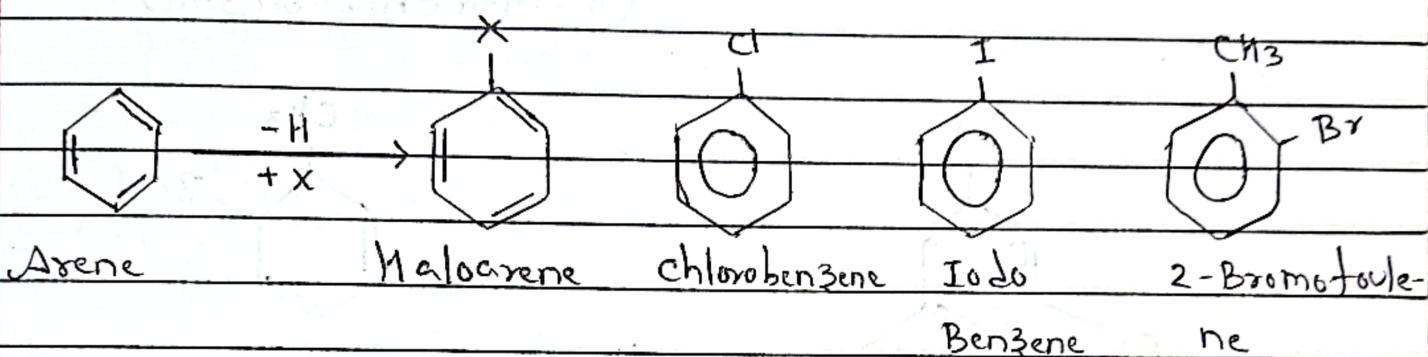


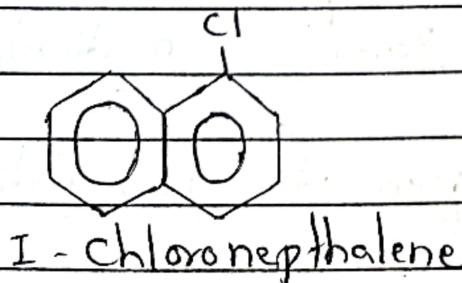
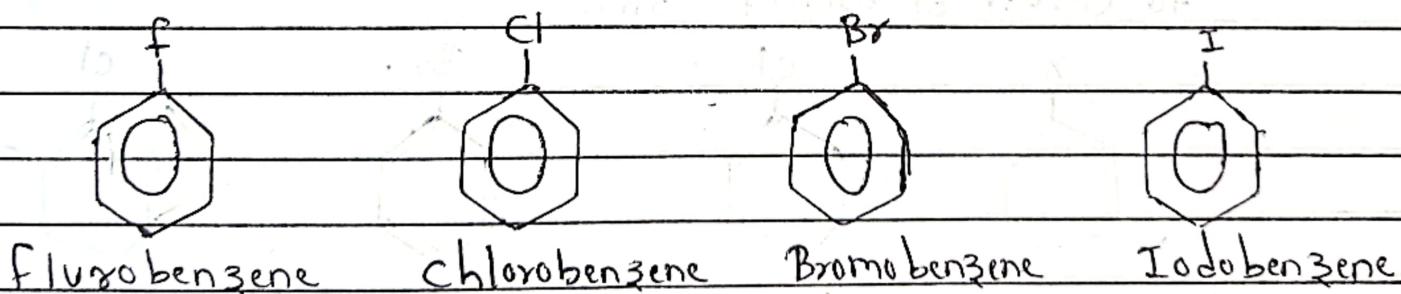
Introduction

- Haloarenes are compounds in which halogen atom is directly attached to aromatic ring.
- They are represented by $\text{Ar}-x$ where $\text{Ar}-$ is an aryl group ($\text{Ar}-$ Phenyl or substituted phenyl).

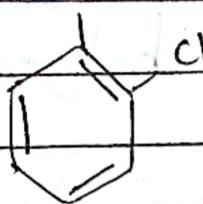


Nomenclature

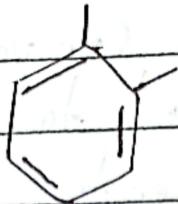
- According to IUPAC system, the haloarene is named by indicating halo first and then aromatic ring.
- IUPAC name = Halo + arene = Haloarene



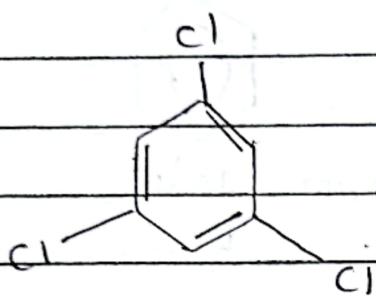
- If more than one substituent are present, the number is given for locant.



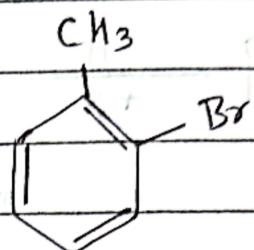
1,2 - dichlorobenzene



2-nitrochlorobenzene
(o-Nitrochlorobenzene)



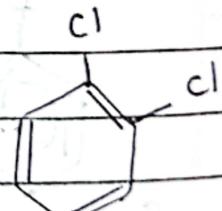
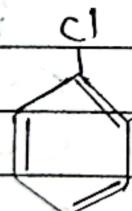
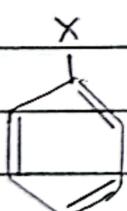
1,3,5 - Trichlorobenzene



2 - bromotoluene
(o-bromotoluene)

Classification of Haloarenes

1. Aryl Halide: The halogen atom is directly bonded to carbon of aromatic ring.



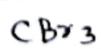
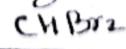
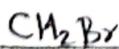
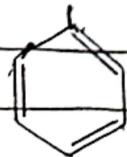
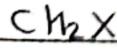
Chlorobenzene

Bromobenzene

1,2 - dichlorobenzene

o - dichlorobenzene

2. Aryl alkyl halide: The halogen atom is not directly bonded to carbon of aromatic ring.



Benzyl Bromide

Benzal bromide

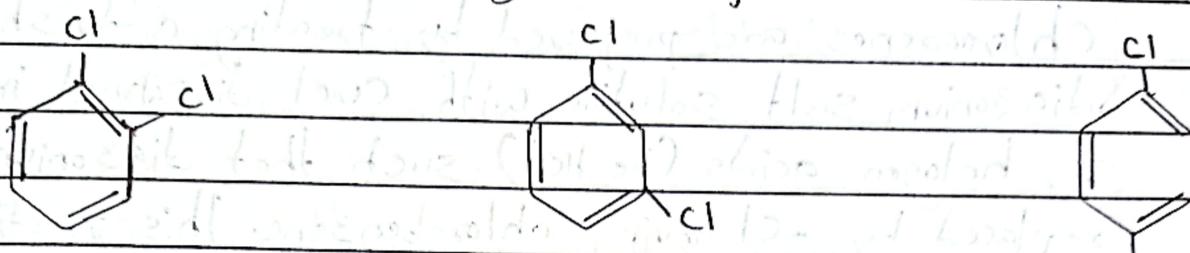
Benzo Tribromide

Dibromomethyl benzene

Tribromomethyl Benzene

Isomerism in Haloarenes

- If two halogen atoms are present in same benzene ring, the compounds are named as ortho (1,2), meta (1,3) and para (1,4) according to the position of locants.



1-2 dichlorobenzene

1-3, dichlorobenzene

o-dichlorobenzene

m-dichlorobenzene

Cl

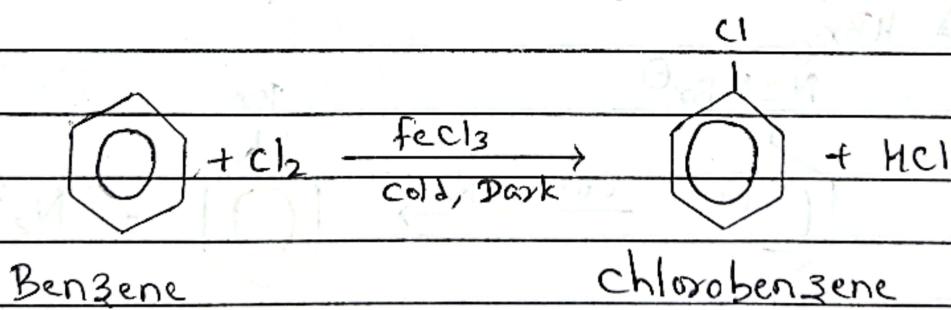
1,4 dichlorobenzene

p-dichlorobenzene

General Methods of preparation of Haloarenes

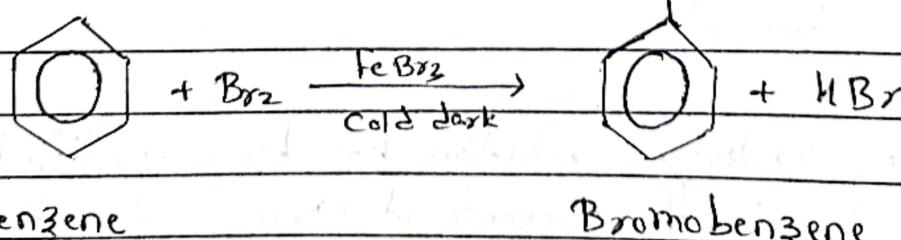
1. From Benzene

- Haloarenes are prepared by treating benzene with halogen in presence of halogen carrier or lewis acid such as FeCl_3 , FeBr_3 or AlCl_3 as catalyst.



Benzene

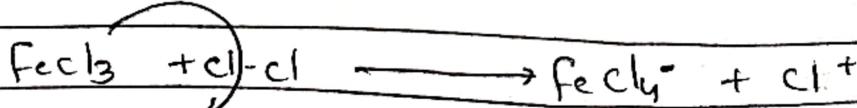
chlorobenzene



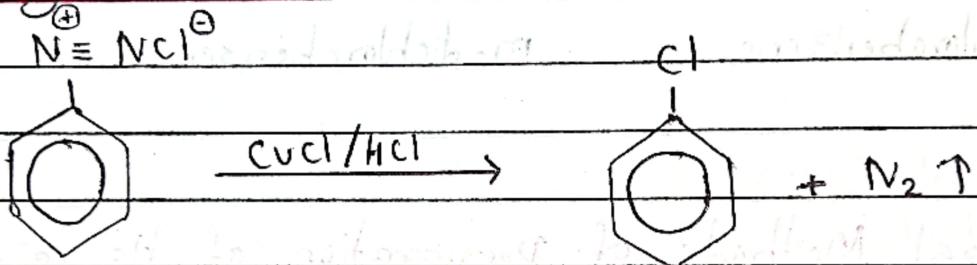
Benzene

Bromobenzene

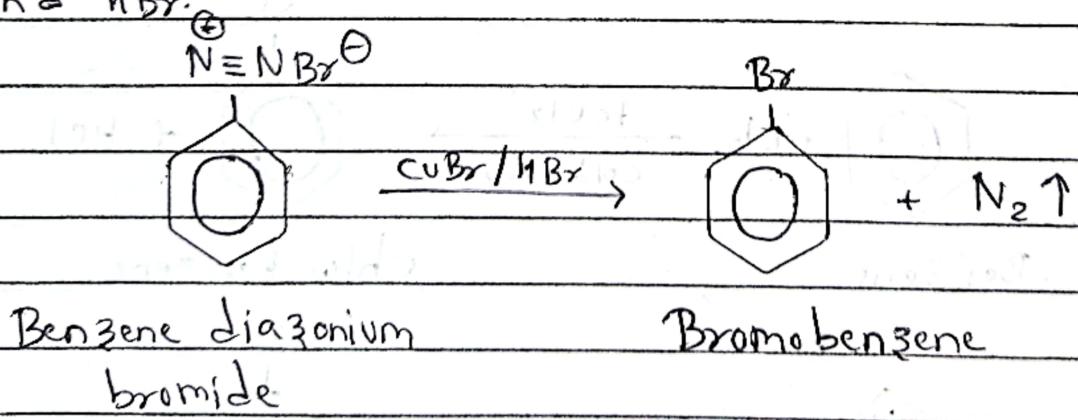
- FeCl_3 helps to generate Cl^+ (chloronium) electrophile easily from Cl_2 .



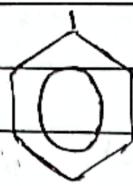
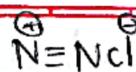
- Chloronium ion (Cl^+) displaces H^+ from benzene to give chlorobenzene.
 - 2. From benzene diazonium chloride
 - Chloroarenes are prepared by treating a freshly prepared diazonium salt solution with CuCl dissolved in corresponding halogen acids (i.e. HCl) such that diazonium group is replaced by $-\text{Cl}$ giving chlorobenzene. This reaction is called Sandmeyer reaction.



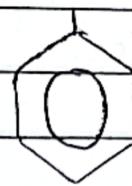
- Similarly Bromoarenes can be prepared by using CuBr and HBr.



- The Sandmeyer reaction has been modified by using copper powder in the presence of corresponding halogen acid (i.e. HCl) in place of cuprous chloride ($CuCl$). The modified reaction is called as Gattermann reaction.



$\xrightarrow{\text{Cu/HCl}}$



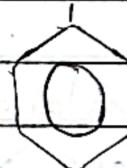
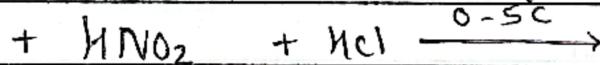
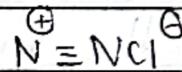
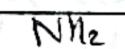
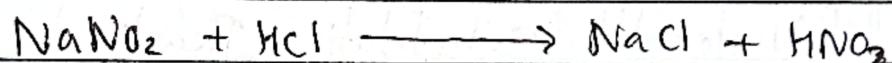
+ $\text{N}_2 \uparrow$

Benzene diazonium chloride

chlorobenzene

Note:

The diazonium salt required for this purpose are prepared by treating a cold acid solution of aniline with a well cooled aqueous solution of sodium nitrite, maintaining the temperature below 5°C. The reaction is known as diazotization reaction.



Aniline

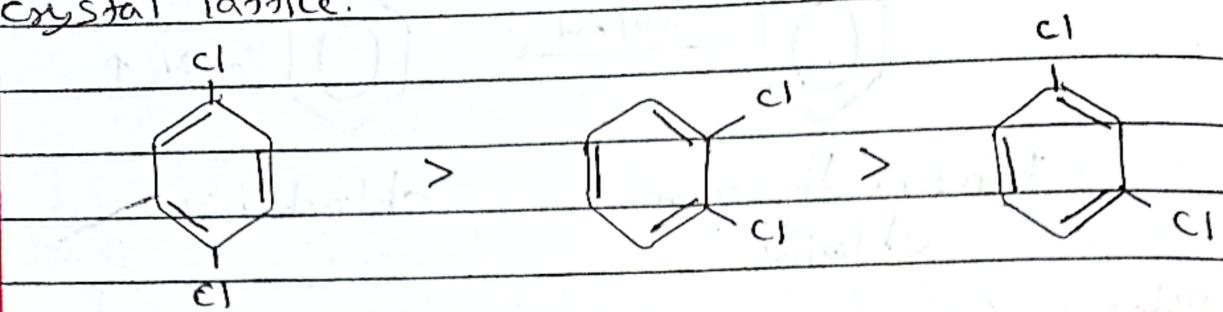
Acidic substitution

Benzene diazonium chloride

Properties of Haloarenes

- They are colorless oily liquid or crystalline solid with characteristic pleasant smell.
- They are insoluble in water and soluble in organic solvent.
- They are heavier than water and density increase continuously with increase in molecular mass of halogen atoms.
- Their melting and boiling point increases regularly with rise in molecular mass.
- In isomeric dihaloarene boiling point are nearly similar however melting point of para isomer is greater than that of ortho and meta isomers. This is due to symmetrical

structure which leads to more close packing in the crystal lattice.



p-dichlorobenzene

M.P. = 52°C

o-dichlorobenzene

M.p. = -17°C

m-dichlorobenzene

M.P. = -24°C

Chemical Properties:

Reaction due to Halogen (chloride) atom
(Nucleophile Substitution Reaction)

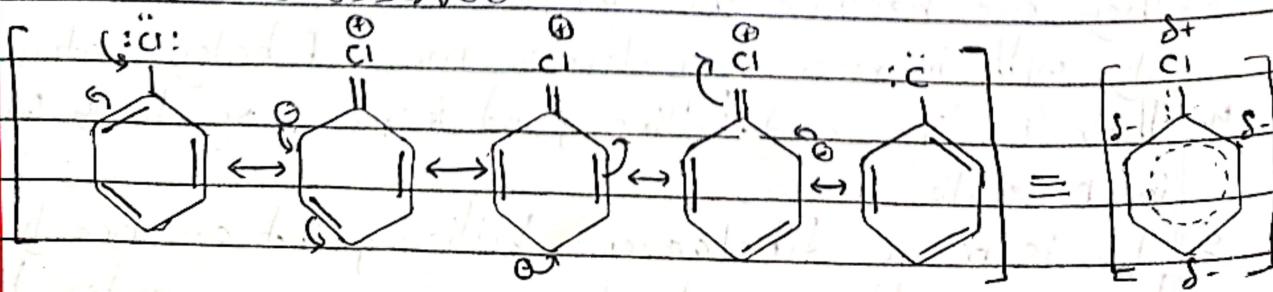
- Haloarenes like chlorobenzene are less reactive towards the nucleophilic substitution reaction than alkyl halides

Explanation

- Less reactivity of Haloarenes (chlorobenzene) towards nucleophilic substitution reaction can be explained on the basis of following effect.

Resonance Effect

- In Haloarenes (chlorobenzene), as halogen (chlorine) atom has a tendency to share its lone pair of electron with aromatic benzene ring as a result, following resonating structures are observed.



