

Alkyl Halide and Aryl Halide

Page No. _____

Date _____

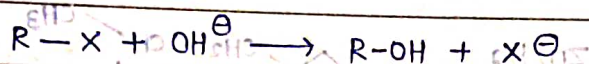
- