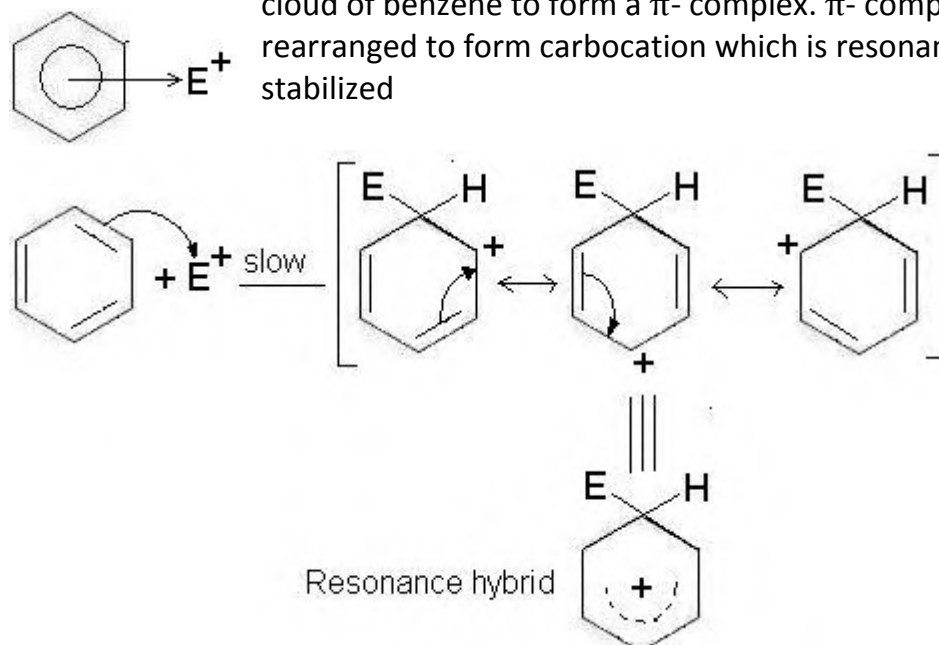


General mechanism

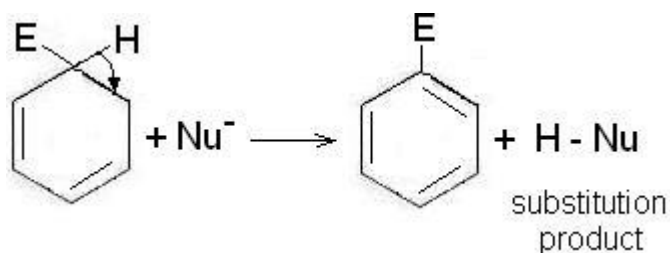
Step I : Attacking electrophile is generated from the reagent



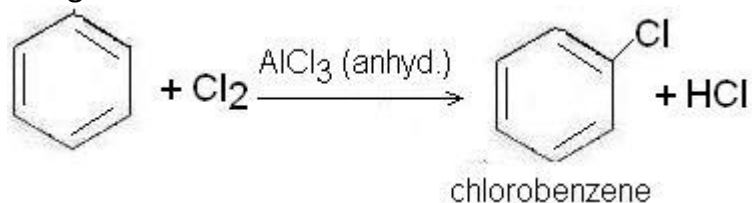
Step II : As soon as the electrophile is generated, it is attracted by π electron cloud of benzene to form a π - complex. π - complex is then rearranged to form carbocation which is resonance stabilized



Step III: The carbocation intermediate loses a proton to the nucleophile (Nu^-) present in reaction mixture to form substitution product.



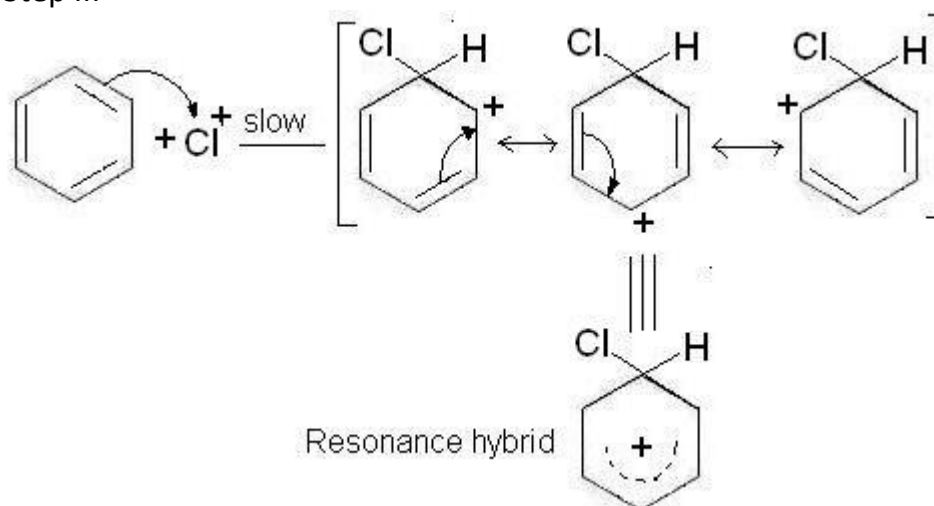
1. Halogenation



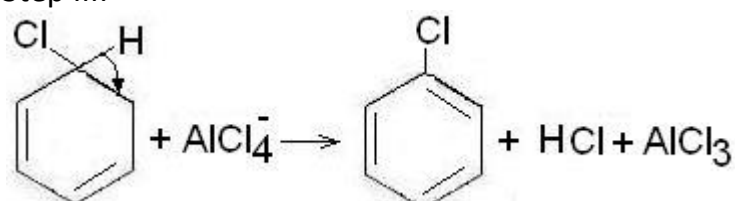
Mechanism



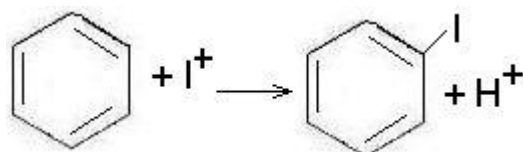
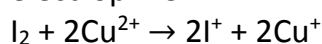
Step II:



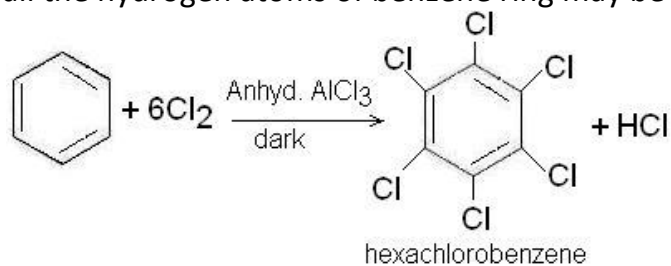
Step III:



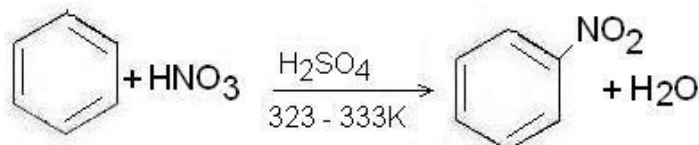
- Fluorine is extremely reactive and gives very poor yield under similar conditions
- Iodination is carried out in presence of oxidizing agents such as hydrogen peroxide or cupric chloride which oxidize molecular iodine into an electrophile



With excess of halogens in presence of anhydrous AlCl_3 (catalyst) and dark, all the hydrogen atoms of benzene ring may be successively replaced.

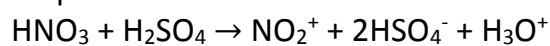


2. Nitration

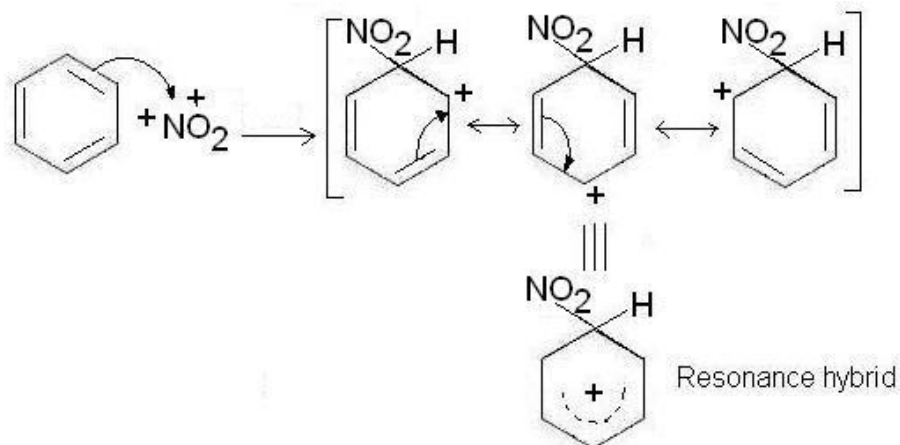


Mechanism

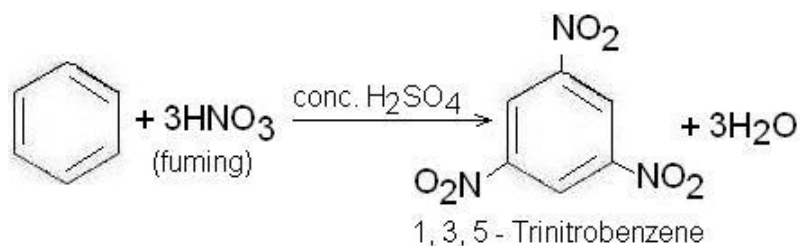
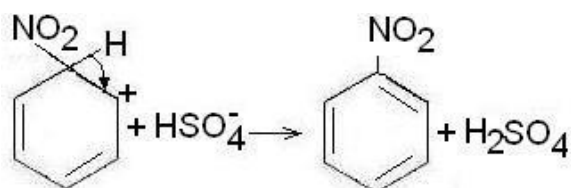
Step I



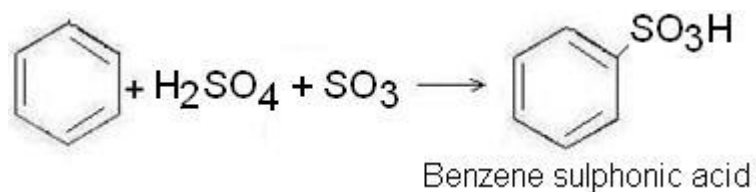
Step II



Step III

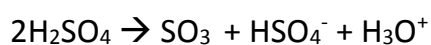


3. Sulphonation

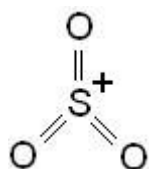


Mechanism

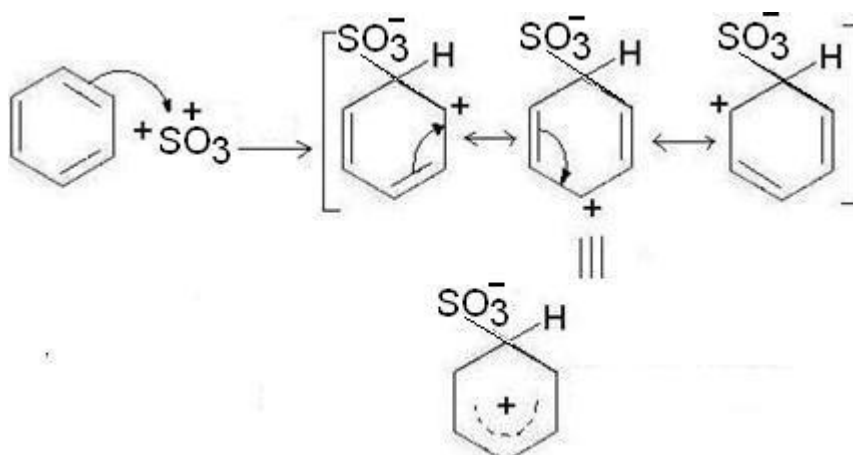
Step I



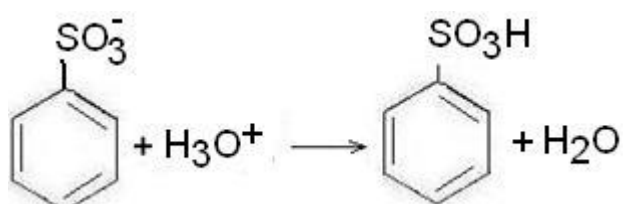
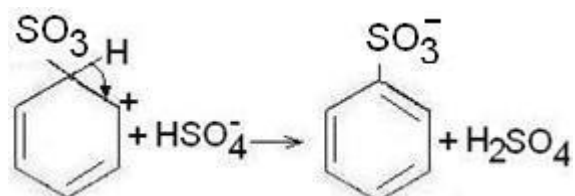
In sulphonation SO_3 acts as attacking electrophile since sulphur atom in SO_3 is electron deficient



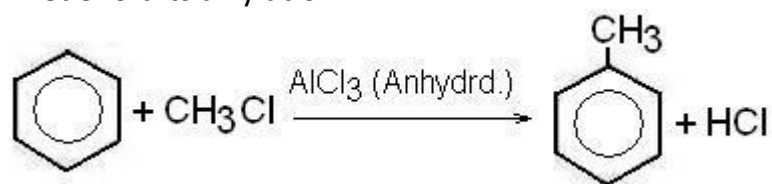
Step II



Step III

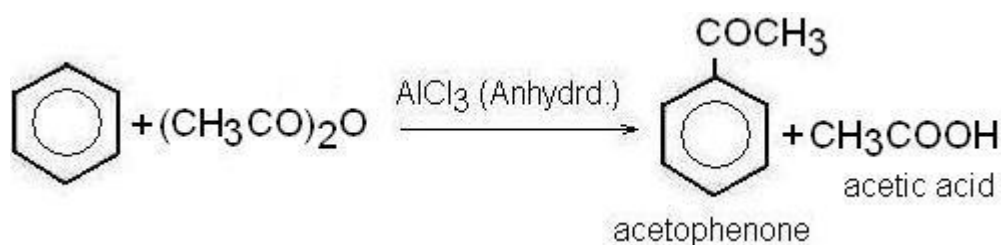
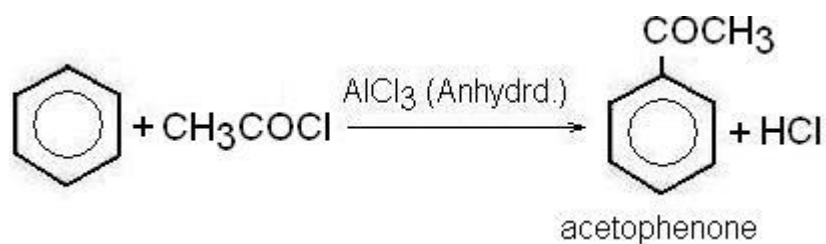
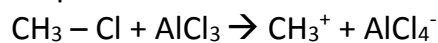


4. Friedel Crafts alkylation



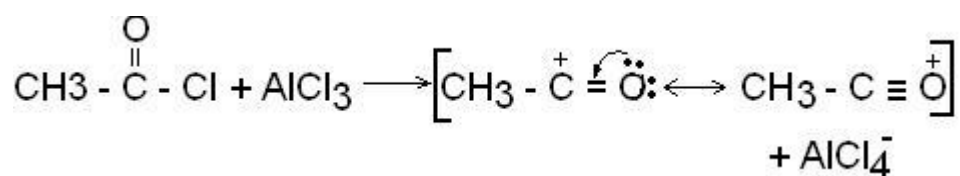
Mechanism

Step I

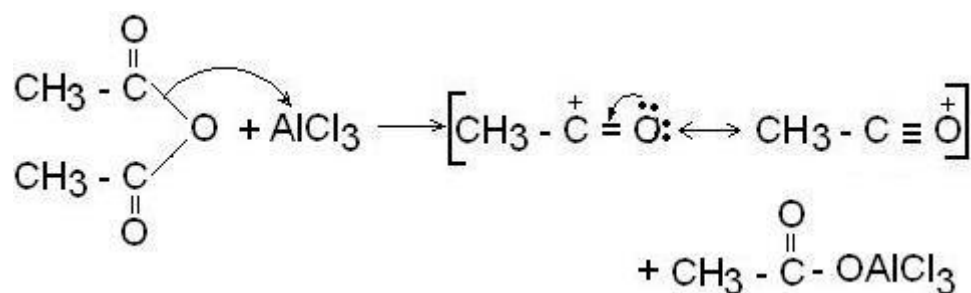


Mechanism

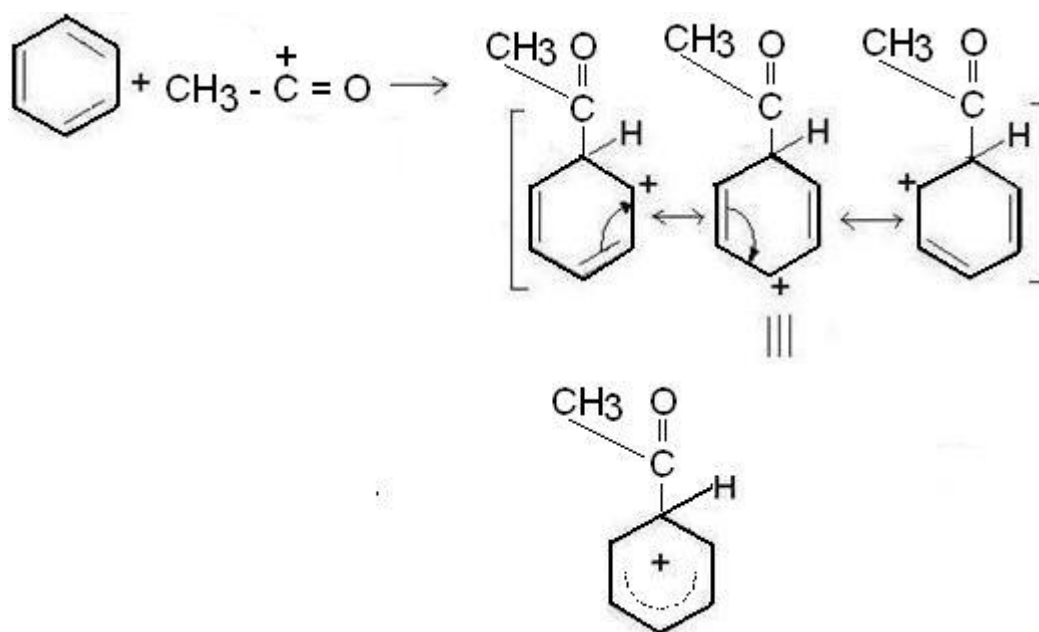
Step I



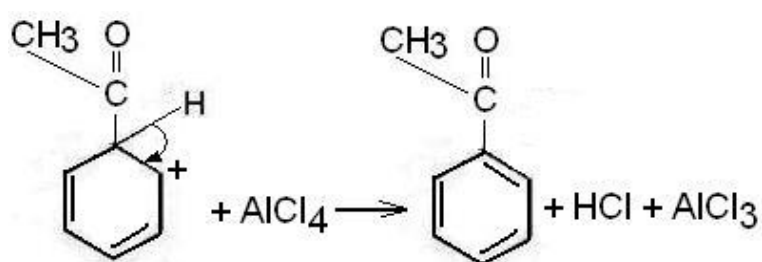
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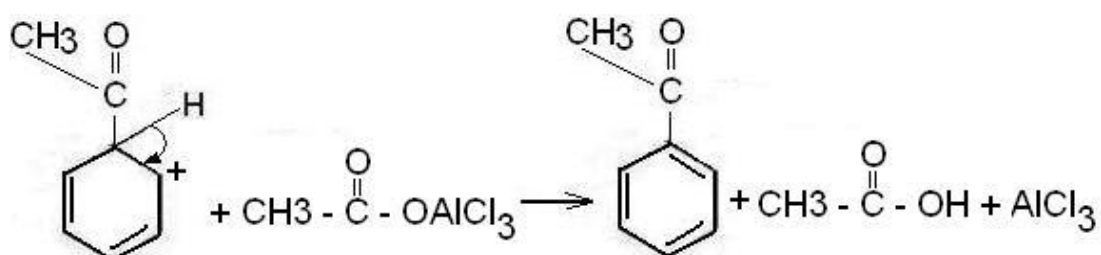
Step II



Step III

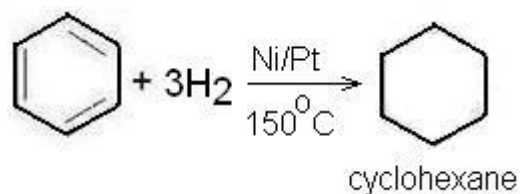


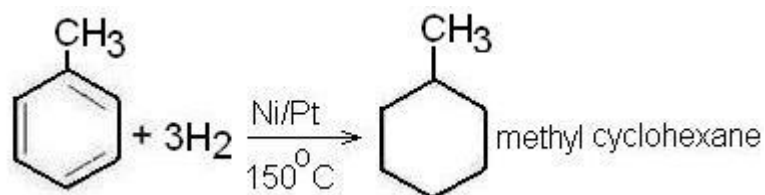
OR



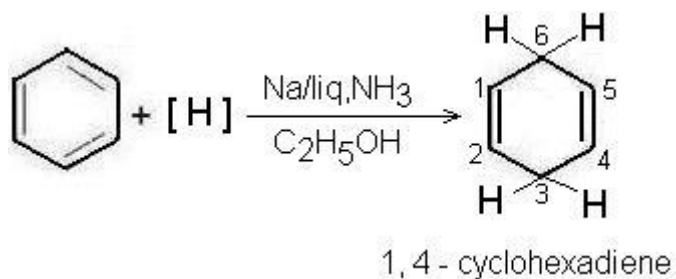
II) Addition reactions

1. Catalytic hydrogenation

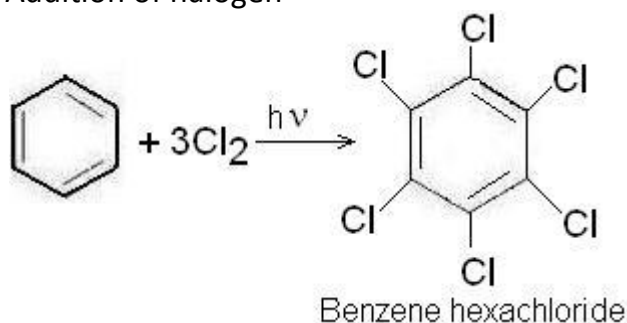




Birch reduction takes place in presence of Na metal and liquid NH_3



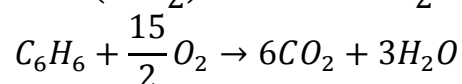
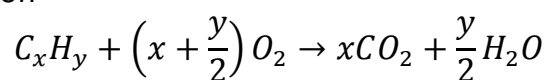
2. Addition of halogen



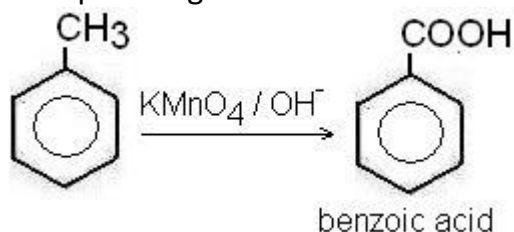
Benzenehexachloride is used as powerful insecticide under the name of gammexane or 666 or lindane

III) Oxidation

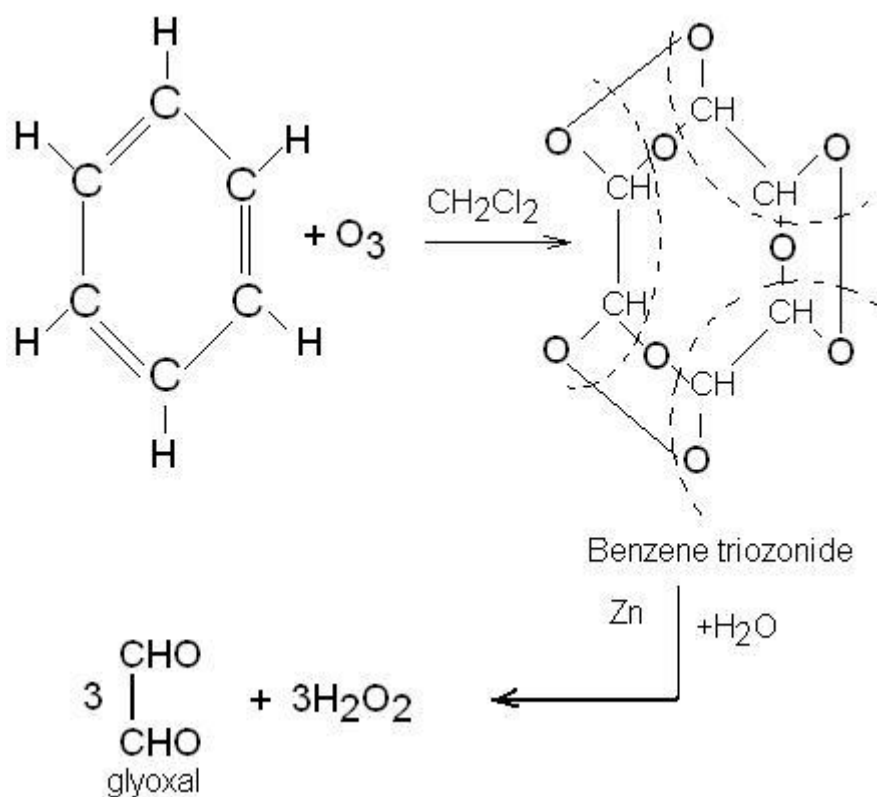
1. Complete combustion



2. Oxidation with potassium permanganate

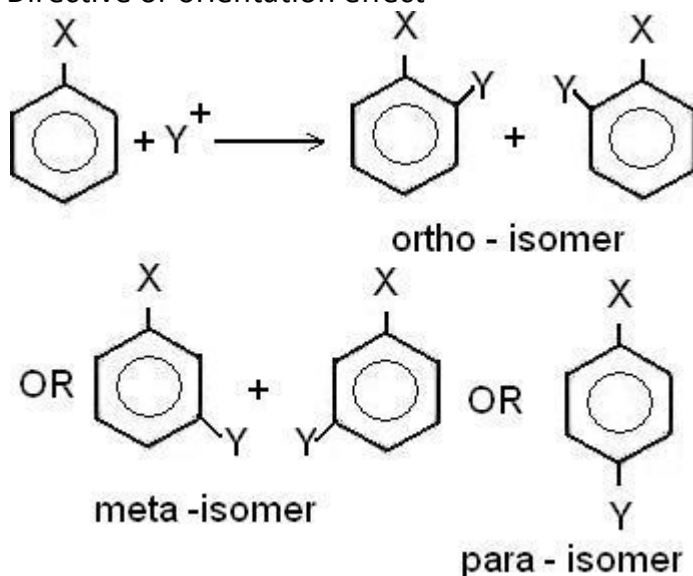


(IV) Ozonolysis



DIRECTIVE INFLUENCE OF A FUNCTIONAL GROUP IN MONOSUBSTITUTED BENZENE

1. Directive or orientation effect



(i) o, p – directing groups

The substituent's or groups which direct the incoming group to ortho and para positions are called o,p – directing groups

Example: -R (alkyl), -C₆H₅, -OH, -SH, -NH₂, -NHR, -NR₂, -NHCOR, -OR(alkoxy), -Cl, -Br, I.

- In general electron-donating group are o,p directing. Halogens (-Cl, -Br, -I) and nitroso (-N=O) are exception to it which are electron withdrawing but o,p – directing.
- Out of ortho- and para-, gerally para- substitution predominates because ortho – substitution is accompanied with steric hindrance.

(ii) m- directing groups

The substituents or groups which direct the incoming group at the meta position are called m-directing groups.

Example: -SO₃H, -COOH, -COOR, -COR, -CHO, -CCl₃, -CF₃, -CN, -COCl, -NO₂, -N⁺H₃, -N⁺H₂R, -N⁺HR₂, -N⁺R₃, -SO₂Cl, -N⁺H₃Cl

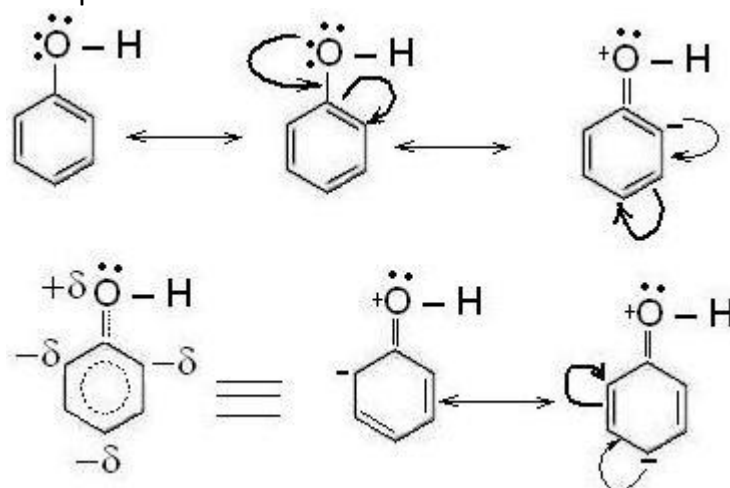
- In general all electron withdrawing are m-directing

2. Activity effect (Effect of substituent on reactivity)

(i) Activating groups

- Electron releasing group i.e. o,p-directing groups activate the benzene ring by increasing its nucleophilicity for further substitution.

