Unit - X

Haloalkanes And Haloarenes

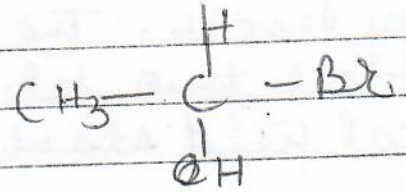
* Haloalkane or alkyl halide → are t
halogen derivatins of alkanes repre
by RX where R is alkyl group and X
halogen.
eg:→ CH_3Cl , CH_3Br
C_2H_5Br , C_3H_7I

Types of haloalkanes :→
(a) Depending upon the number of ha
atom → Depending upon the numbe
of halogen atom we have following typ
haloalkanes:
1) monohalo compound eg:→ CH_3Br , C_2H_5
2) Di halo compound eg:→ CH_2Cl_2 , C_2H_5

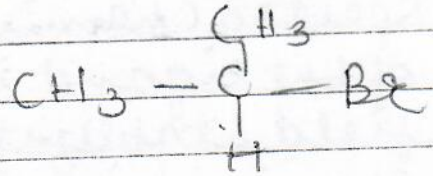
3) Tri halocompound eg ⇒ $CHCl_3$
4) Tetra halocompound eg ⇒ CCl_4

(b) Depending upon the nature of carbon atom to which halogen is attached ⇒

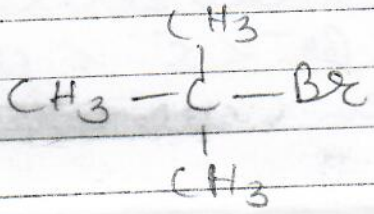
1) Primary (1°)



2) secondary (2°)



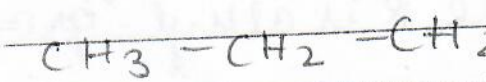
3) Tertiary (3°)



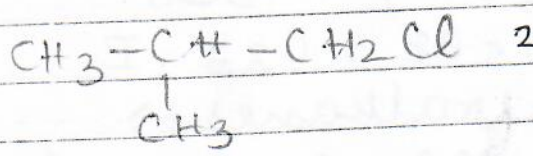
* Isomerism in haloalkane ⇒ Haloalkane shows following type of isomerism

1) Chain isomerism → Haloalkane containing four or more than four carbon atom shows chain isomerism.

eg ⇒ C_4H_9Cl



1-chloro butane



2 methyl 1 chloro propane

2) Position isomerism ⇒ Haloalkanes containing three or more than three

Carbon atoms shows position isomerism

eg ⇒ C_3H_7Br

$CH_3-CH_2-CH_2Br$ 1-Bromopropane

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ 2-Bromopropane

* Methods of preparation

⇒ From Hydrocarbons

1) From alkane → Alkane when react with halogen in presence of a sunlight forms haloalkanes as a product.

$CH_4 - Cl_2 \xrightarrow{UV/hv/sunlight} CH_3Cl + HCl$
(Chloromethane)

$CH_3Cl + Cl_2 \xrightarrow{UV} CH_2Cl_2 + HCl$
(dichloromethane)

$CH_2Cl_2 + Cl_2 \xrightarrow{UV} CHCl_3 + HCl$
(Trichloromethane)
or
(chloroform)

$CHCl_3 + Cl_2 \xrightarrow{UV} CCl_4 + HCl$
(Carbontetrachloride)

In case of higher alkane isomeric products are formed →

$CH_3CH_2CH_3 + Cl \xrightarrow{U.V.} CH_3CH_2CH_2Cl$ (1-Chloropropane) $+ CH_3\underset{\underset{Cl}{|}}{CH}CH_3$ (2-Chloropropane)

2) From Alkene ⇒ Alkene when react with halogen acid forms haloalkanes

as a product.

$CH_2=CH_2 + HX \longrightarrow CH_3-CH_2X$ (X = Cl, Br, I)

eg ⇒ $CH_2=CH_2 + HBr \rightarrow CH_3-CH_2Br$
ethene — Bromoethane

* Markonikov's Rule → Acc. to this rule when a reagent is added to unsymetrical alkene the -ve part of the attacking reagent will goes to the carbon atom containing less no. of hydrogen atom and +ve part of the attacking reagent will goes to the carbon atom containing more no. of hydrogen atoms.

$CH_3-CH=CH_2 + HBr \xrightarrow{M.R} CH_3-\underset{Br}{CH}-CH_3$
propene — 2 Bromo propane

Anti markonikov's Rule / Peroxide effect / Kharasch effect ⇒ ~~when~~ Acc. to this rule when a reagent is added to unsymetrical alkene (in presence of peroxide) the -ve part of the attacking reagent will goes to the carbon containing more no. of hydrogen atom and +ve part ~~will goes to the~~ carbon of the attacking reagent will goes to the carbon atom containing more less no. of hydrogen atom.

$CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3-CH_2-CH_2Br$
Propene — 1 Bromo Propane

⇒ From alcohol → Alcohol when react with halogen acid forms haloalkane as a product.

$$ROH + HX \longrightarrow RX + H_2O$$
(alkyl group)

eg ⇒ Chloroalkanes can be prepared by treating with HCl

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$
(ethanol) (chloroethane)

$$CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$
(ethanol) (Bromoethane)

⇒ By halogen exchange reactions → This rxn is mainly used to prepare iodo alkanes.

Bromo or chloro alkanes when react with sodium iodide (NaI) in presence of acetone forms iodo alkanes as a product. This rxn is also Finkelstein reaction.

$$R-Cl + NaI \xrightarrow{\text{acetone}} R-I + NaCl$$
(Iodoalkane)

eg ⇒ $CH_3CH_2Cl + NaI \xrightarrow{\text{acetone}} CH_3CH_2I + NaCl$
(chloroethane) (iodoethane)

$$CH_3CH_2CH_2Br + NaI \longrightarrow CH_3CH_2CH_2I + NaBr$$
(Bromopropane) (Iodopropane)

⇒ From salt of acid → Silver salt of carboxylic acid ($RCOOAg$) when react with bromine in presence of carbon tetra chloride (CCl_4) bromo alkane is formed

as a product. This rxn is also Hund's dieuher rxn or Borodine Hund's diecher rxn.

$$RCOOAg + Br_2 \xrightarrow{CCl_4} \underset{(\text{Bromoalkane})}{R\text{-}Br} + CO_2 + AgBr$$

eg $\Rightarrow CH_3COOAg + Br_2 \xrightarrow{CCl_4} \underset{(\text{Bromomethane})}{CH_3Br} + CO_2 + AgBr$

* Properties (chemical rxns) of haloalkanes →
= Haloalkane gives following rxns

A) Nucleophilic substitution rxns
B) Elimination rxns
C) Reaction with metals
D) Reduction

⇒ Nucleophilic substitution rxns ⇒

1) substitution by OH group (formation of alcohols) ⇒ when haloalkanes react with aqueous KOH or moist AgOH alcohol is formed as a product.

$$RX + KOH(aq) \longrightarrow ROH + KX$$

eg ⇒ $\underset{(\text{Bromoethane})}{CH_3CH_2Br} + KOH(aq) \longrightarrow \underset{(\text{ethanol})}{CH_3CH_2OH} + KBr$

$$CH_3-\overset{CH_3}{\overset{|}{C}}-Br + KOH(aq) \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}-OH + KBr$$
$$\qquad\qquad CH_3 \qquad\qquad\qquad\qquad CH_3$$

2) substitution by alkoxy group ⇒ formation of ethers) → when haloalkanes react with Na alkoxide ether is formed as a product. This rxn is also williamson

Synthesis rxn -

$$R-X + NaOR \longrightarrow ROR + NaX$$

eg $\Rightarrow$ $CH_3Br + NaOCH_3 \longrightarrow CH_3OCH_3 + NaBr$
(Methoxymethane)

3) Substitution by CN group (formation of alkyl cyanide) $\rightarrow$ when alkyl halides react with KCN alkyl cyanide is formed as a product.

$$R-X + KCN \longrightarrow R-CN + KX$$

eg $\Rightarrow$ $CH_3Cl + KCN \longrightarrow CH_3CN + KCl$
(Methyl cyanide)

Alkyl cyanide are very important compounds for the synthesis of other organic compounds.

(i) Alkyl cyanide on reduction with different reducing agents gives amines as product.

$$R-C\equiv N$$

Reduction
Na/C_2H_5OH
H_2

$$R-CH_2-NH_2 \text{ (Amines)}$$

(ii) Alkyl cyanide on partial hydrolysis gives amide as a product.

$$R-C\equiv N$$

Conc HCl/H_2O
Partial hydrolysis

$$R-CONH_2 \text{ (Amide)}$$

(iii) Alkyl cyanide on complete hydrolysis gives carboxylic acid as product.

$$R-C\equiv N \xrightarrow[2H_2O]{\text{Complete Hydrolysis}} RCOOH + NH_3 \text{ (Carboxylic acid)}$$

(4) Substitution by amino group (formation of amines) → when alkyl halide react with ammonia amines are formed as a product. This rxn is also called Hoffmans ammonolysis.