Resonating Hybrid

Resonance Hybrid

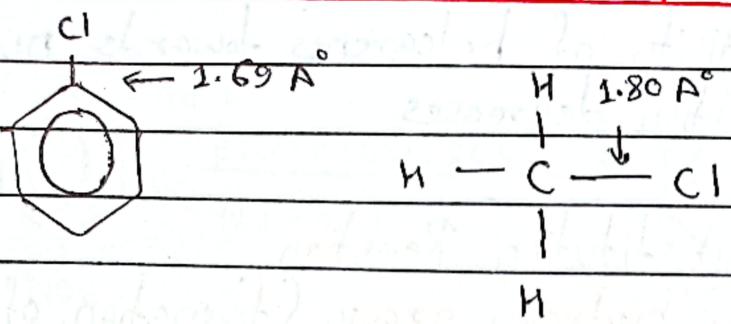
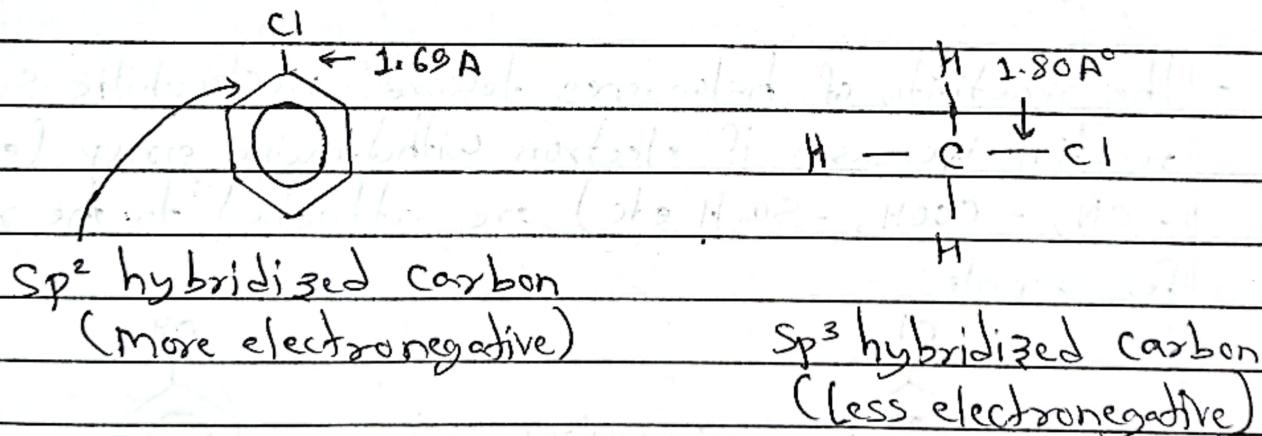


Fig: C-Cl bond in Haloarene and haloalkane

From the above resonating structure, it is cleared that the carbon and halogen (chlorine) atom have developed partial double bond character, which is shorter. Hence stronger than single covalent bond. As a result, the halogen atom is highly tightly held with aromatic ring. It makes the halogen atom more difficult to substitute by attacking nucleophile.

Hybridization Effect



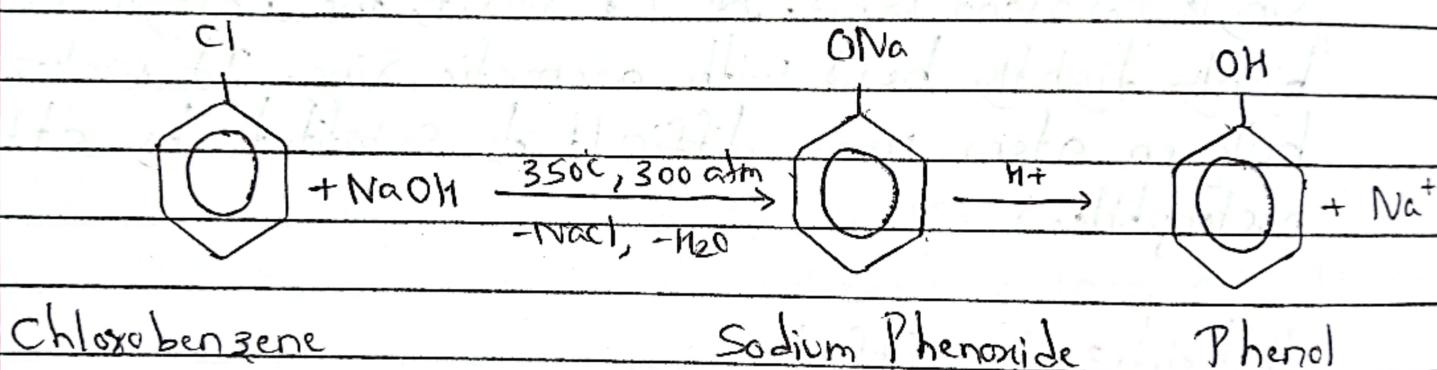
- In chlorobenzene (haloarene) Carbon is sp^2 -hybridized while in haloalkane it is sp^3 hybridized. sp^2 hybridized carbon (s-character 33%) is more electronegative than sp^3 -hybridized (s-character 25%), as a result, the shared paired of electron between carbon and halogen are pulled effectively towards benzene ring, due to which carbon halogen bond length decreases. so it makes the -Cl atom more difficult to substitute by attacking nucleop-

hile. Thus, reactivity of haloarenes towards nucleophilic substitution reaction decreases.

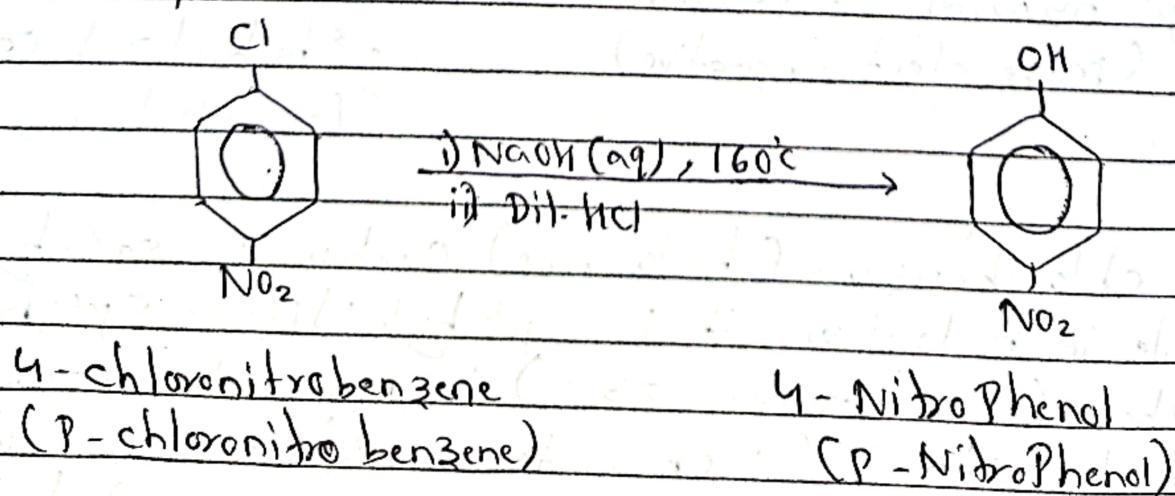
A. Nucleophilic Substitution Reaction

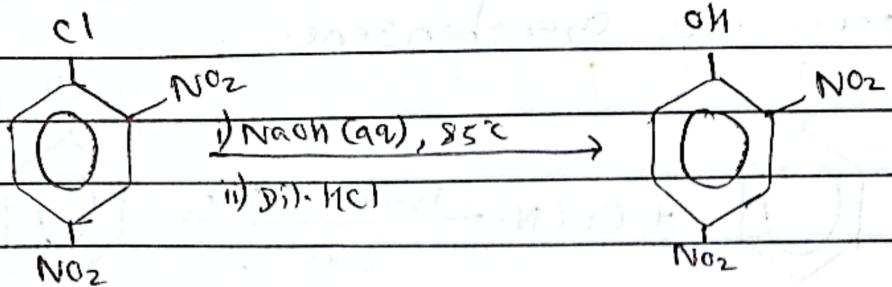
1. Substitution by hydroxy group (formation of Phenol): Dow's Process

- Chlorobenzene on heating with an aqueous solution of NaOH at 350°C under 300 atmospheric pressure gives sodium phenoxide which on subsequent acidification produces phenol.



