Alkyl Halide and Aryl Halide

Page No.
Date

- **Nucleophilic Substitution Reaction :**

Nucleophile ⟶ Nucleolus loving species.

Condition ⟶ ① octet complete

② Minimum 1 lone pair.

Ex : Cl, OH, SH, N^{-3}, H_2O, NH_3, OH.

$$R-X + OH^{\ominus} \longrightarrow R-OH + X^{\ominus}$$

- Reaction in two-methods :

① $R-X \xrightarrow{R.D.S} R^{+} + X^{\ominus} \longrightarrow ROH + X^{\ominus}$ — SN_1 — Unimolecular — $Nu^{\ominus}$ — Subs. Reaction. (Molecularity – 01)

② $R-X + OH^{\ominus} \xrightarrow{R.D.S} HO-R--X \longrightarrow ROH + X^{\ominus}$ — SN_2 — Bimolecular — $Nu^{\ominus}$ — Subs. Reaction (Molecularity – 02)

- SN_1 Reaction

① $R-X \longrightarrow R^{\oplus} \xrightarrow{Nu^{\ominus}} R-Nu$

Carbocation (T.S)

② Kinetics.

$R-X \xrightarrow{R.D.S} R^{\oplus}$

a) 2-step rxn.

b) Intermediate step.

c) Rate = $K[R-X]^1$

d) Molecularity – 01

e) Order of Reaction – 01

SN_2 Reaction

$R-X + Nu^{\ominus} \longrightarrow Nu-R--X \longrightarrow HOR + X^{\ominus}$

T.S

Kinetics

$R-X + Nu^{\ominus} \xrightarrow{R.D.S} HOR + X^{\ominus}$

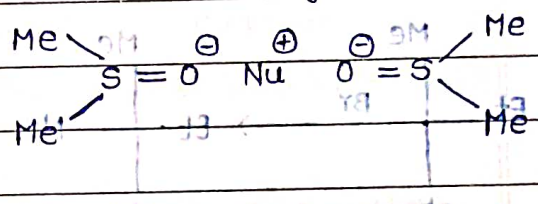
1-step reaction

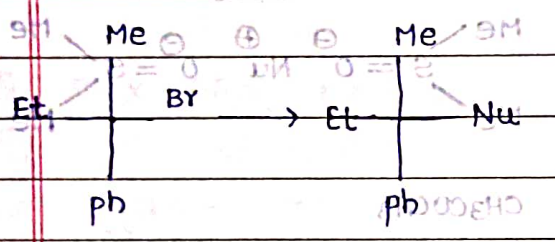
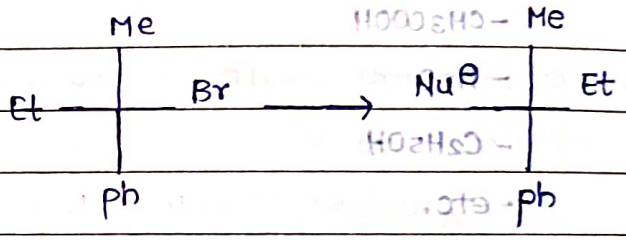
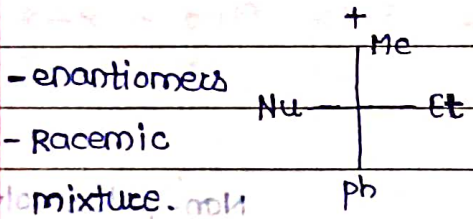
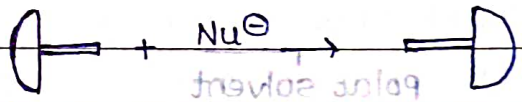
Transition state

Rate = $K[R-X]^1[Nu^-]^1$

Elementary rxn.

M = 2 ; Order of Reaction = 2.

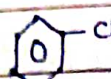
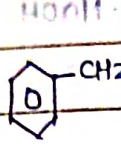
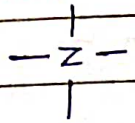
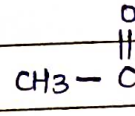
SN1 Reaction	SN2 Reaction.
③ Rate of SN1 ∝ stability of Carbocation	Rate of SN2 ∝ $\frac{1}{\text{Bulkness}}$
④ Effect of Nucleophile – No effect	Rate ∝ strength of Nucleophile ① L → R → Nucleophilicity decreases ② Down the group → $Nu^{\ominus}$ increases ③ $Nu^{\ominus}$ ∝ $\frac{1}{\text{Bulkness (same type ions)}}$
⑤ Effect of Solvent Favour polar protic solvent: – CH_3COOH – H_2O – C_2H_5OH – etc.	Effect of Solvent Favour polar aprotic solvent ⑤ DMSO → Dimethyl sulphoxide.  CH_3COCH_3
Polar solvent ($\mu \neq 0$)	Non-polar solvent * Hydrocarbon * CCl_4, CS_2
Polar protic solvent ← – O – H – S – H – N – H – F – H	Polar aprotic solvent absence of – O – H – S – H – F – H } Bond

	S_N1 Reaction	S_N2 Reaction
①	Effect of leaving group Good leaving group. Rule ① : Neutral molecules are good leaving molecule. Rule ③ :- Weak Base are good leaving group.	Effect of leaving group Good leaving group. Rule ② : Down the group leaving group tendency increases. Rule ④ : leaving tendency ∝ stability of leaving is $F < Cl < Br < I$ ↓ poor ↓ good leaving group
②	Stereochemistry of S_N1 - Both side attack is possible	Stereochemistry of S_N2 - Only Back attack is possible.
		
	 - enantiomers - Racemic mixture.	- Welden Inversion 
③	Effect of substrate ∝ Bulky group.	Effect of substrate ∝ small group.

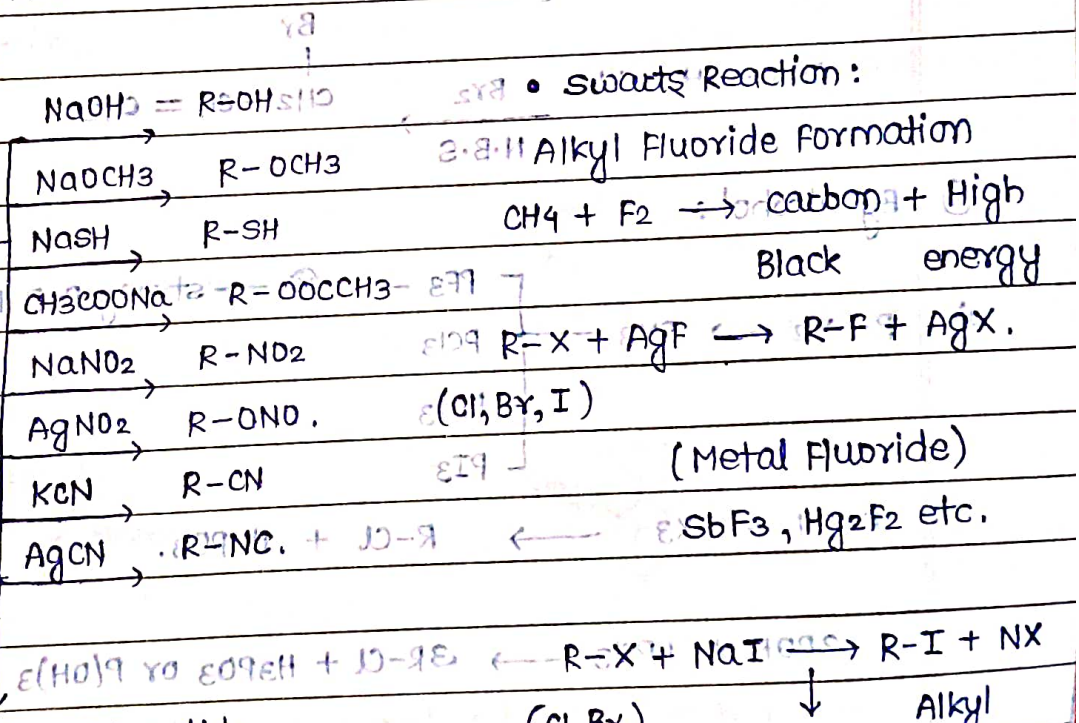
• ① $C=C-X$ ②  ⟶ do not show S_N1 and S_N2

• Molecule { H–O–X, H–a–, H–F }

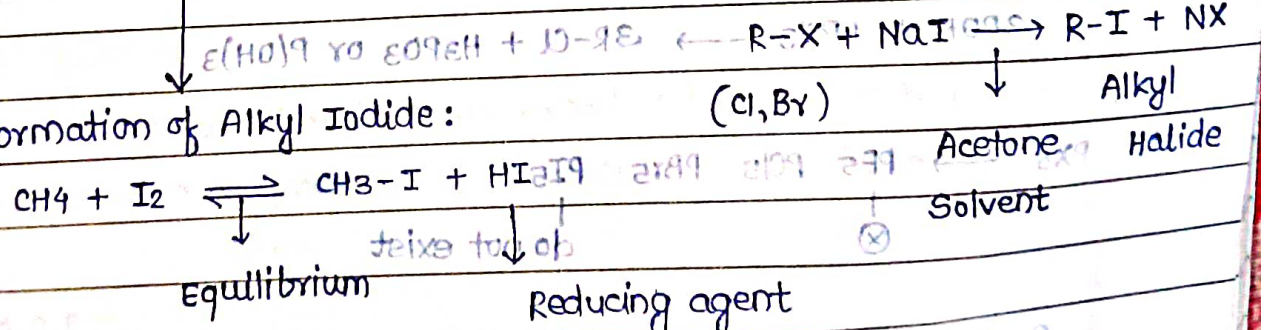
		S_N1		S_N2
①	$CH_2 = CH - CH_2 - X$	Yes	<	Yes
②	$CH_2 = \underset{\underset{CH_3}{|}}{C} - CH_2 - X$ Branch allylic Condition	Yes	>	Yes

③		Yes	< Yes
④		If o⁻ and p⁻ directing group attached with Benzyl halide	Yes > Yes.
⑤	 (where → Z = O, N)	Excellent	Yes (poor)
⑥	 β-keto Halide	Yes (poor)	Excellent

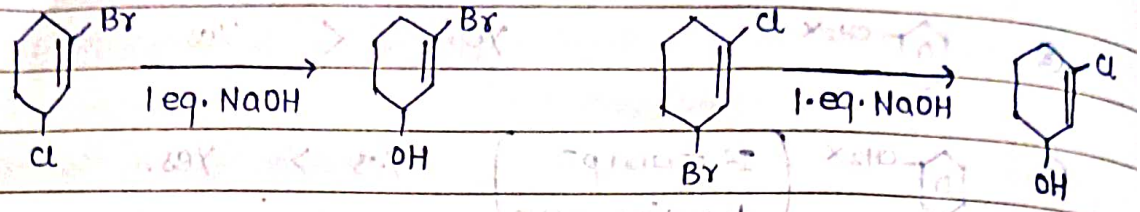
- Swarts Reaction:



- Formation of Alkyl Iodide:



Note: Equilibrium shifted Further CH3I ko
Forward direction in reduce kar deta
presence of oxidising agent hain:
(HNO3)



Note: If more than one L.G. present then remove best L.G But X Best L.G attached with doubled bonded carbon then remove other L.G.

- Method of preparation → Alkyl Halide:

① Addition of HBr in Alkene

② Bromination in Allylic position

$CH_3-CH=CH_2 \xrightarrow[N.B.S]{Br_2} CH_2(Br)-CH=CH_2$

① Free Radical Formation.

③ By alcohol:-

a) $P + X_2 \longrightarrow PX_3$ (PF_3 ⊗ strong P-F Bond., PCl_3, PBr_3, PI_3)