$$R-X + NH_3 \longrightarrow \underset{(1^\circ \text{ amine})}{R-NH_2} + HX$$

$$R-NH_2 + R-X \longrightarrow \underset{(2^\circ \text{ amine})}{R_2NH} + HX$$

$$R_2NH + R-X \longrightarrow \underset{(3^\circ \text{ amine})}{R_3N} + HX$$

$$R_3N + R-X \longrightarrow \underset{(\text{salt})}{R_4N^+X^-}$$

eg $\rightarrow$ $CH_3Cl + NH_3 \longrightarrow CH_3NH_2 + HCl$

$CH_3NH_2 + CH_3Cl \longrightarrow (CH_3)_2NH + HCl$

$(CH_3)_2NH + CH_3Cl \longrightarrow (CH_3)_3N + HCl$

$(CH_3)_3N + CH_3Cl \longrightarrow (CH_3)_4N^+Cl^-$

5) Substitution by carboxylic group (formation of ester) ⇒ Alkyl halides when react with salt of carboxylic acid forms esters as a product.

$$R-X + RCOOAg \longrightarrow \underset{\text{(esters)}}{RCOOR} + AgX$$

Eg ⇒ $CH_3Br + CH_3COOAg \rightarrow CH_3COOCH_3 + AgBr$

⇒ Elimination reactions ⇒

Dehydrohalogenation → when haloalkanes react with alcoholic KOH dehydrohalogenation occurs and alkene is formed as a product.

$$CH_3-CH_2Br + alc.KOH \xrightarrow{\Delta} \underset{\text{(alkene)}}{CH_2=CH_2} + HBr$$

When dehydrohalogenation in alkyl halide occurs in two different ways then that alkene is preferred which is more alkylitic. This rxn is known as Saytzeff's rule.

$$CH_3-CH_2-\underset{Br}{CH}-CH_3 + alc.KOH \longrightarrow CH_3-CH=CH-CH_3 + HBr$$

(2 Bromo butane)

⇒ Reaction with metals ⇒

1) Reaction with Mg (formation of grignard reagents) → Haloalkanes react with Mg and forms grignard reagent ($RMgX$) as a product.

$$R-X + Mg \longrightarrow \underset{\text{(G.R.)}}{RMgX}$$

eg :- $CH_3Br + Mg \rightarrow CH_3MgBr$

2) Reaction with sodium → when two molecules of alkyl halide react with Na metal in presence of ether higher alkane formed as a product. This rxn is known as wurtz's rxn.

$$R-X + 2Na + X-R \xrightarrow{\text{ether}} R-R + 2NaX$$

eg :- $CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{ether}} CH_3-CH_3 + 2NaBr$
(ethane)

⇒ Reduction :- Haloalkanes on reduction forms alkane using different reducing agents.

1) with H_2 in presence of Ni / Pt

$CH_3CH_2Br + H_2 \xrightarrow{Ni/Pt} CH_3-CH_3 + HBr$
(bromoethane) (ethane)

2) with Zn/Cu & C_2H_5OH

$CH_3CH_2Br + 2[H] \xrightarrow{Zn/Cu, C_2H_5OH} CH_3-CH_3 + HBr$

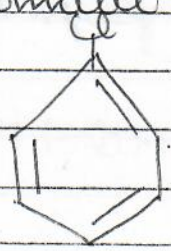
$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 + 2[H] \xrightarrow{Zn/Cu, C_2H_5OH} CH_3-CH_2CH_3 + HCl$

3) with HI in presence of red phosphorus

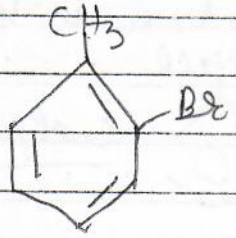
→ HI in presence of red phosphorus is used for the reduction of iodo alkanes.

$CH_3CH_2I + HI \xrightarrow{Red\,P} CH_3CH_3 + I_2$
(iodoalkane) (alkane)

* **Haloarenes** ⇒ Are the halogen derivative of aromatic compounds.



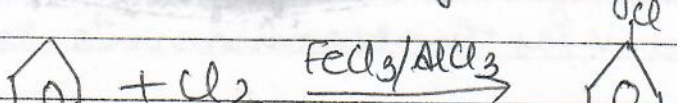
Chlorobenzene



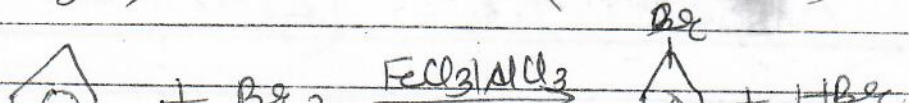
Ortho bromotoulene
2 Bromotoulene

Methods of preparation →

1) By direct halogenation of aromatic ring
→ Chloro and bromo benzene can be prepared by the reaction of benzene with halogen (Br, Cl) in presence of halogen carrier $FeCl_3/AlCl_3$

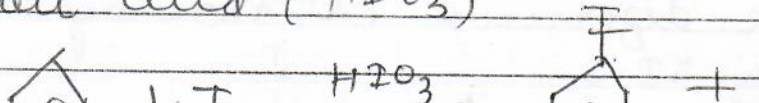


(benzene) (Chlorobenzene)



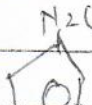
(benzene) (Bromobenzene)

iodo benzene can be prepared by treating iodine with halo benzene in presence of iodic acid (HIO_3)



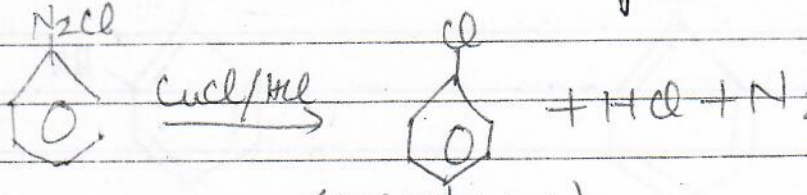
(iodobenzene)

2) From diazonium salt →

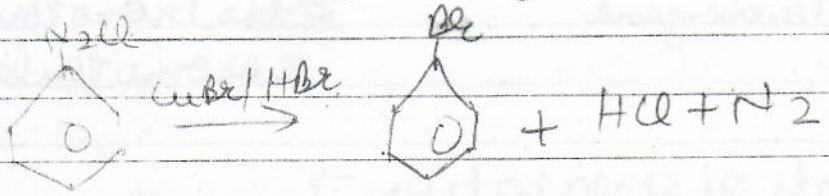


→ benzene diazonium chloride

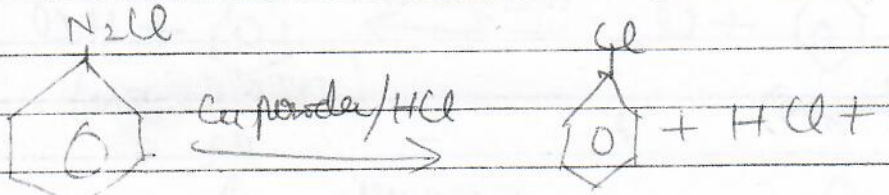
- When diazonium salt is treated with cuperous chloride ($CuCl$) or bromide ($CuBr$) in presence of corresponding halogen acid chloro benzene and bromobenzene is formed as a product. This rxn is known as Sandmeyer's rxn.



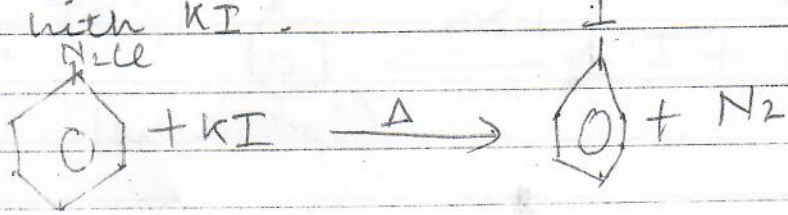
(Chlorobenzene)



- Gattermanns rxn (modified form of sandmeyer rxn) → When diazonium salt is treated with Cu powder and halogen acid chloro benzene and bromobenzene is formed as a product. This rxn is known as Gattermann's rxn.

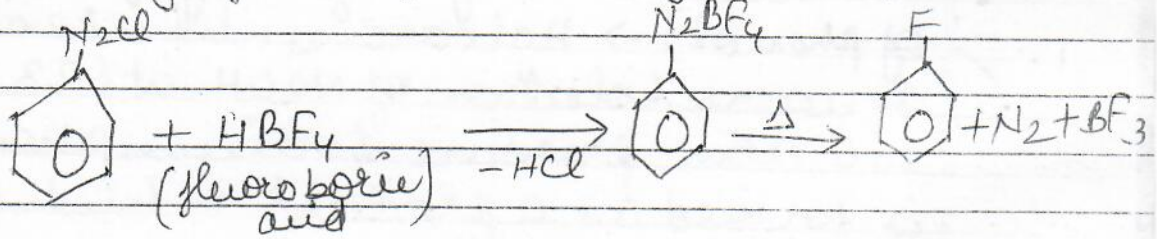


- Iodobenzene can be prepared from benzene diazonium chloride by heating it with KI.