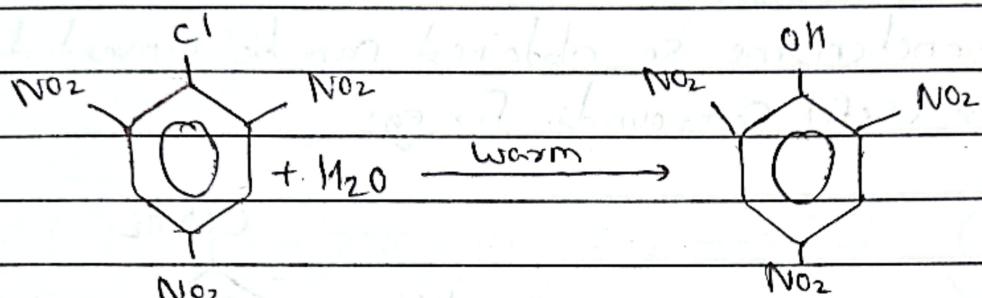
- The reactivity of haloarenes towards nucleophilic substitution reaction increases if electron withdrawing group (e.g. -NO₂, -CN, -COOH, -SO₃H etc.) are attached to the ring.
- For example:





2,4-dinitrochloro
Benzene

2,4-dinitrophenol



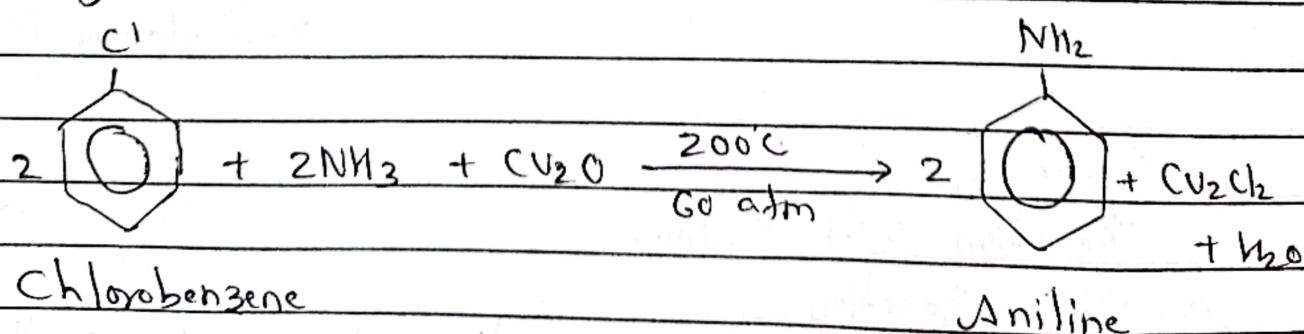
2,4,6-Trinitrochloro
Benzene

2,4,6-Trinitrophenol

Thus, the reactivity of halogenes increases with increasing no. of electron withdrawing substituents.

2. Substitution by amino group (formation of aniline)

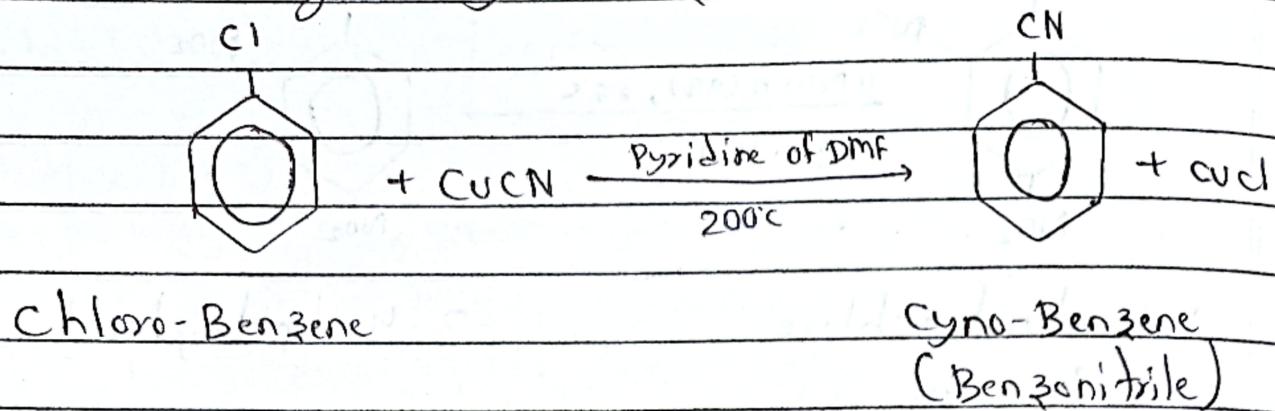
Chlorobenzene on heating with aqueous ammonia at about 200°C under 60 atm pressure and in the presence of catalyst Cu₂O yields aniline.



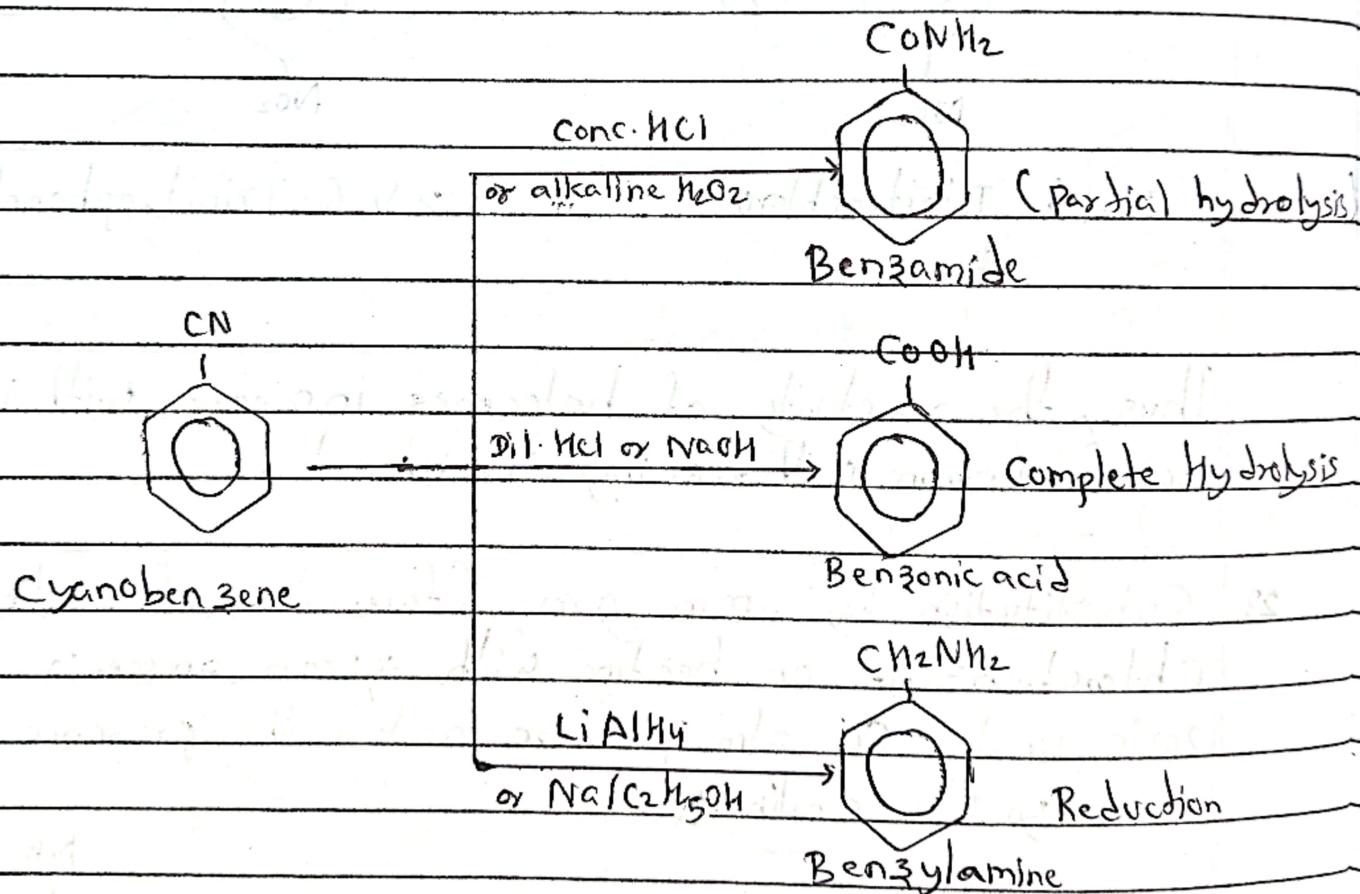
3. Substitution by cyano group (formation of cyanobenzene)

Chlorobenzene on heating with anhydrous cuprous cyanide in the presence of pyridine or dimethylformamide (DMF) at

about 200°C gives cyanobenzene.



The cyanobenzene so obtained can be converted into no. of other useful compounds. For eg.:

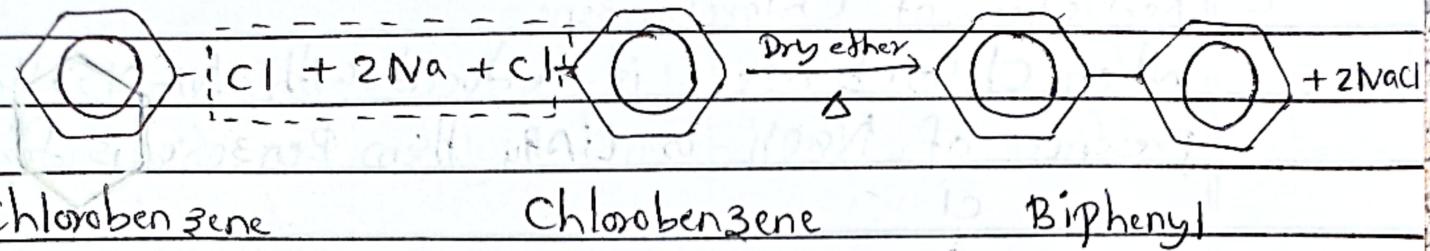


B. Reaction with Metals

Reaction with Sodium

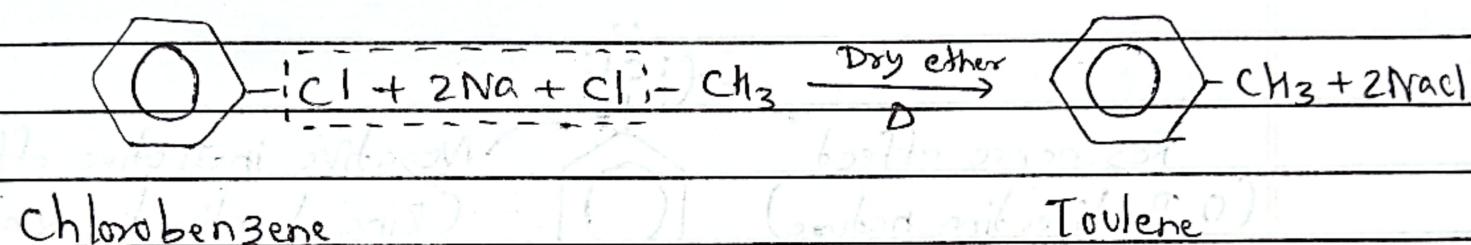
a. Fittig Reaction

Halobenzene on heating with sodium metal in the presence of dry ether form biphenyl. This reaction is called fittig reaction.



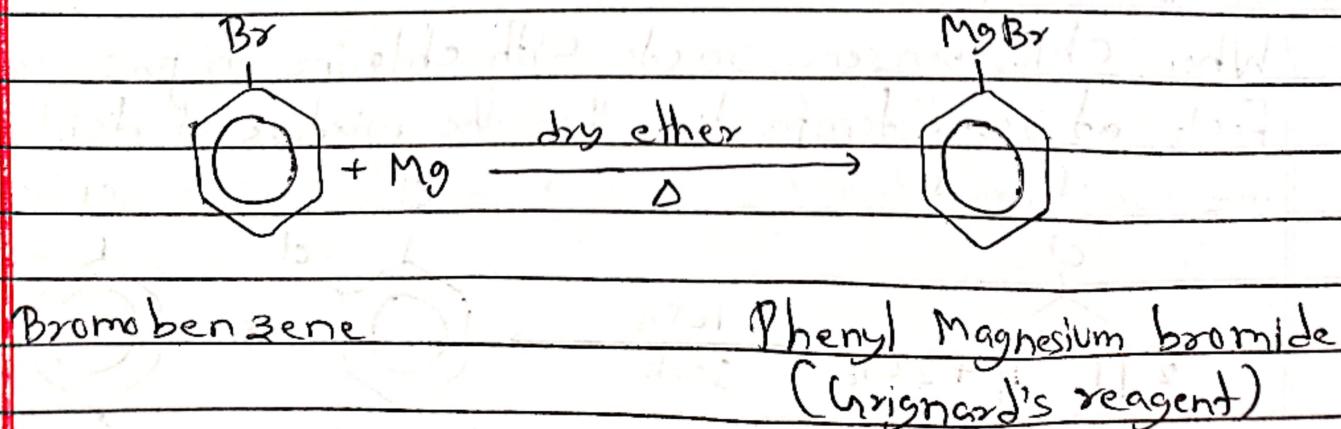
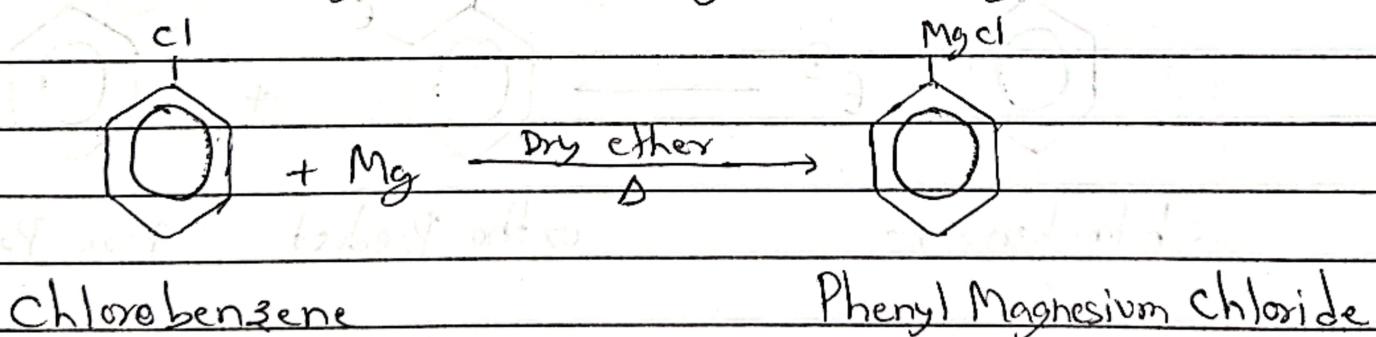
b. Wurtz - Fittig Reaction

However, halobenzene when heated with haloalkanes and sodium metal in dry ether undergo Wurtz - Fittig reaction forming alkyl benzene.



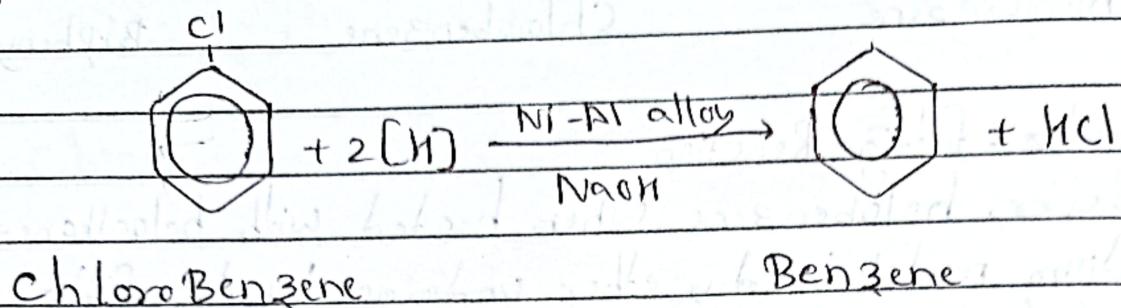
Reaction with Magnesium (Grignard Reagent)

When halocarbenes are heated with magnesium metal in presence of dry ether or THF then aryl magnesium halide is formed which is commonly called as Grignard's reagent.



c. Reduction of Chlorobenzene

Reduction of Chlorobenzene
When chlorobenzene is reduced with Ni-Al alloy in presence of NaOH or LiAlH₄, then Benzene is formed.



D. Electrophilic Substitution reaction

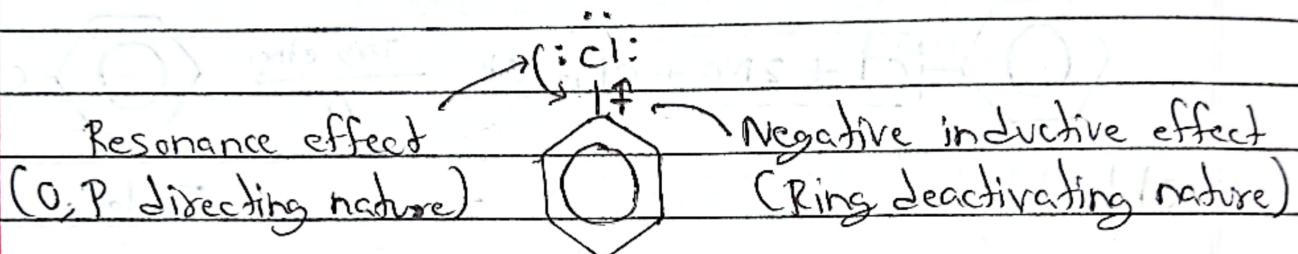
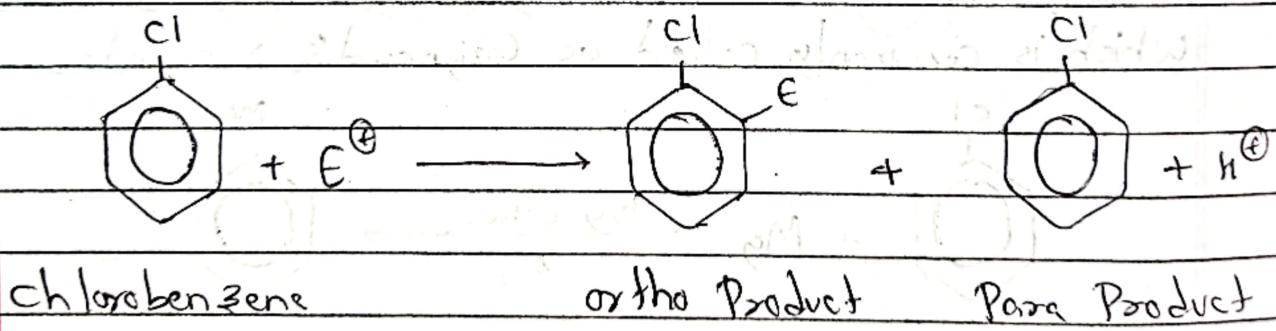
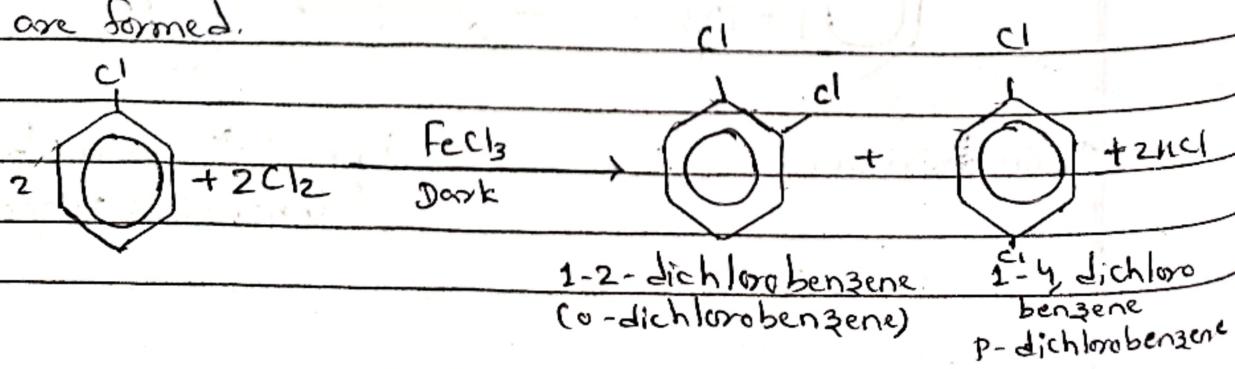


Fig: O, P directing and ring deactivating nature of Benzene



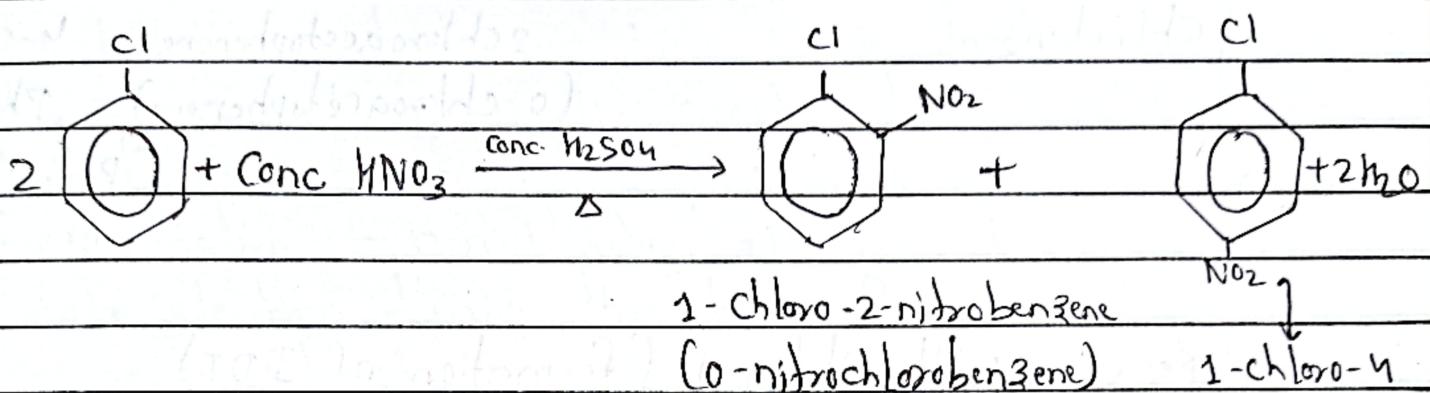
1 || Halogenation

When chlorobenzene reacts with chlorine in presence of FeCl_3 at room temperature then the mixture of dichloro-benzene are formed.



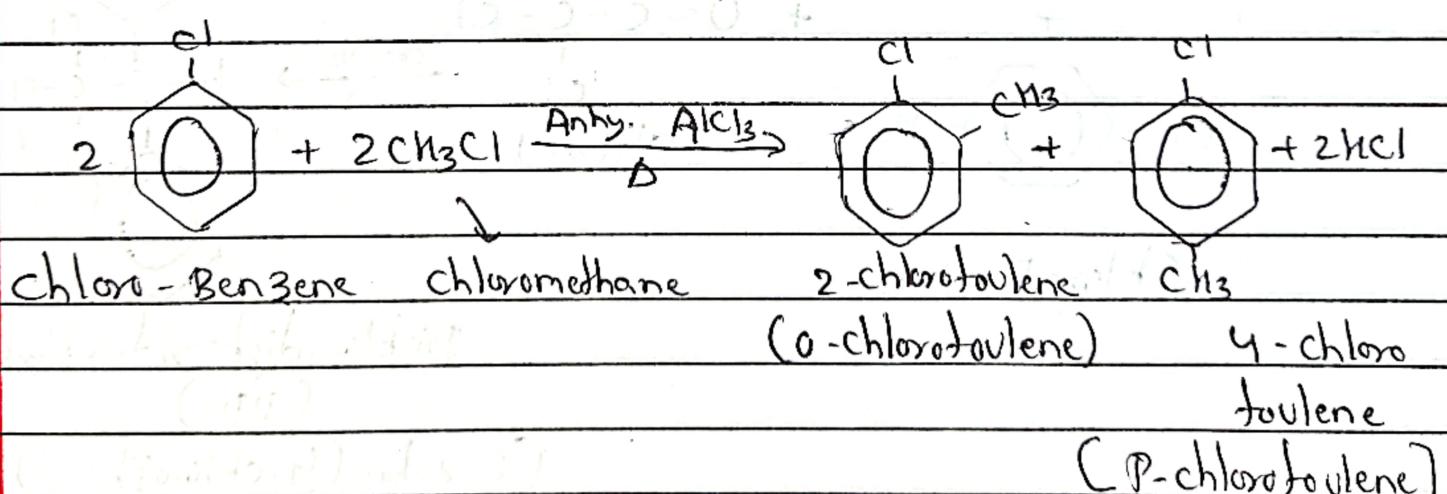
2. Nitration

When chlorobenzene is heated with conc. Nitric acid and conc. Sulphuric acid as catalyst then the mixture of nitrochlorobenzenes are formed.



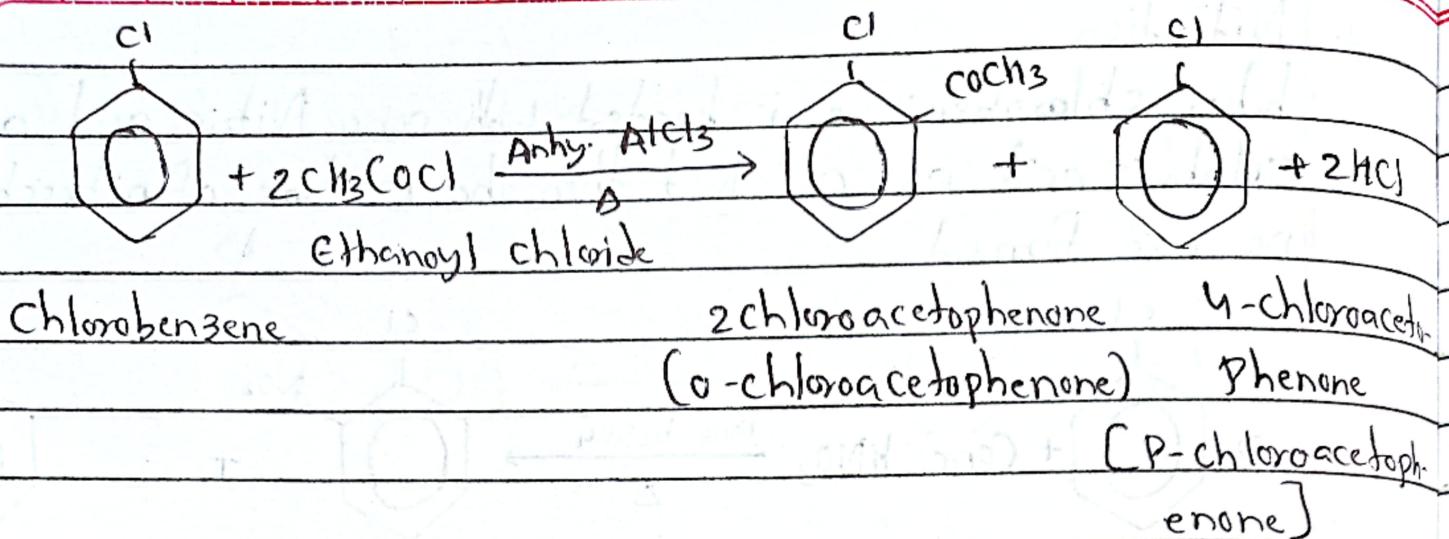
3. Sulphonation

When chlorobenzene is heated with conc. Sulphuric acid then the mixture of chlorobenzene sulphonic acid are formed.