$R-OH + PX_3 \longrightarrow R-Cl + H_3PO_3$

$\therefore 3ROH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$ or $P(OH)_3$

b) PX_5 → PF_5 ⊗, PCl_5, PBr_5, PI_5 do not exist

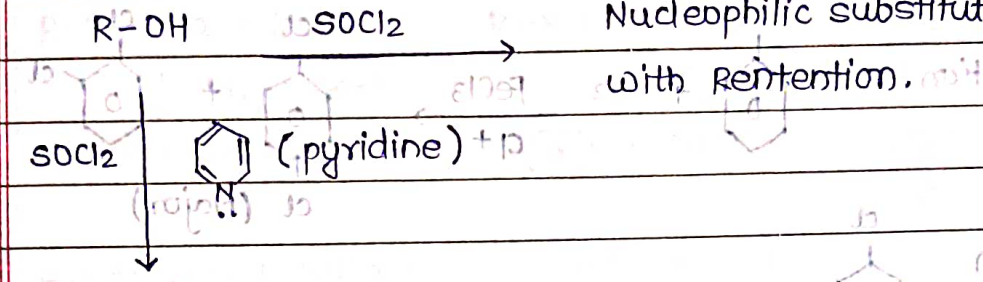
$R-OH + PX_5 \longrightarrow R-Cl + POCl_3$

$\therefore 1ROH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

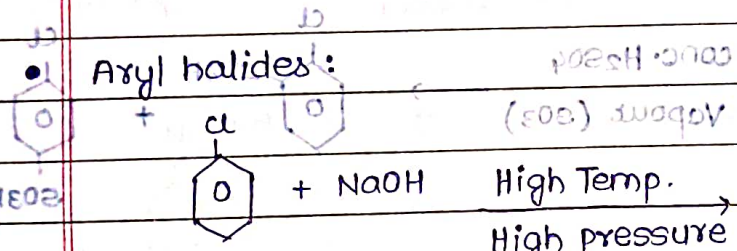
(c) $SOCl_2$ (Darzen Method)

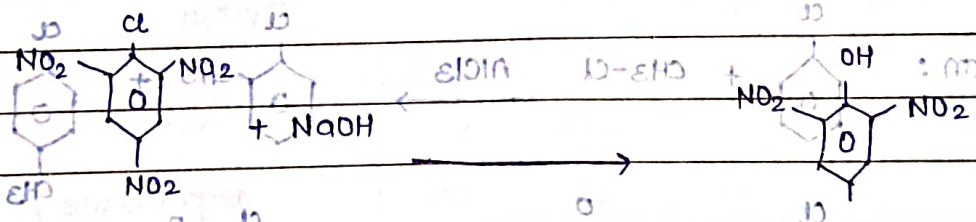
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$$

- Best method for preparation of Alkyl halide.



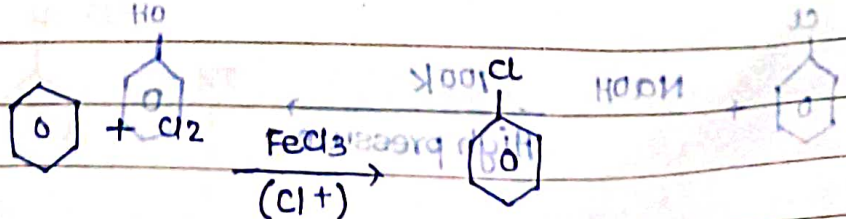
- Aryl halides:



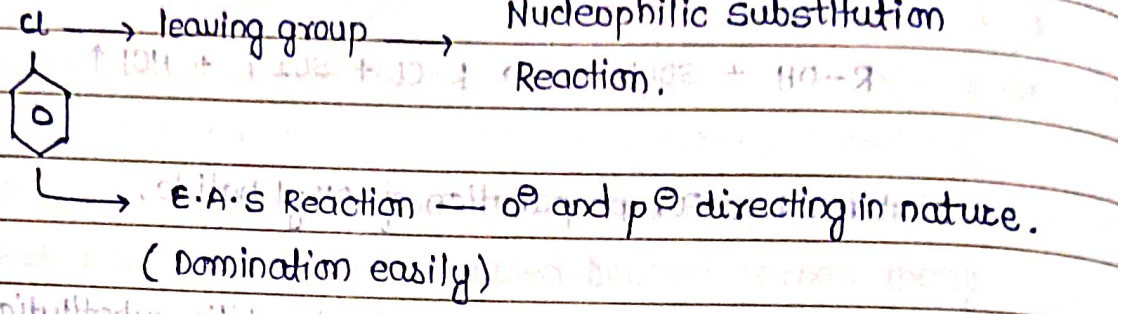


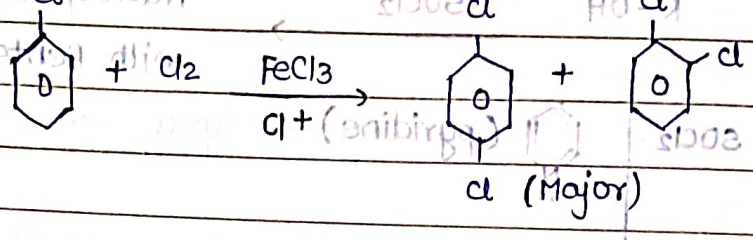
Note: Aromatic halides gives Ar_SN^1 and Ar_SN^2 at high temp and pressure or in presence of number of meta directing group.

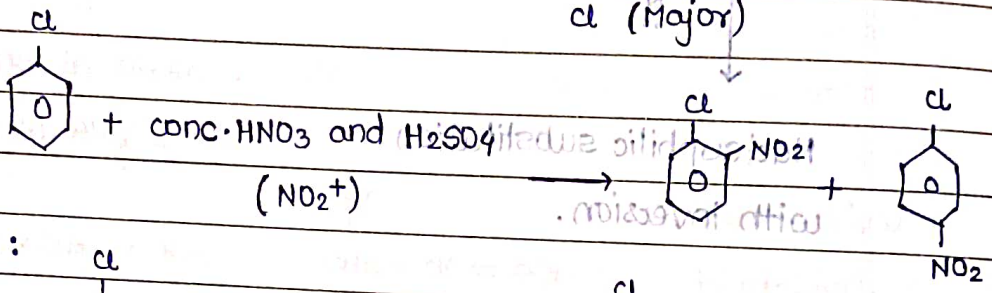
- M.O.P:

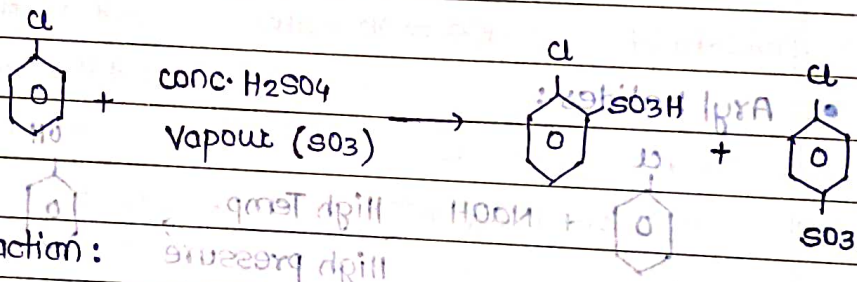


- **Chemical properties:**

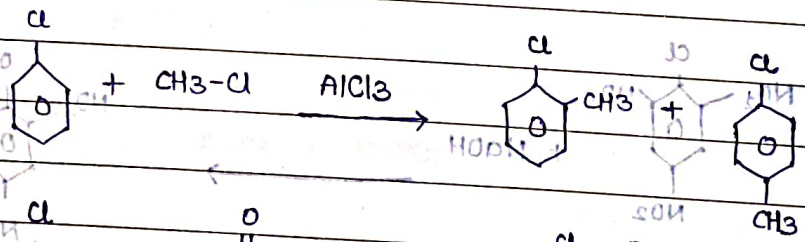


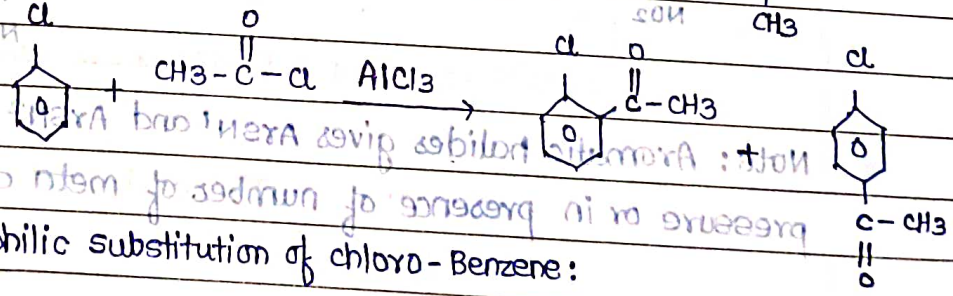
① Halogenation 

② Nitration 

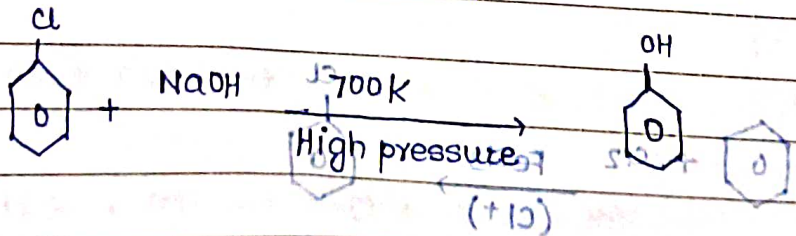
③ Sulphonation: 

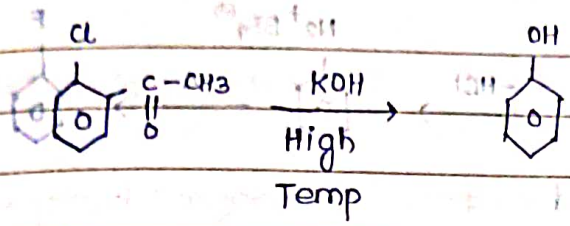
- **Friedal craft Reaction:**

① Alkylation: 

② Acylation: 

- **Rate of Nucleophilic substitution of chloro-Benzene:**





- Wurtz Reaction (Both aliphatic)

$$R-X + Na + R-X \xrightarrow[\text{(dry ether)}]{} R-R + 2NaX$$

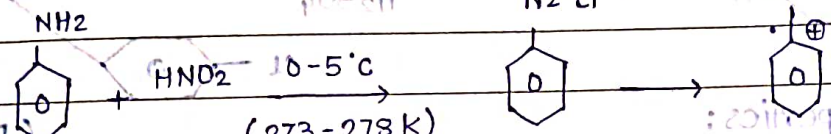
Wurtz-Fittig Rxn (one aromatic and one aliphatic)

$$R-X + Na + R-C_6H_5 \xrightarrow[\text{(dry ether)}]{} R-C_6H_5 + 2NaX.$$

Fittig Reaction (Both Aromatic)

$$C_6H_5-X + Na + X-C_6H_5 \xrightarrow[\text{(dry ether)}]{} C_6H_5-C_6H_5 + 2NaX.$$

- Sandmeyer Reaction:

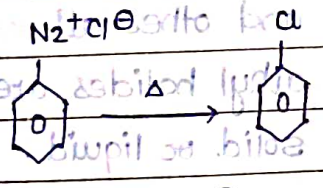


Benzene Diazonium chloride

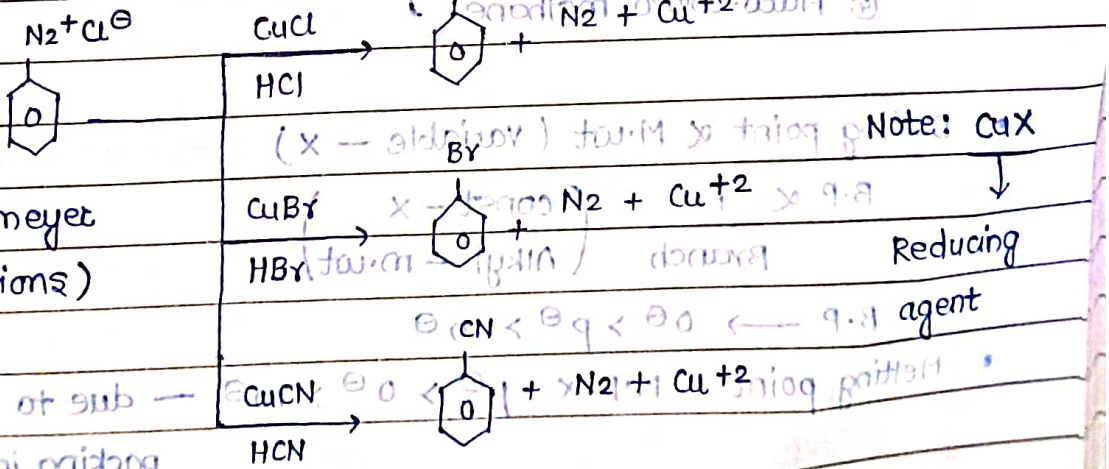
Free Radical or carbocation.

