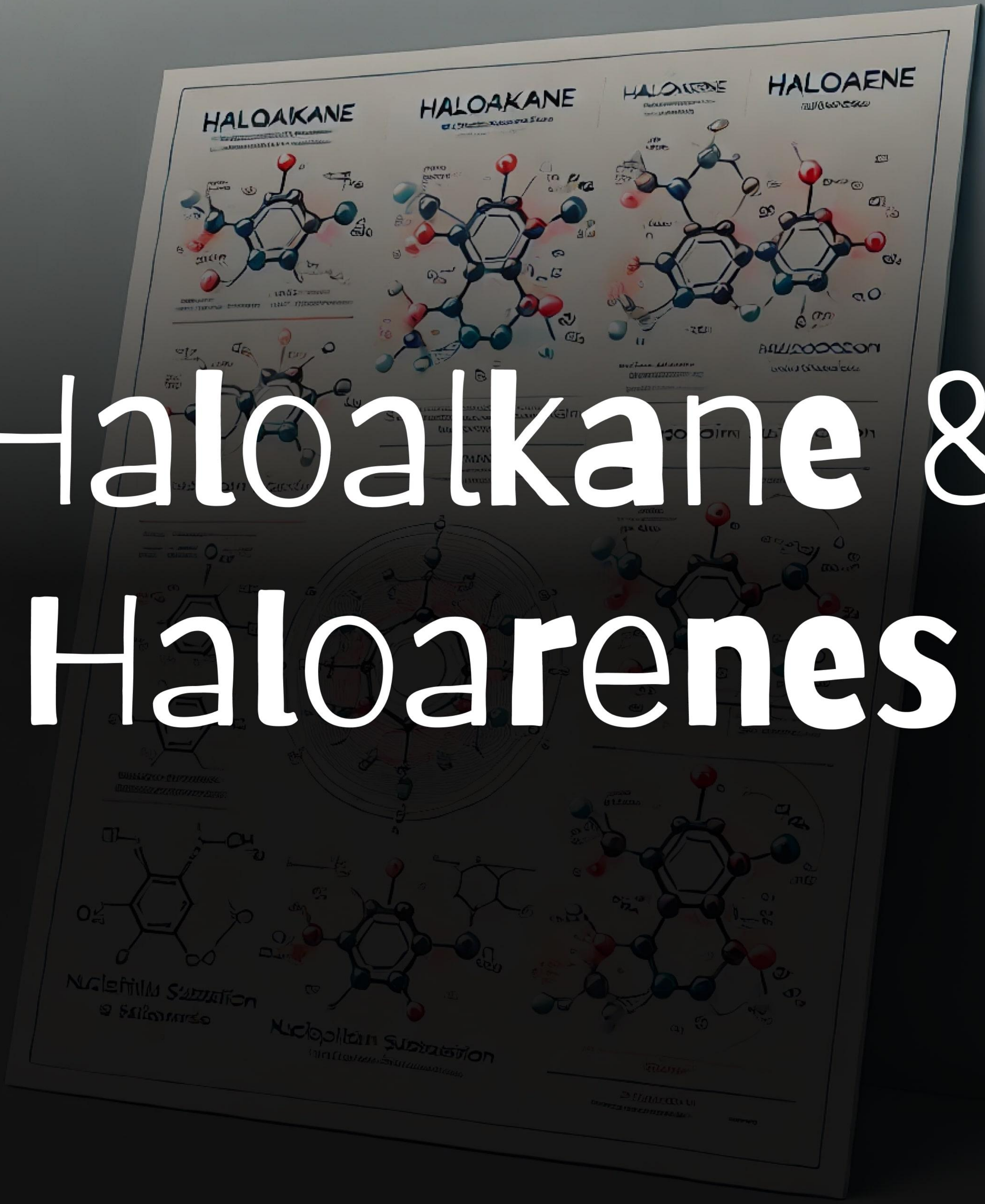


Haloalkane & Haloarenes

Alkyl Halide and Aryl Halide

- 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.

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

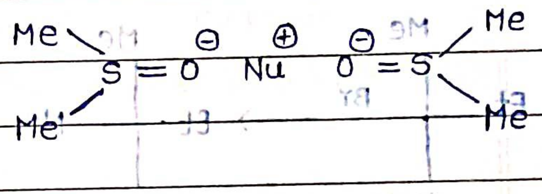
- Reaction in two-methods :

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	SN_2 Reaction
①	$R-X \longrightarrow R^{\oplus} \xrightarrow{Nu^{\ominus}} R-Nu$ $\downarrow$ Carbocation (T.S)	$R-X + Nu^{\ominus} \longrightarrow Nu-R--X \longrightarrow HOR + X^{\ominus}$ $\downarrow$ T.S
②	Kinetics. $R-X \xrightarrow{R.D.S} R^{\oplus}$	Kinetics $R-X + Nu^{\ominus} \xrightarrow{R.D.S} HOR + X^{\ominus}$
a)	2-step rxn.	1-step reaction
b)	Intermediate step.	Transition state
c)	Rate = $K[R-X]^{1}$	Rate = $K[R-X]^{1}[Nu^{-}]^{1}$
d)	Molecularity – 01	Elementary rxn.
e)	Order of Reaction – 01	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⊖ increases ③ Nu⊖ ∝ $\frac{1}{\text{Bulkness}}$ (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 DMSO → Dimethyl sulphoxide. CH_3COCH_3



Solvent

Polar solvent	Non-polar solvent
($\mu \neq 0$)	* Hydrocarbon * CCl_4, CS_2

Polar protic solvent ←	Polar aprotic solvent absence of
—O—H	× —O—H
—S—H	—S—H
—N—H	—F—H
—F—H	

} Bond

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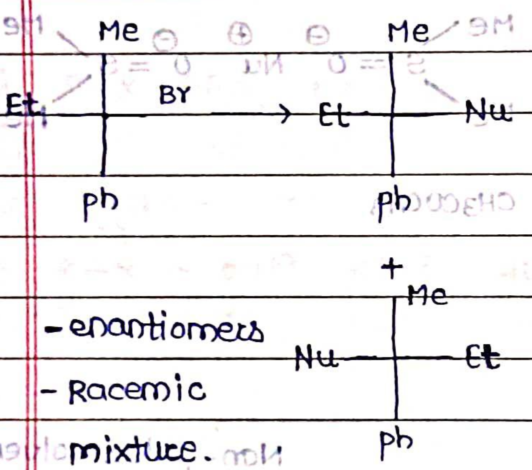
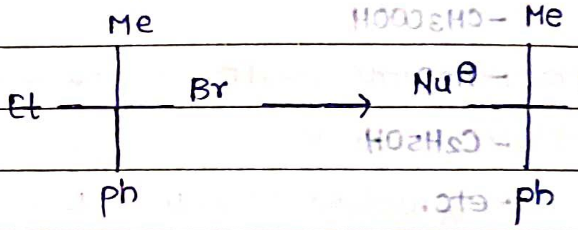
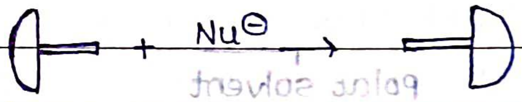
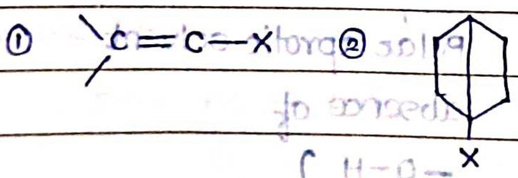
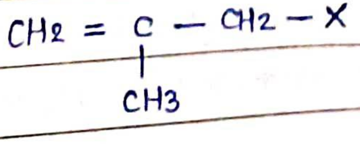
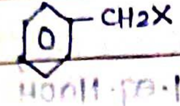
	SN1 Reaction	SN2 Reaction
①	Effect of leaving group Good leaving group. Rule ① : Neutral molecules are good leaving molecule. Rule ③ :- weak Base are good leaving group.	Effect of leaving group Good leaving group. Rule ② : Down the group leaving group tendency increases. Rule ④ : leaving tendency ∝ stability of leaving ion F < Cl < Br < I ↓ poor ↓ good leaving group
②	Stereochemistry of SN1 - Both side attack is possible  - enantiomers - Racemic mixture.	Stereochemistry of SN2 - Only Back attack is possible.  - Welden Inversion 
③	Effect of substrate ∝ Bulky group.	Effect of substrate ∝ small group.