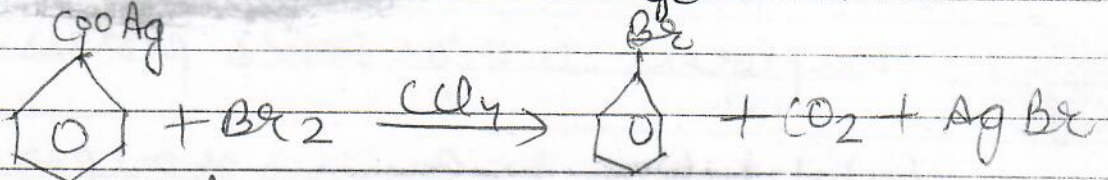


Balkemen rexn →

- Fluorobenzene (fluoroarenes) → Benzene diazonium chloride when react with fluoro boric acid forms an additional compound which on heating gives fluoro benzene as a product.



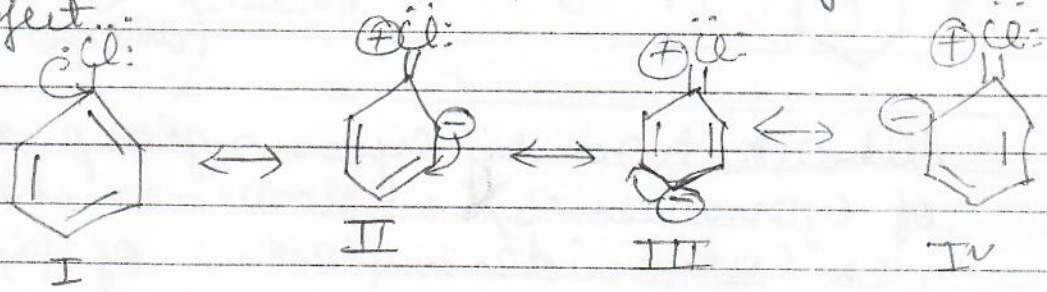
3) From salt of aromatic carboxylic acid → when silver salt of aromatic carboxylic acid is treated with bromine in presence of CCl_4 bromobenzene is formed as a product. This rxn is also known as Hund's dycher rxn.



(C_6H_5COOAg)

Properties of haloarenes :→

- Haloarenes are less reactive than haloalkanes :→ The less reactivity of haloarenes can be explain on the basis of resonance effect...



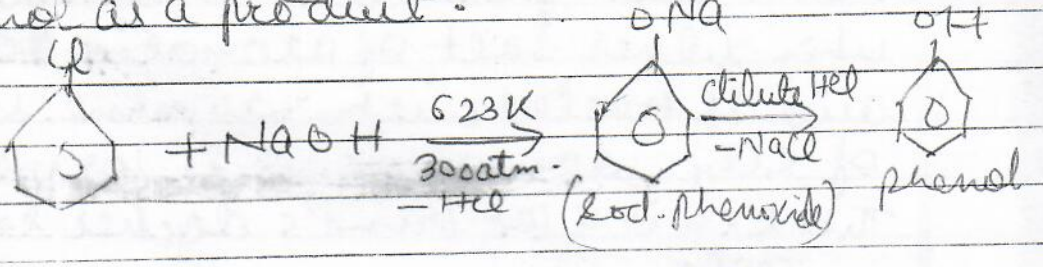
It is clear from the resonating structures II, III and IV that there is a double bond b/w the carbon and halogen in case

of haloalkanes there is a single bond b/w the carbon and halogen. Thus haloarenes is less reactive than haloalkane.

Haloarenes shows following type of rxn ⇒

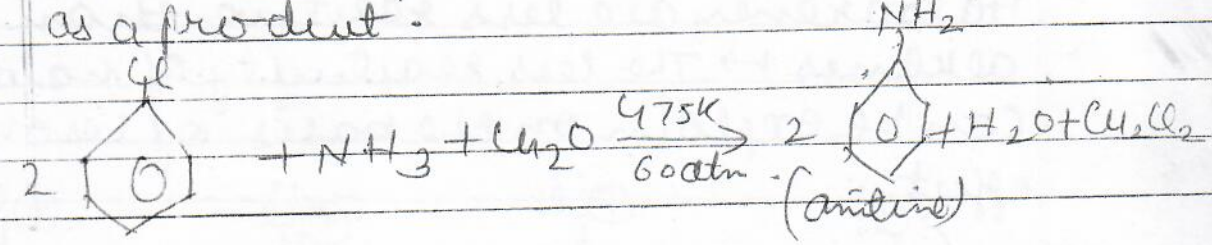
1) Nucleophilic ~~ex~~ substitution rxn ⇒

Substitution by hydroxy group (formation of phenol) → Haloarenes when react with aqueous solution of NaOH at 623K and 300 atm. pressure sodiumphenoxide is formed as a product which on acidification with dilute HCl forms phenol as a product.