↓

Nucleophile add kar dena.

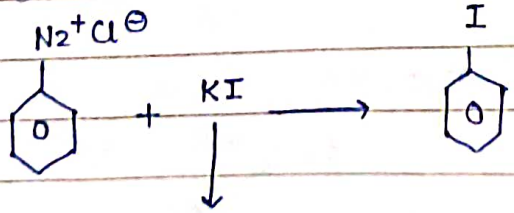


(Sandmeyer Reactions)

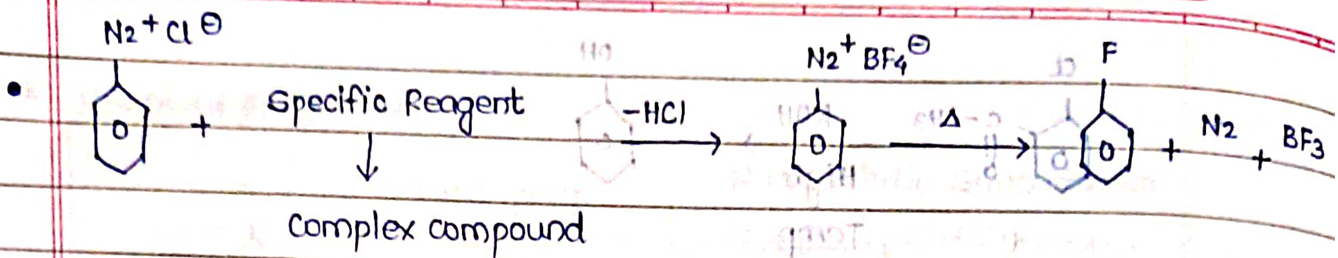


Note: CuX ↓ Reducing agent

- Note:



($I^{\ominus}$ - self mein Reducing agent ka kaam krta hai)

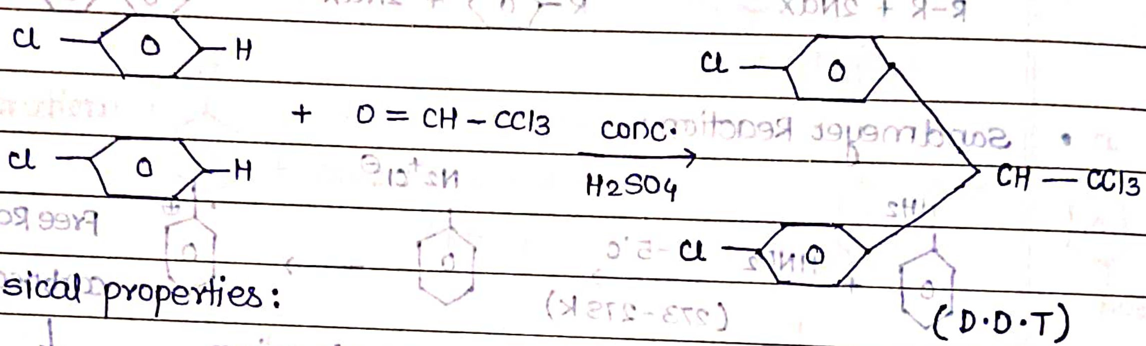


of Fluoride

$HBF_4 \longrightarrow H^+ + BF_4^\ominus$

$HSbF_6 \longrightarrow H^+ + SbF_6^\ominus$

- Formation of DDT :



- Physical properties :

① CH_3F
② CH_3Cl
③ C_2H_5-Cl
④ Fluoro-chloro-methane

} Gas

and other all alkyl halides are solid or liquid.

- Boiling point ∝ M.wt (variable – X)

$B.P \propto \frac{1}{Branch}$ (const – X / Alkyl – m.wt)

B.P ⟶ $O^\ominus > P^\ominus > m^\ominus$

- Melting point → M.P ∝ $P^\ominus > O^\ominus > m^\ominus$ — due to packing in solid state.