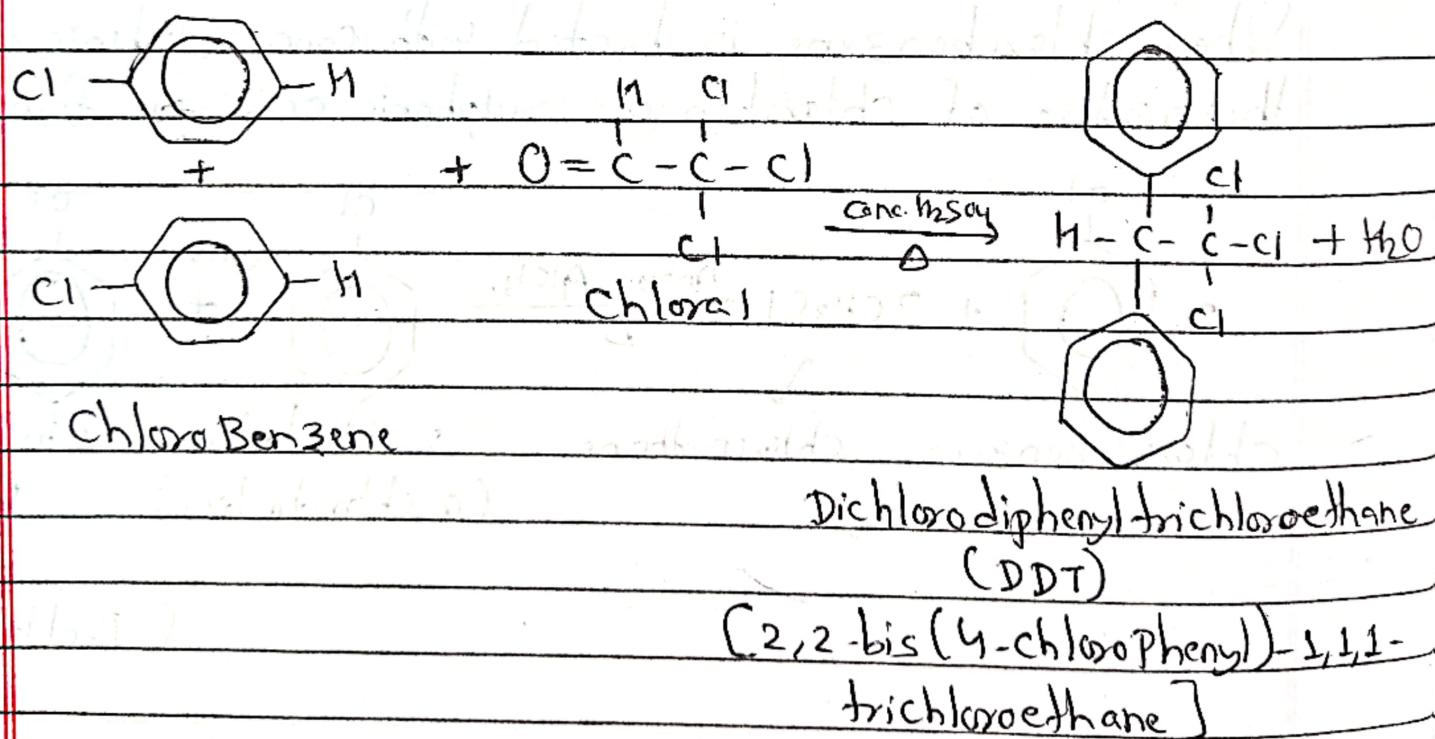
5. Friedel-Craft's acylation

When chlorobenzene is heated with acetyl chloride or acetic anhydride in presence of anhydrous AlCl_3 then the mixture of chloroacetophenone are formed.



Reaction with chloral (formation of DDT)

When chlorobenzene is heated with chloral in presence of conc. H_2SO_4 then a crystalline solid of DDT is formed which is used as an insecticides.



Uses of Haloarenes

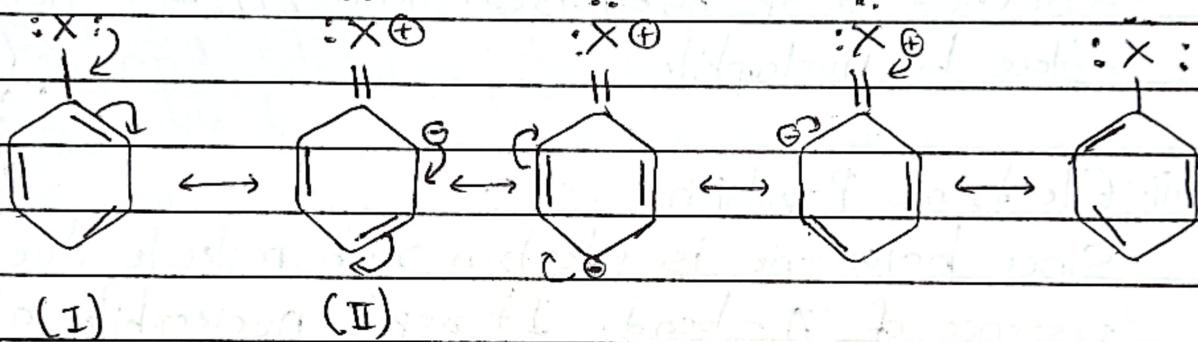
- They are largely used to prepare phenol, aniline, chlorotoluene, DDT, BHC, fungicides, preservatives etc.

Some Important Questions:

1. Why is haloarene less reactive than benzene in electrophilic Substitution reaction?

Ans: In haloarene, halogroup is a weak deactivating group. This means haloarene is less reactive toward electrophiles than benzene. Due to the presence of density through the formation of non-bonding electron, halo group can donate electron density through the formation of π bond.

Resonance structure of Haloarene

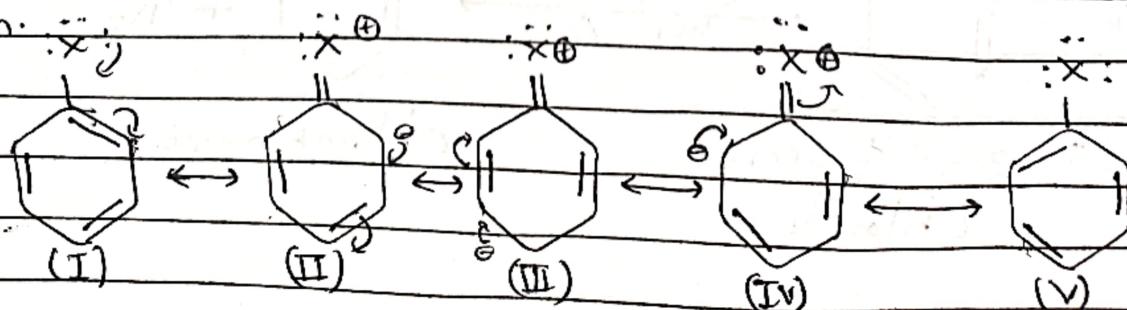


2. Why is haloarene less reactive than towards nucleophilic Substitution reaction than haloalkane?

Ans: Haloarene is less reactive towards nucleophilic substitution reaction than haloalkane due to the following reason.

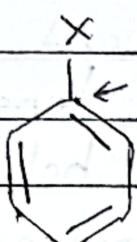
i. Resonance effect

In haloarene, the lone pair of electron on halogen atom is delocalized on the benzene ring. Due to this partial double bond is developed between carbon and halogen atom.



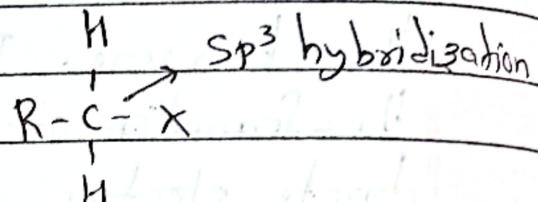
Hence, it is difficult to break down the carbon-halogen bond double bond in haloarene than in haloalkane for nucleophilic reaction.

ii. Difference of hybridization of carbon atom in C-X bond



Haloarene

$\leftarrow \text{sp}^2 \text{ hybridization}$



Haloalkane

$\rightarrow \text{sp}^3 \text{ hybridization}$

In haloarene the carbon atom to which the X-group is attached is sp^2 hybridized. Hence, it is difficult to replace by nucleophile.

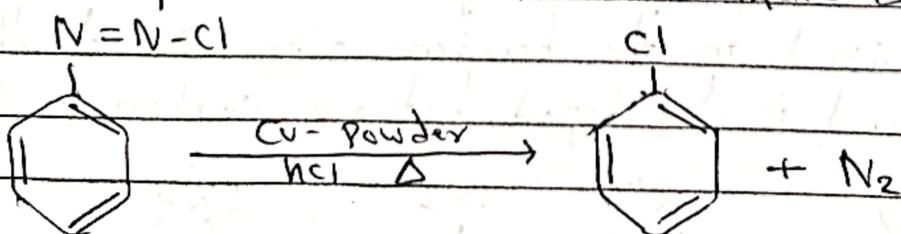
iii. Electronic Repulsion

Since haloarene is electron rich molecule due to the presence of π -bond. It repels nucleophile attacking.