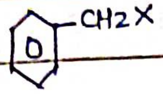
- 

→ do not show SN1 and SN2

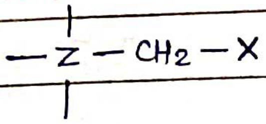
	Molecule		SN1		SN2
①	$CH_2 = CH - CH_2 - X$		Yes	<	Yes
②	 $CH_2 = \underset{CH_3}{\underset{\vert}{C}} - CH_2 - X$	$\xrightarrow[\text{allylic}]{\text{Branch}}$ Condition	Yes	>	Yes

③ 

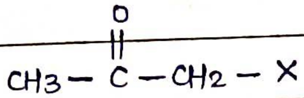
Yes < Yes

④ 

{If o- and p- directing group attached with Benzyl halide} Yes > Yes.

⑤ 
$-\overset{|}{\underset{|}{Z}}-CH_2-X$ Excellent Yes (poor)

(Where → $Z = \ddot{O}, \ddot{N}$)

⑥ 
$CH_3-\overset{O}{\overset{||}{C}}-CH_2-X$ Yes (poor) Excellent

β-keto Halide

- R–X —
  - $\xrightarrow{NaOH}$ R–OH
  - $\xrightarrow{NaOCH_3}$ $R-OCH_3$
  - $\xrightarrow{NaSH}$ R–SH
  - $\xrightarrow{CH_3COONa}$ $R-OOCCH_3$
  - $\xrightarrow{NaNO_2}$ $R-NO_2$
  - $\xrightarrow{AgNO_2}$ R–ONO.
  - $\xrightarrow{KCN}$ R–CN
  - $\xrightarrow{AgCN}$ R–NC.

- Swarts Reaction:

Alkyl Fluoride Formation

$CH_4 + F_2 \rightarrow$ carbon Black + High energy

$R-X + AgF \longrightarrow R-F + AgX$.
(Cl, Br, I)

(Metal Fluoride)
SbF_3, Hg_2F_2 etc.

$R-X + NaI \longrightarrow R-I + NX$
(Cl, Br)
↓ Acetone Solvent
Alkyl Halide

- Formation of Alkyl Iodide:

$CH_4 + I_2 \rightleftharpoons CH_3-I + HI$
↓ Equilibrium
↓ Reducing agent

Note: Equilibrium shifted Forward direction in presence of oxidising agent (HNO_3)

Further CH_3I ko reduce kar deta

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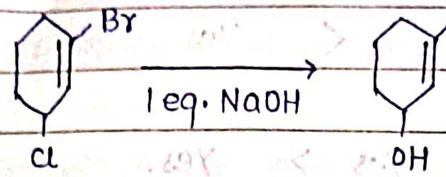
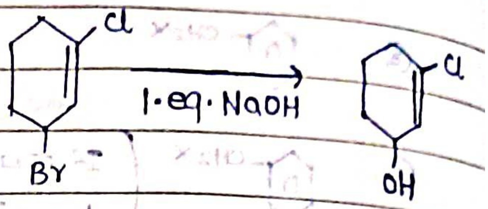
- 



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

$$CH_3-CH=CH_2 \xrightarrow[N\cdot B\cdot S]{Br_2} \overset{Br}{\overset{|}{CH_2}}-CH=CH_2$$

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

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

$$\therefore\ 3ROH + 1PCl_3 \longrightarrow 3R-Cl + H_3PO_3 \text{ or } P(OH)_3$$

b) $PX_5 \longrightarrow$ PF_5 PCl_5 PBr_5 PI_5

PF_5 — ⊗; PI_5 — do not exist

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

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

(c) $SOCl_2$ (Darzen Method)

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

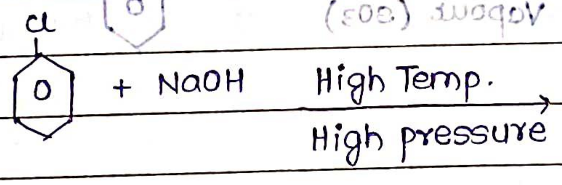
- Best method for preparation of Alkyl halide.

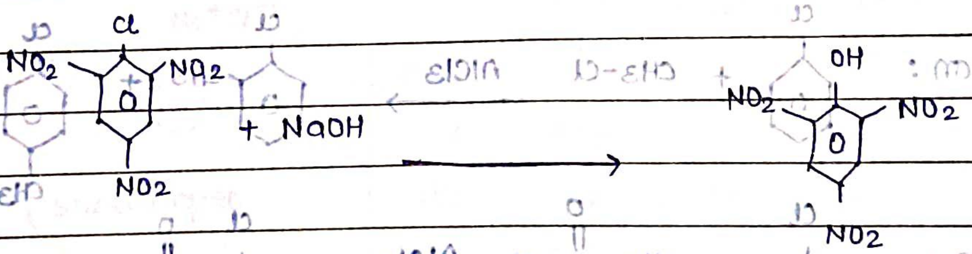
$R-OH \xrightarrow{SOCl_2}$ Nucleophilic substitution with Rentention.

$\downarrow$ $SOCl_2$  (pyridine)

Nucleophilic substitution with inversion.

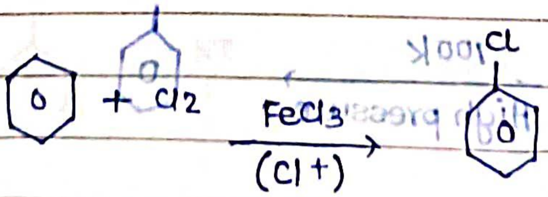
- Aryl halides:



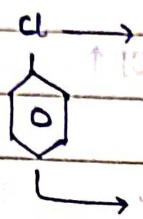


Note: Aromatic halides gives $ArSN^1$ and $ArSN^2$ at high temp and pressure or in presence of number of meta directing group.

- M.O.P:



- Chemical properties :

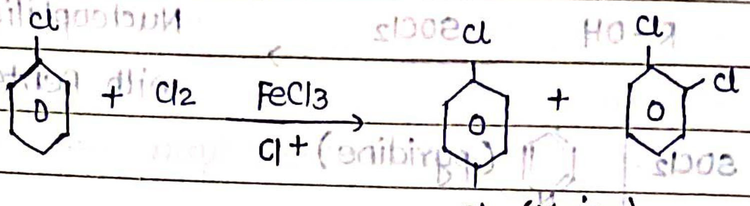


Cl → leaving group → Nucleophilic substitution Reaction.

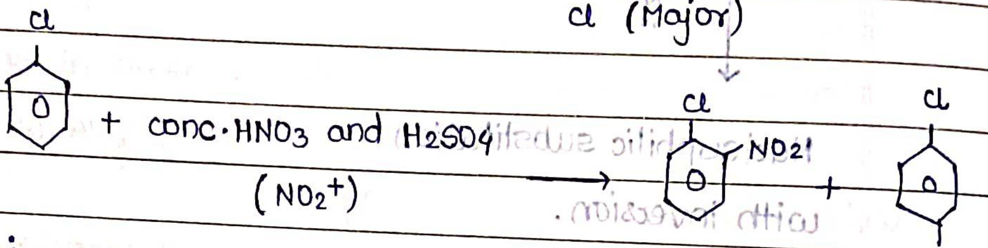
→ E.A.S Reaction — o⊖ and p⊖ directing in nature.

(Domination easily)

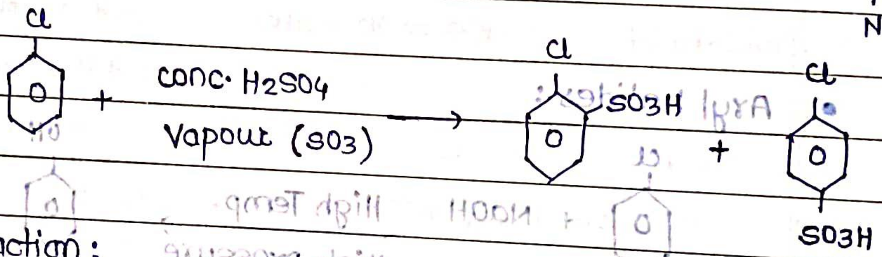
① Halogenation.



② Nitration

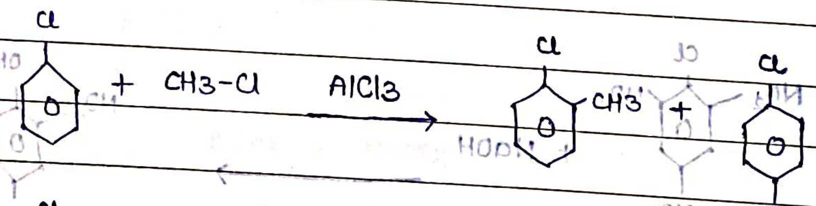


③ Sulphonation :

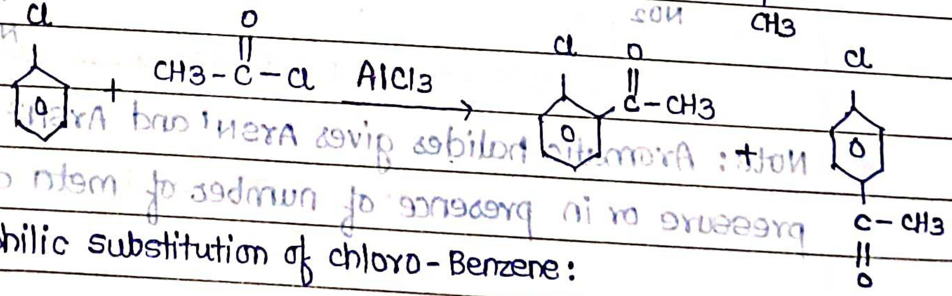


- Friedal craft Reaction :

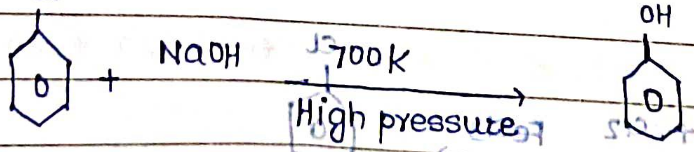
① Alkylation :



② Acylation :



- Rate of Nucleophilic substitution of chloro-Benzene :



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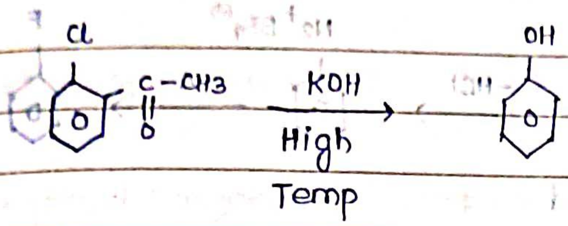
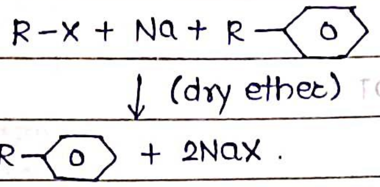
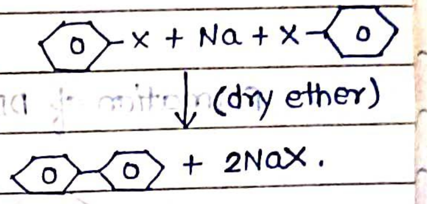
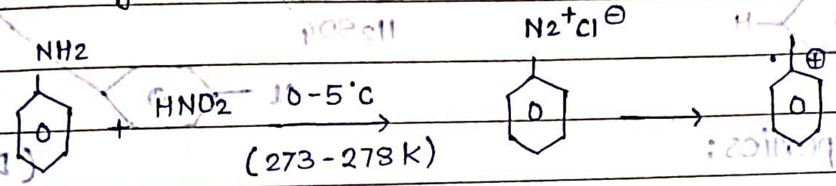


-

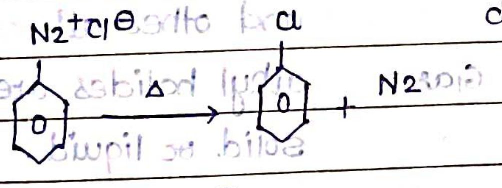
Wurtz Reaction	Wurtz-Fittig Rxn	Fittig Reaction
(Both aliphatic)	(one aromatic and one aliphatic)	(Both Aromatic)
$R-X + Na + R-X$ ↓ (dry ether) $R-R + 2NaX$		

- Sandmeyer Reaction :

