

HALOALKANES AND HALOARENES

HALOARENES:

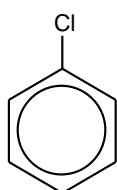
NEB Syllabus:

Haloarenes:

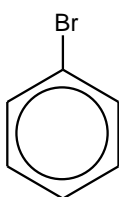
- Preparation of chlorobenzene from (i) Benzene (ii) Benzene diazonium chloride
- Physical properties
- Chemical properties
 - Low reactivity of haloarene as compared to haloalkane in term of nucleophilic substitution reaction
 - Reduction of chlorobenzene
 - Electrophilic substitution reaction
 - Action with Na, Mg, and chloral etc
- Uses

Introduction:

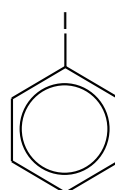
Halogen derivatives of aromatic hydrocarbons in which halogen atom is directly attached with aromatic ring are called haloarenes or aryl halides.



Chlorobenzene



Bromobenzene

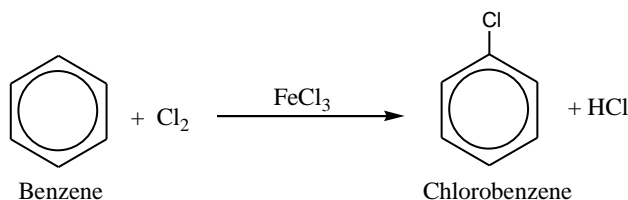


Iodobenzene

Preparation of aryl halide (Haloarene)

1) From benzene:

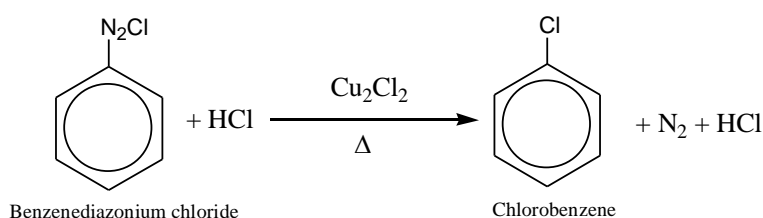
Benzene reacts with Cl_2 in presence of Lewis acid AlCl_3 or FeCl_3 as catalyst, chlorobenzene is formed.

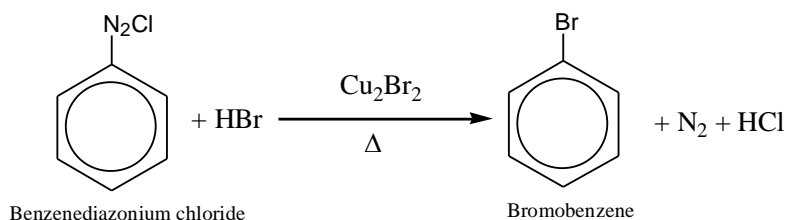


2) From benzene diazonium chloride:

a) Sandmeyer reaction:

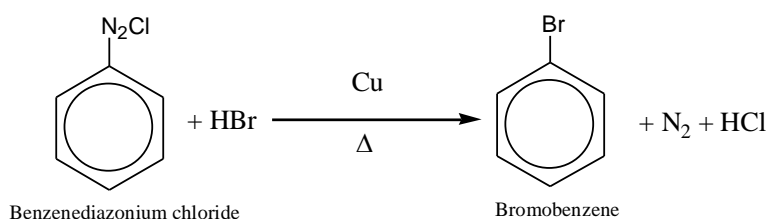
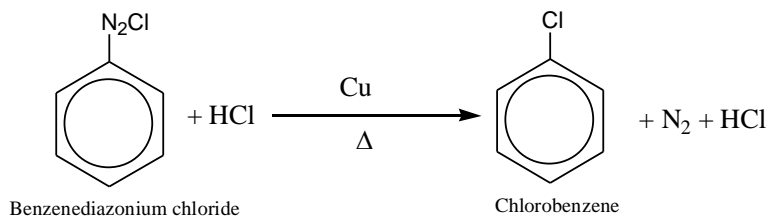
When benzene diazonium chloride is heated with Cu_2Cl_2 or Cu_2Br_2 in presence of corresponding halogen acid (HCl or HBr), chlorobenzene or bromobenzene is formed.





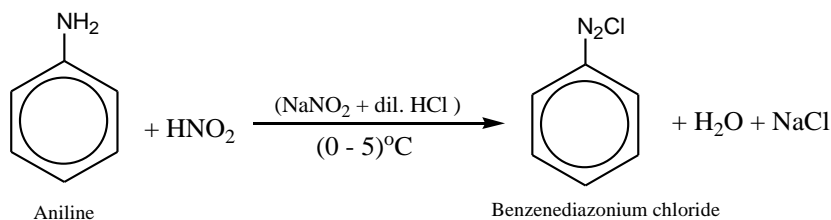
b) Gattermann reaction:

When benzene diazonium chloride is heated with Cu in presence of HCl or HBr, chlorobenzene or bromobenzene is formed.



Preparation of benzenediazonium chloride (Diazotization reaction)

When aniline is treated with nitrous acid, HNO_2 ($\text{NaNO}_2 + \text{dil. HCl}$) at ice cold condition, benzene diazonium chloride is formed.



Physical properties:

Physical character:

State: oily liquid or crystalline solid

Color: colorless

Odour: chlorobenzene has pleasant odour

Boiling point: B.pt. of haloarene is higher than benzene. B.pt. increases with the increase in molecular mass.

Solubility: insoluble in water but soluble in organic solvent.

Chemical Properties:

1) Nucleophilic substitution reactions:

Why is haloarene less reactive towards nucleophilic substitution reaction than haloalkane? (NEB 2075)

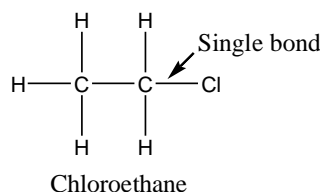
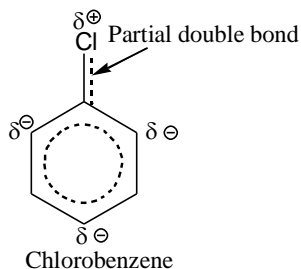
Why is nucleophilic substitution difficult in haloarene? (NEB 2072)

Why is nucleophilic substitution reaction in chlorobenzene difficult as compared to chloroethane? (NEB 2064)

Answer: It is very difficult to undergo the nucleophilic substitution reactions in Haloarenes (For example in Chlorobenzene) than haloalkane (For example – chloroethane) under normal condition due to the following reasons:

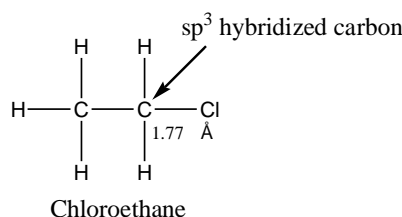
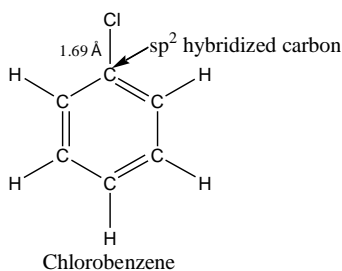
i) Resonance Effect:

C-Cl bond in chlorobenzene (haloarene) has partial double bond character due to resonance & hence difficult to break whereas C-Cl bond in chloroethane (haloalkane) has single bond & easy to break.



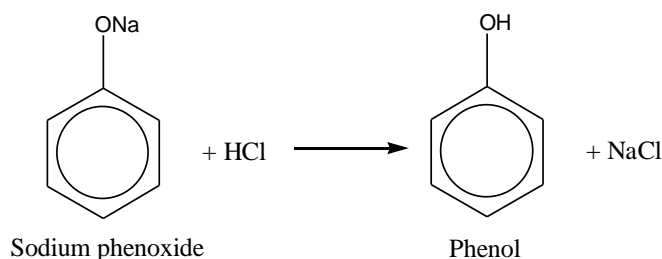
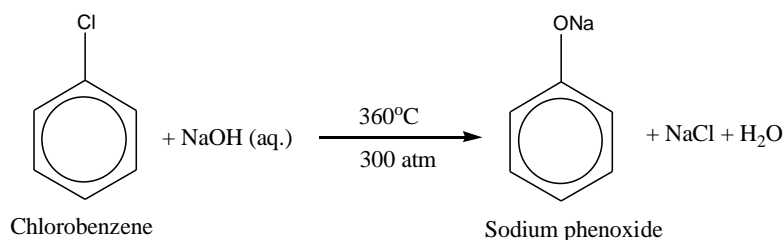
ii) Hybridization effect:

C-atom bonded with Cl atom in chlorobenzene is sp^2 hybridized which is more electronegative (33.33% s character), less polar & difficult to break whereas C-atom bonded with Cl atom in chloroethane is sp^3 hybridized (25% s character), more polar & easy to break.