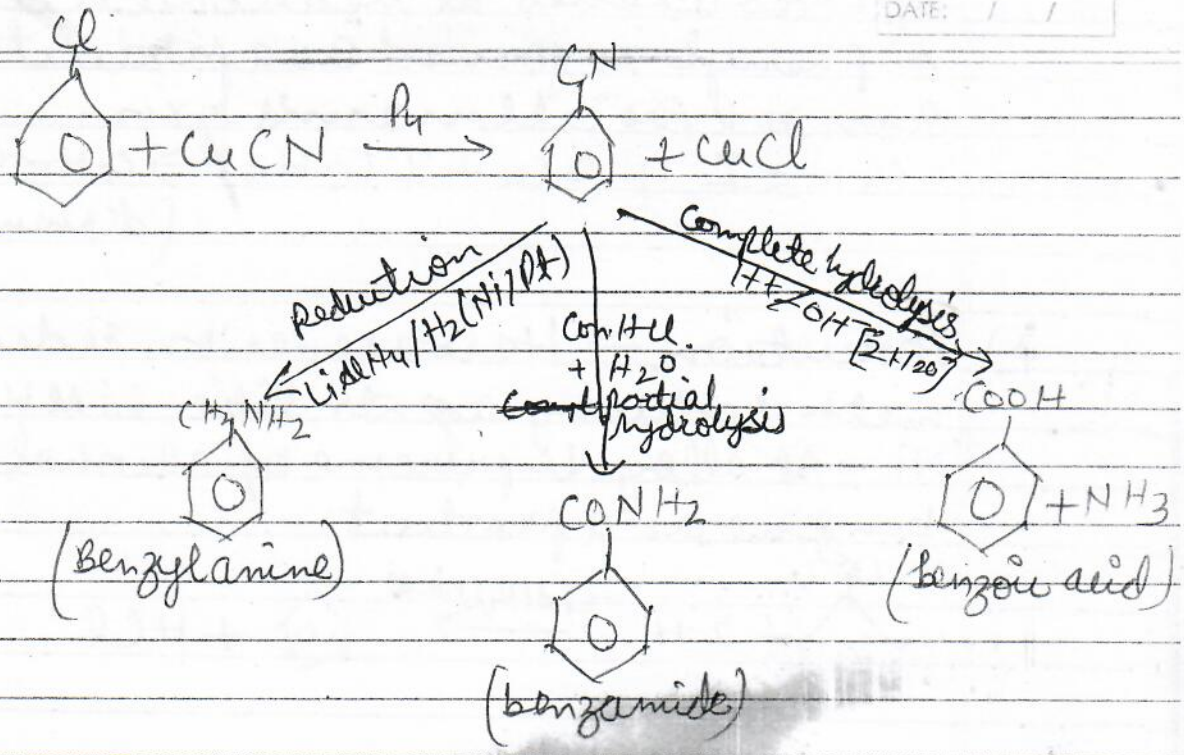


This process is also Dow's process.

Substitution by amino group → (formation of aniline) → when halo arenes react with ammonia in presence of Cu_2O at 475K and 60 atm. pressure aniline is formed as a product.



Substitution by cyano group ⇒ (formation of cyano arenes) → Haloarenes when react with Cu cyanide in presence of pyridine forms cyano arenes as a product.



2) Reaction with metals :-

Reaction with Mg :- Haloarenes when react with Mg and forms an additional compound K/as grignard reagent.

$C_6H_5Cl + Mg \xrightarrow{ether} C_6H_5MgCl$
(chlorobenzene) (phenyl mg chloride)

$C_6H_5Br + Mg \xrightarrow{ether} C_6H_5MgBr$
(phenyl mg bromide)

- Reaction with Na → when the molecule of haloarenes react with Na metal in presence of ether diphenyl is formed as a product. This rxn is K/as fittig rxn.

$C_6H_5Cl + 2Na + ClC_6H_5 \rightarrow C_6H_5-C_6H_5 + 2NaCl$
(di phenyl)

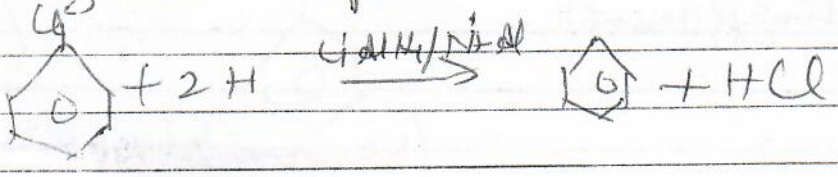
- when a molecule of halo alkane react with a molecule of halo arene in presence of Na metal aromatic compound is formed as a product. This rxn is K/as wurtz fittig rxn.

$C_6H_5Cl + 2Na + ClCH_3 \rightarrow C_6H_5-CH_3 + 2NaCl$
(Toluene)

- Reaction with Cu ⇒ when two molecules of Iodo arenes is heated with cu powder di phenyl is formed as a product. This rxn is also known as ullmann's rxn.

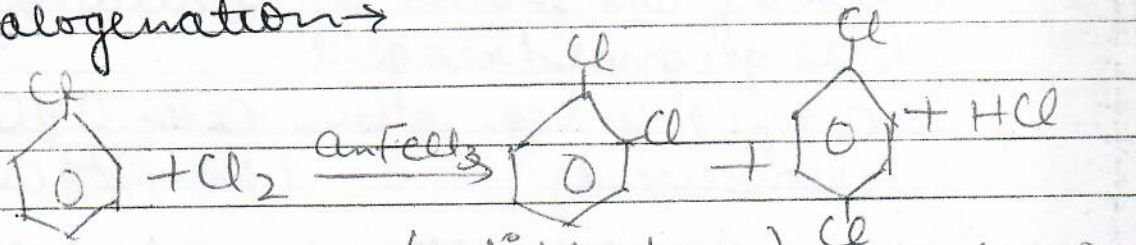
$$C_6H_5I + 2Cu + ICH_5 \xrightarrow{\Delta} C_6H_5-C_6H_5 + CuI_2$$
(di phenyl)

3) Reduction ⇒ Haloarenes on reduction with reducing agents like $LiAlH_4$ or Ni – Al alloy in presence of alcohol forms benzene as a product.



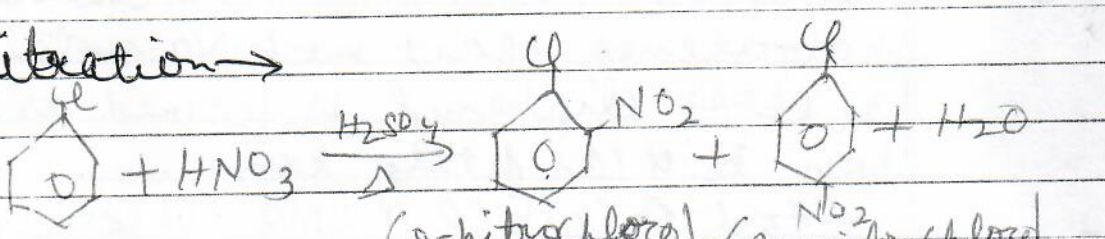
4) Reaction due to ring (electrophilic substitution rxn) ⇒

- Halogenation →



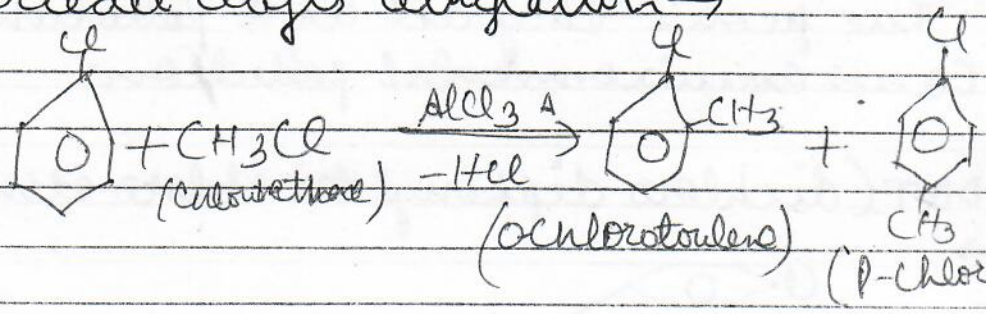
(o-dichlorobenzene) (1,2 dichloro benzene)
(1,4 dichloro benzene) (p-dichlorobenzene)