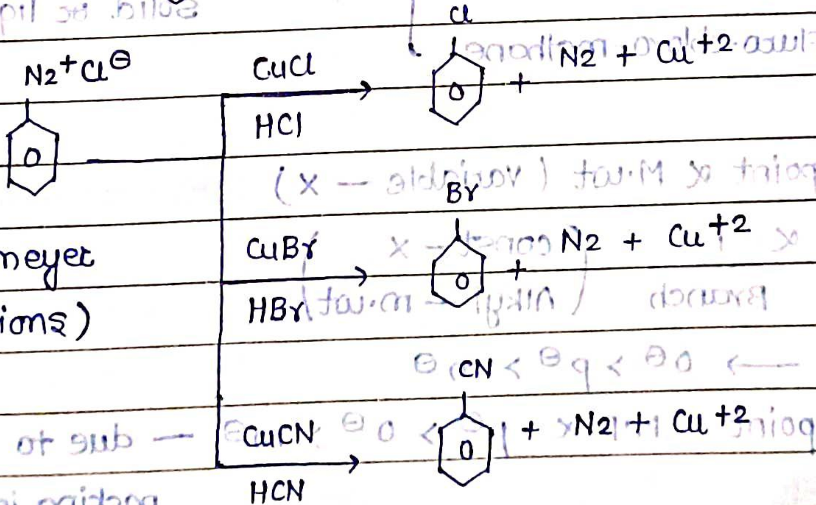


Free Radical or carbocation.
↓
Nucleophile add kar dena.

Benzene Diazonium chloride



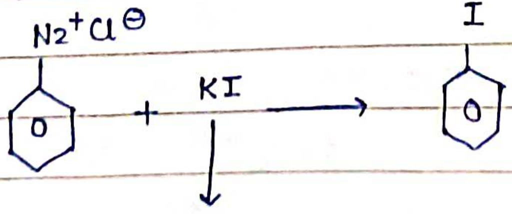
①



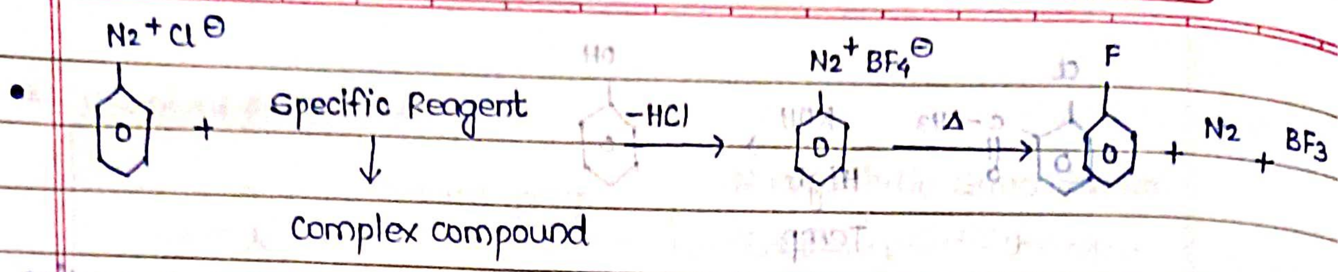
(sandmeyer Reactions)

Note: CuX
↓
Reducing agent

- Note :



(I⊖ - self mein Reducing agent ka kaam krta hai)

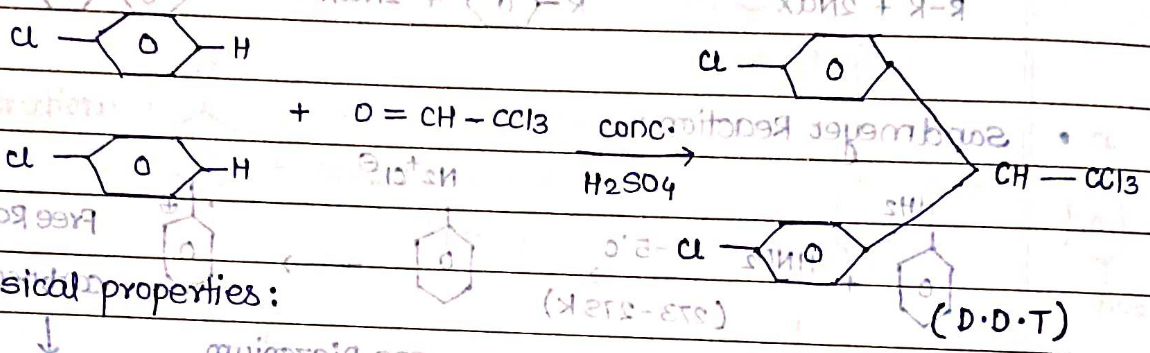


of Fluoride

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

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

- 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)

$$B\cdot P \propto \frac{1}{\text{Branch}} \begin{pmatrix} \text{const} - x \\ \text{Alkyl} - m\cdot wt \end{pmatrix}$$

$B\cdot P \longrightarrow o^\ominus > p^\ominus > m^\ominus$

- Melting point → $M\cdot P \propto p^\ominus > o^\ominus > m^\ominus$ — due to packing in solid state.