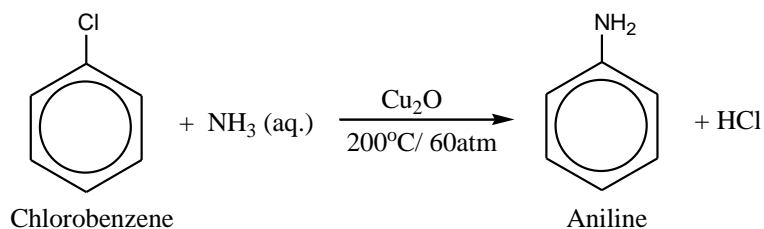


Examples of Nucleophilic substitution reaction:

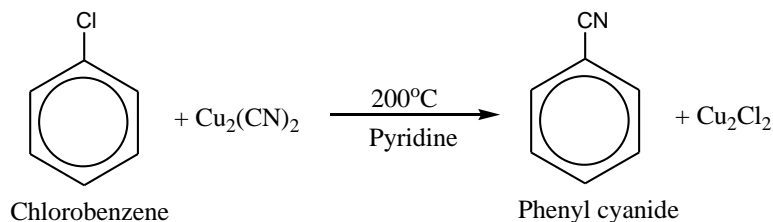
1) Reaction with aqueous NaOH or KOH : Hydrolysis



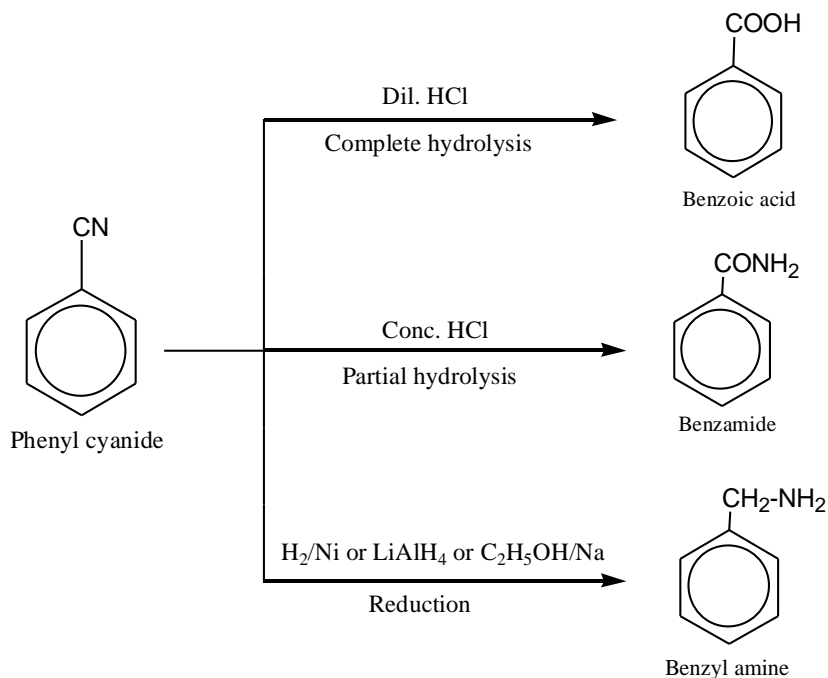
2) Reaction with NH_3 :



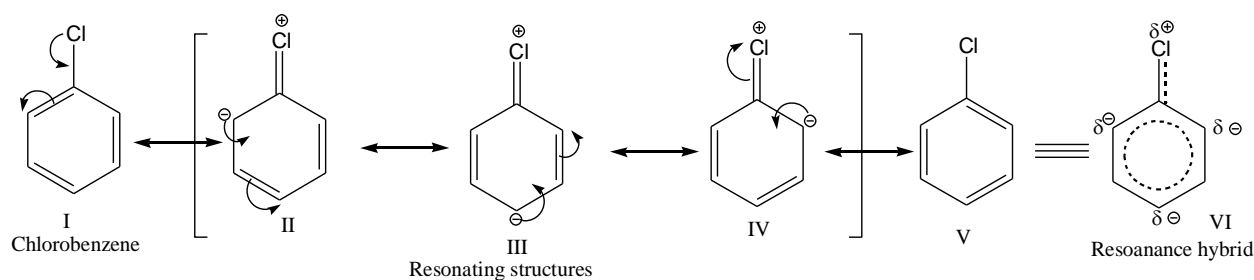
3) Reaction with $\text{Cu}_2(\text{CN})_2$:



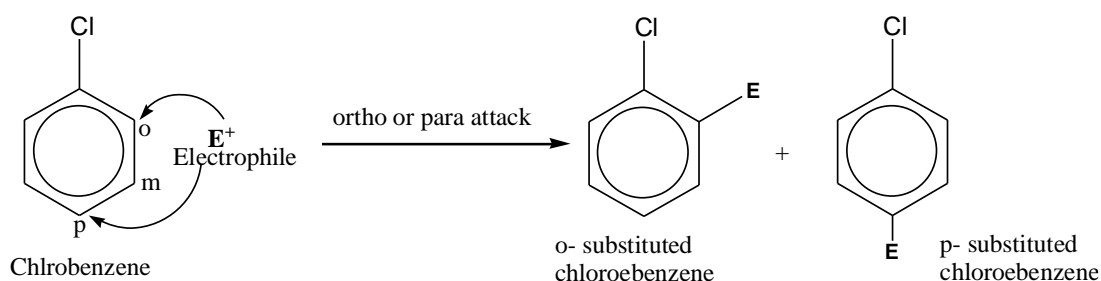
Application of Phenyl cyanide:



2. Electrophilic substitution reactions in chlorobenzene:

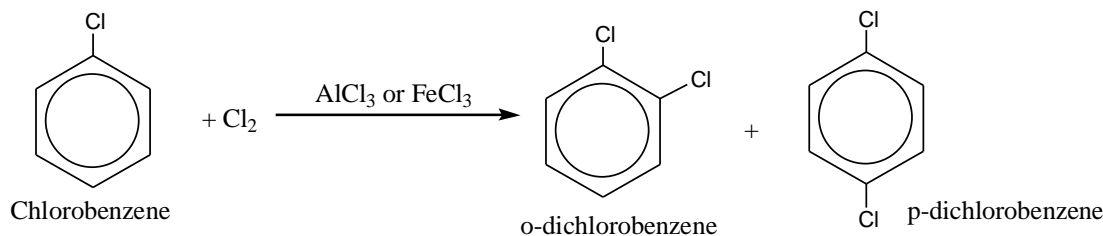


Due to resonance in chlorobenzene, the electron density at ortho and para carbon atoms increases as compared to meta carbon atoms, therefore incoming electrophile will prefer to attack at these carbon atoms during the electrophilic substitution reactions.

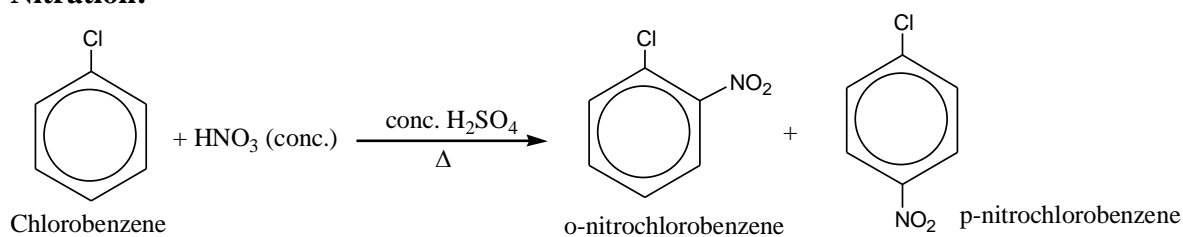


Examples of electrophilic substitution reactions:

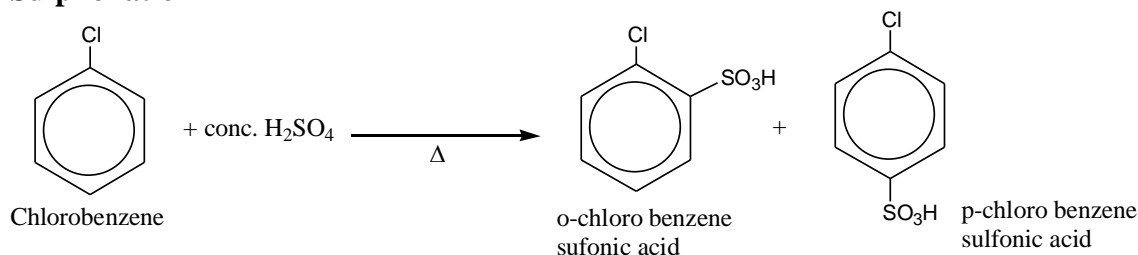
1. Chlorination :



2. Nitration:

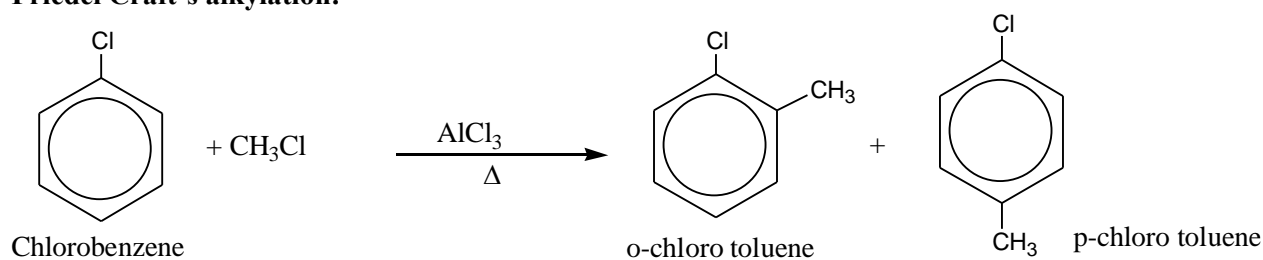


3. Sulphonation

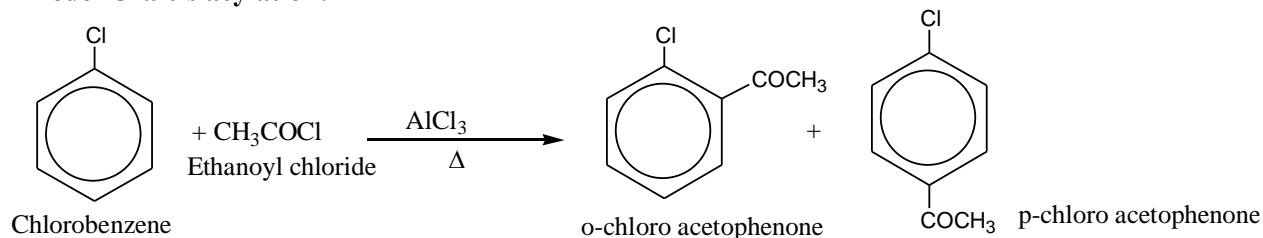


4. Friedel Crafts reactions:

a) Friedel Craft's alkylation:

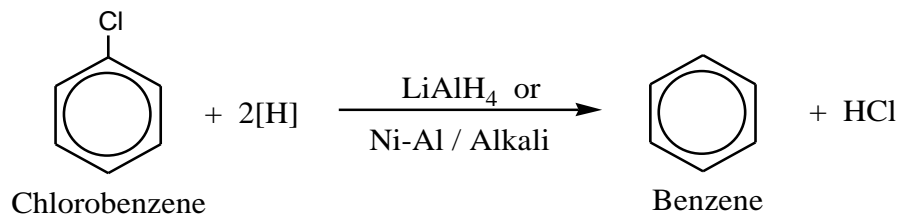


b) Friedel Craft's acylation:



In place of ethanoyl chloride we can even use ethanoic or acetic anhydride.