Q. What product would you expect when;

- Benzene diazonium chloride is heated with copper powder in presence of HCl.
- Chlorobenzene is heated with 2,2,2-trichloroethanol.

Ans: i) When benzene diazonium chloride is heated with copper powder in presence of HCl, chlorobenzene is obtained.



Benzene diazonium
chloride

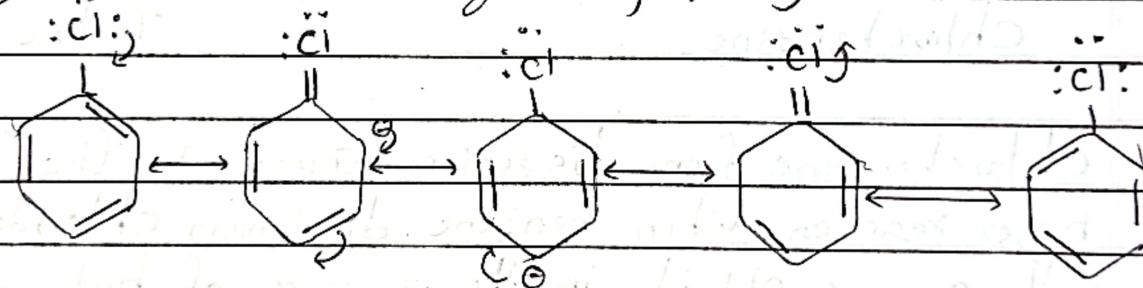
Chlorobenzene

$$2 \text{C}_6\text{H}_5\text{Cl} + \text{H}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{Cl})-\text{C}(\text{Cl})-\text{Cl} \xrightarrow[\text{-H}_2\text{O}]{\text{Conc. H}_2\text{SO}_4} \text{H}-\overset{\text{Cl}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}(\text{Cl})-\text{C}(\text{Cl})-\text{Cl}$$

 2,2,2-trichloroethanol
 (chloral)

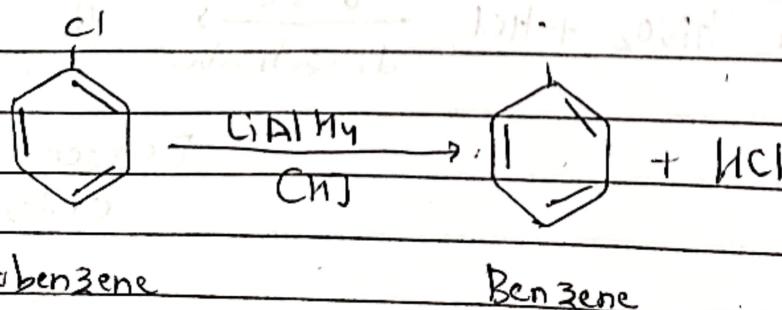
d. Why is nucleophilic substitution difficult in halocarbenes?

Ans: In haloarenes, carbon attached with halogen is sp^2 hybridization and stabilized by resonance. Due to the resonance, a double bond is developed between carbon and halogen atom and having less polarity of C-Cl bond.

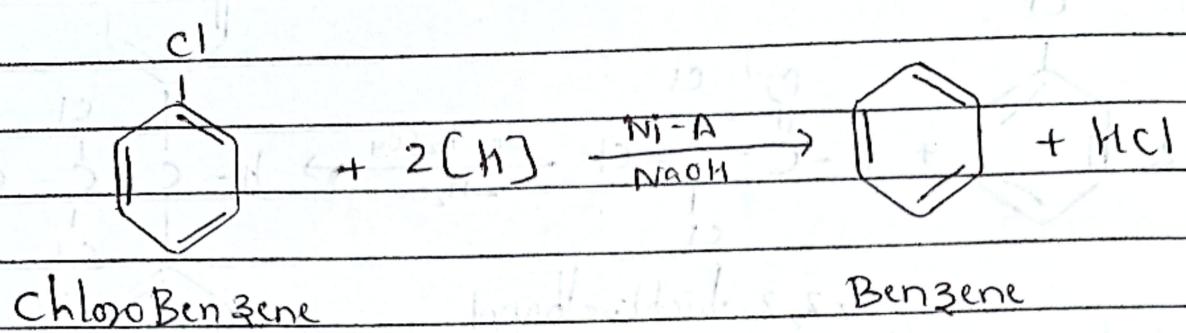


In case of haloalkane, there is no resonance and no double bond is developed between carbon and halogen atom. Therefore, haloarene doesn't easily undergo nucleophilic substitution as compared to haloalkane.

5i. Convert Benzene from chlorobenzene.

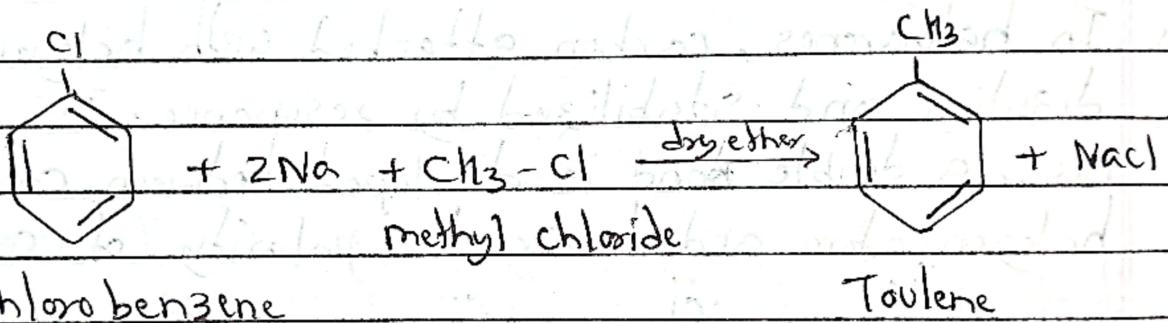


ii) Chlorobenzene is heated with Ni-Al in alkaline medium.

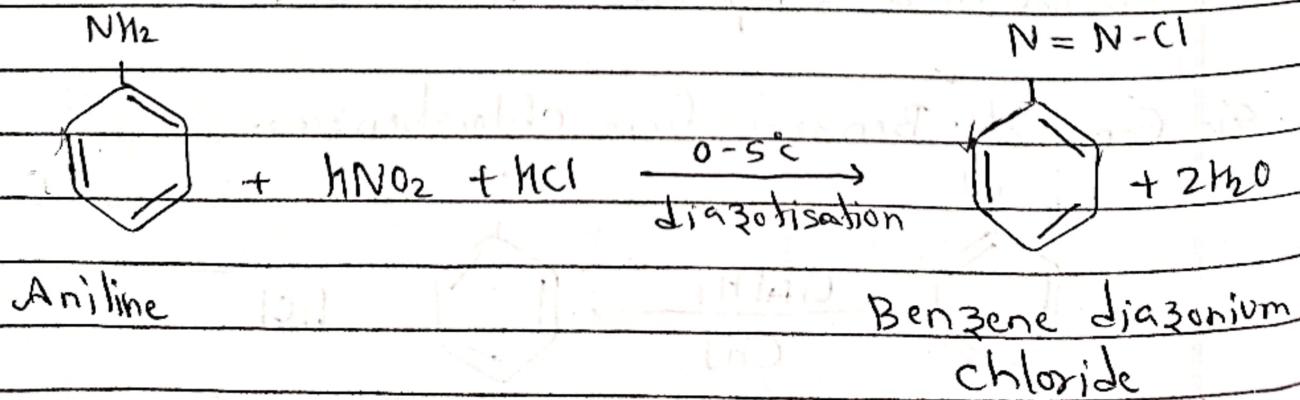


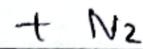
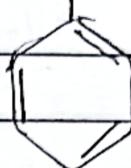
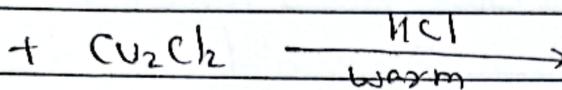
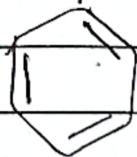
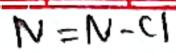
iii. Chlorobenzene into Toulene

When eth chlorobenzene and methyl chloride is heated with sodium metal in the presence of dry ether toulene is formed.



iv. Chlorobenzene from diazonium compounds (i.e Sandmeyer reaction), When benzene diazonium chloride is warmed with cuprous chloride in the presence of halogen acids, chlorobenzene is obtained. This reaction is known as Sandmeyer reaction. Benzene diazonium chloride is prepared from aniline by diazotization.





Chlorobenzene

6. Why does chlorobenzene give ortho and para products during electrophilic substitution reaction? Give its action on choral.

Ans: In the resonance of chlorobenzene, negative charge is developed on the ortho and para position. So, the electrophilic is attracted towards the negative charge and chlorobenzene is ortho and para director in electrophilic substitution.