Example

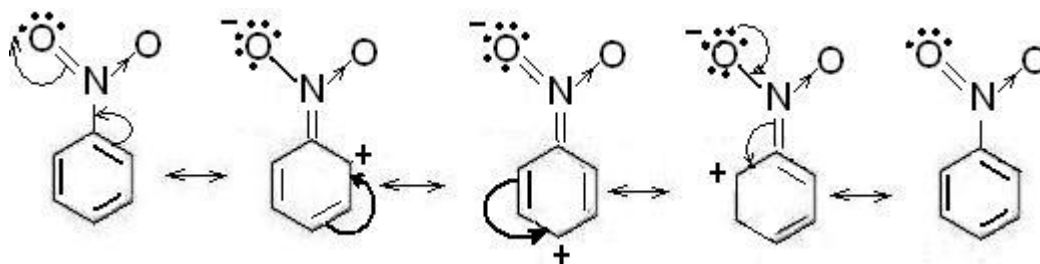


It is clear from the above resonating structures that the electron density is more on o- and p- positions

- Halogens (-Cl, -Br, -I) and nitroso group (- N = O) which are o, p – directing but deactivates the benzene ring being electron withdrawing
- Order of electron donating capability
 $-O^- > -NR_2 > -OH > -NH_2 > -OCH_3 > -NHCOCH_3 > -CH_3$

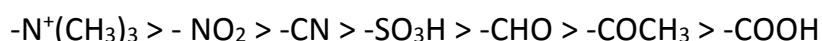
(ii) Deactivating group

Electron withdrawing groups i.e. m-directing group deactivate the ring by decreasing nucleophilicity for further substitution.

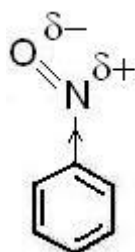


In this case, the overall electron density on benzene ring decreases making further substitution difficult.

Electron withdrawing ability order:

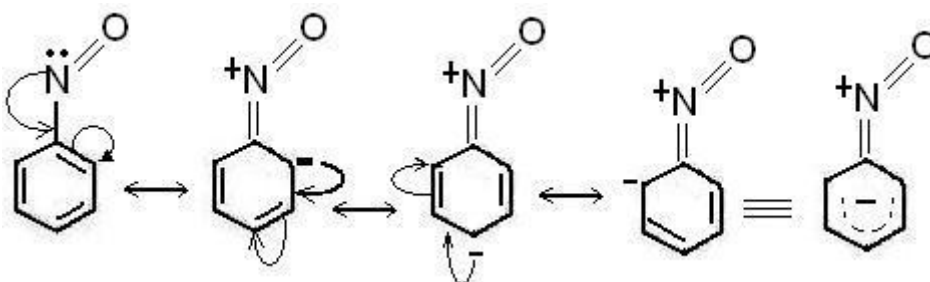


Halogens also come under the category of deactivating group, with the exception that they are o, p- directing. Because of $-I$ effect, halogens are electron withdrawing but o, p- directing due to $+R$ effect.



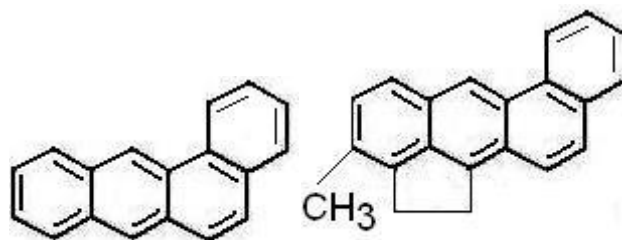
Nitro group ($-N=O$) is also deactivating but o,p-directing. Oxygen is more electronegative than nitrogen and hence NO group as a whole withdraws electrons from benzene ring and produce deactivating effect on the ring.

But lone pair of electrons on the N atom can be donated towards the benzene ring, thus increasing electron density more at o,p-positions rather than at m-position which makes it o,p-directing.

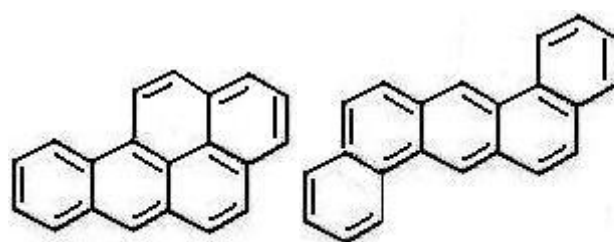


CARCINOGENITY AND TOXICITY OF POLYNUCLEAR HYDROCARBONS

- Polynuclear hydrocarbons are toxic and said to possess cancer producing (carcinogenic) property. In fact, polynuclear hydrocarbons are the products of incomplete combination of organic matter such as coal, petroleum, tobacco etc.
- They enter into the human body and undergo various biochemical reactions and finally damage DNA to cause cancer.



1,2-benzanthracene 3-methyl cholanthrene



1,2-benzopyrene 1, 2, 5, 6 -dibenzanthracene