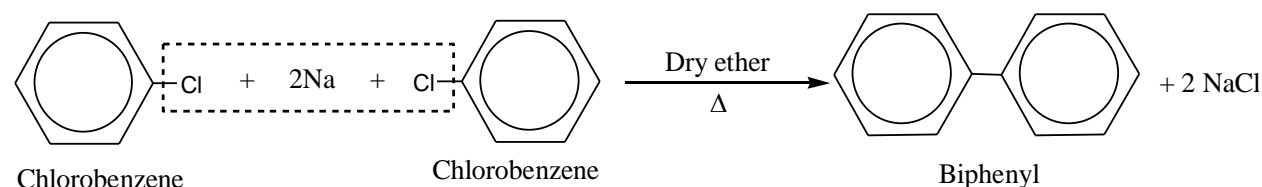
3. Reduction reaction



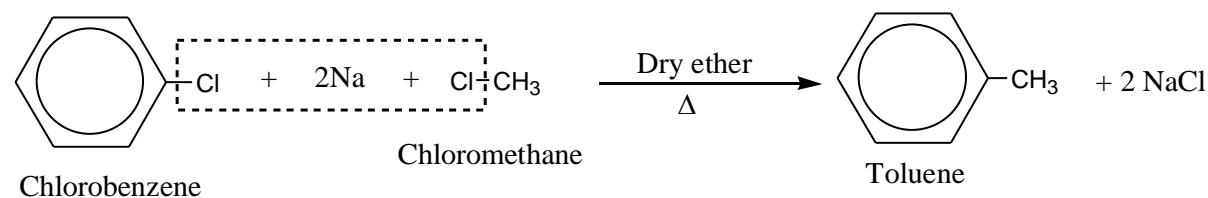
4. Reactions with metals

a) Reaction with Na metal

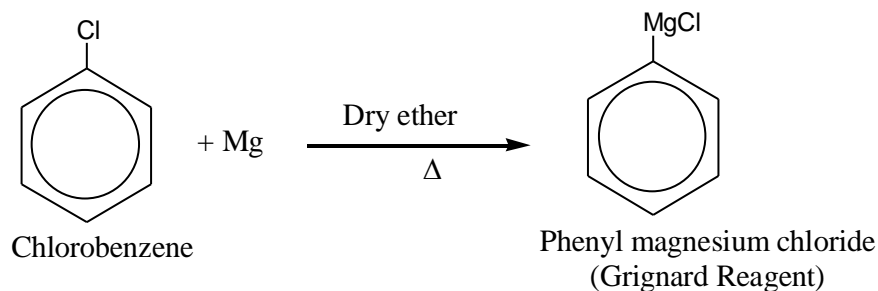
i) Fittig Reaction:



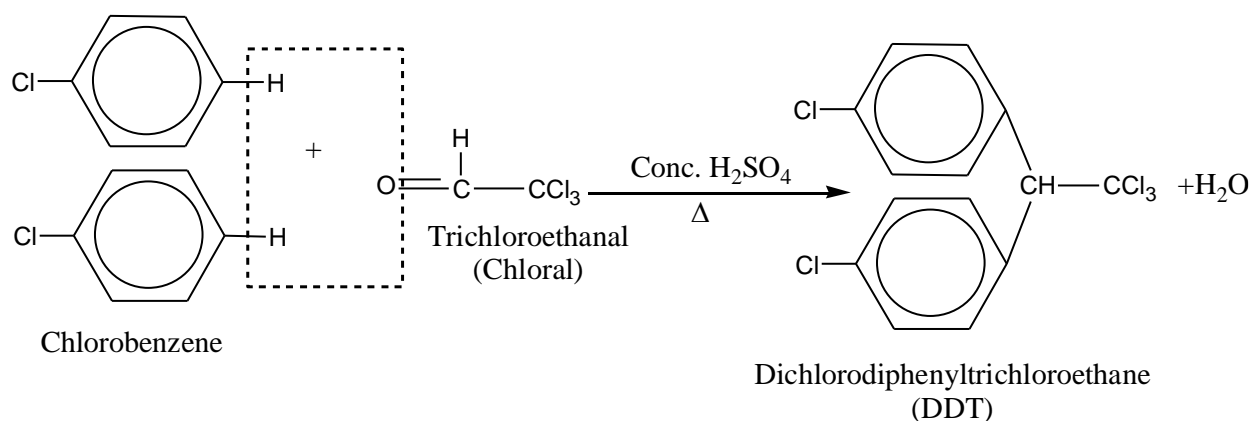
ii) Wurtz- Fittig Reaction:



b) Reaction with Mg metal (Grignard Reaction):



5. Reaction with Chloral



DDT is used as pesticide. But nowadays, it is banned for used because it is not biodegradable.