Nitration →

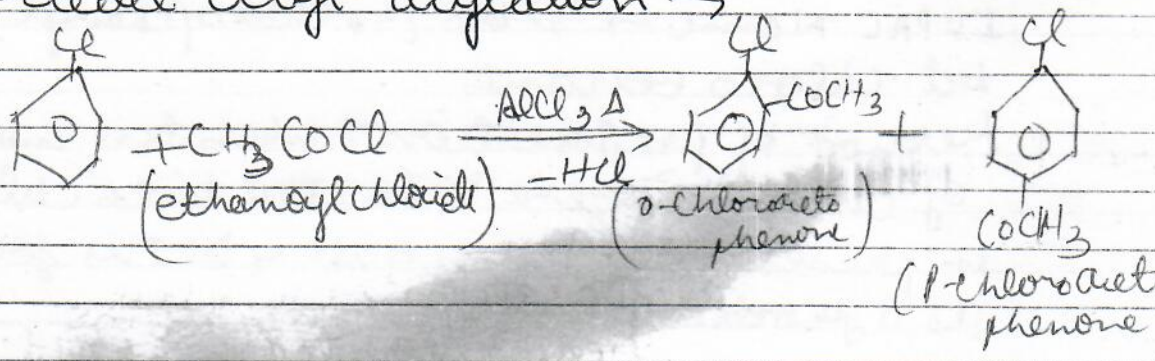


(o-nitrochloro benzene) (1 chloro 2-nitrobenzene)
(p-nitrochloro benzene) (1 chloro 4-nitro benzene)

Friedel crafts alkylation →



Friedel craft acylation →



Q. What is X, Y & Z in the following:

$C_6H_6 \xrightarrow{FeCl_3/Cl_2} X \xrightarrow{CuCN} Y \xrightarrow{H^+/H_2O} Z$

$C_6H_6 \xrightarrow{FeCl_3/Cl_2} C_6H_5Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H^+/H_2O} C_6H_5CO$

$C_6H_5N_2Cl \xrightarrow[\Delta]{KI} X \xrightarrow[\Delta]{Cu} Y$

$C_6H_5N_2Cl \xrightarrow[\Delta]{KI} C_6H_5I \xrightarrow[\Delta]{Cu} C_6H_5-C_6H_5$ (diphe
(Iodobenzene)

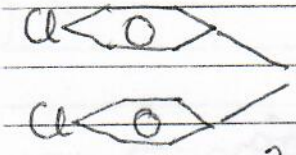
Poly halo compound →
Trichloro methane (CHCl3) (Chloroform)
→ Method of preparation
- Chloroform is strongly oxidised by air in presence of a light to form a poisonous gas i.e. phosgene.

$CHCl_3 + \frac{1}{2}O_2 \longrightarrow \underset{\text{(Phosgene)}}{COCl_2} + HCl$

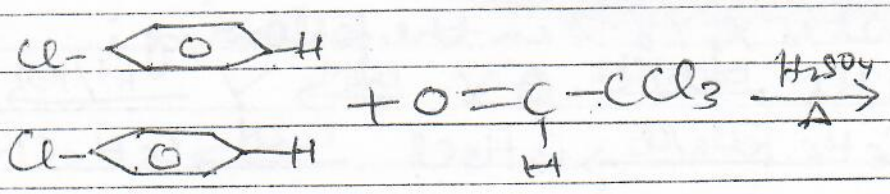
Chloroform is used as a anesthetic agent.

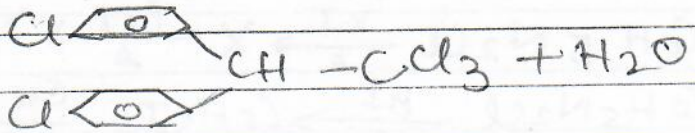
2) Freons → The chloro fluoro derivatives of hydrocarbons are known as freons.
eg :→ $CH_4 \rightarrow CF_2Cl_2 \rightarrow CFCl_3$
These freons they act as a pollutant and cause environmental pollution.

3) DDT (dichloro diphenyl tri chloro ethane)
→



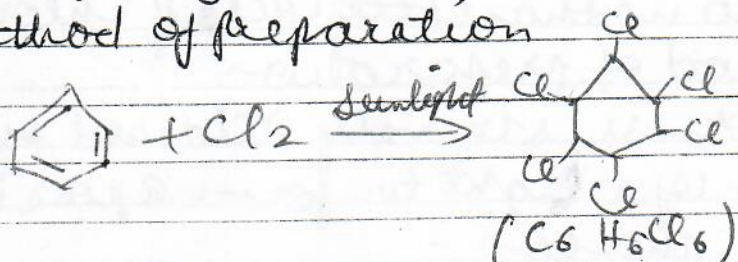
IUPAC Name → 2,2 Bis (4-chlorophenyl) 1,1,1, tri Chloro ethane
Method of preparation → when two molecules of chlorobenzene is heated with chloral in presence of conc. H_2SO_4 DDT is formed as a product.





It is used as insecticides.

4) BHC (Benzene hexa chloride) →
Method of preparation



$(C_6H_6Cl_6)$

It is used as a pestisides.