Uses of Haloarenes

1. Used to prepare pesticides, aniline, phenol etc.

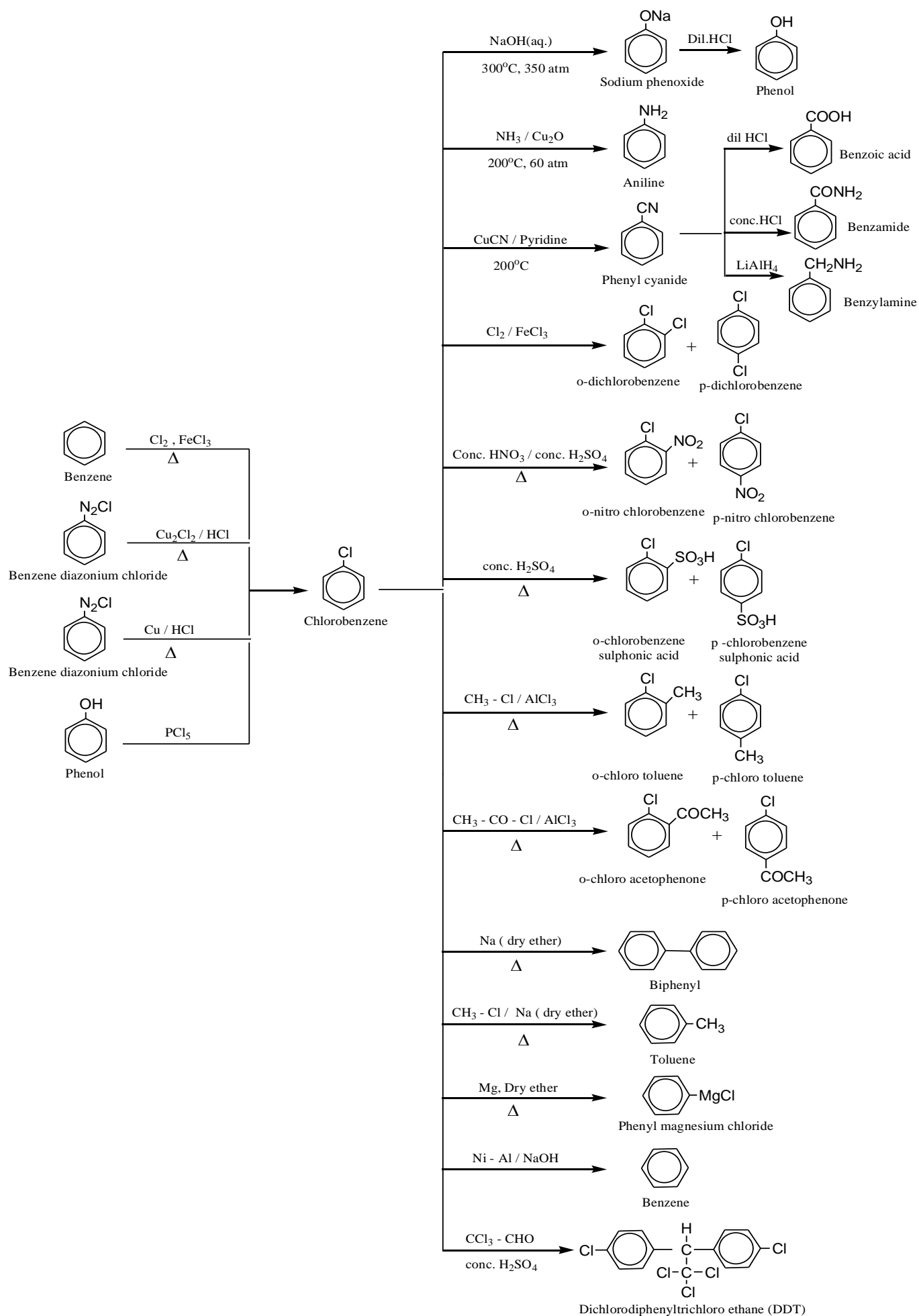
Practice Questions:

Q1. Why is nucleophilic substitution difficult in haloarene?

Q2. What happens when i) Chlorobenzene is heated with sodium in presence of dry ether ii) Chlorobenzene is heated with chloromethane in presence Na/dry ether iii) Chlorobenzene is heated with chloral in presence of conc. Sulphuric acid iv) Chlorobenzene is heated with LiAlH_4

Q3. How would you convert chlorobenzene into a) DDT b) Toluene c) benzoic acid d) benzamide e) benzyl amine f) o-chlorotoluene g) o- chloro acetophenone?

Q4 Write any three methods of preparation of chlorobenzene



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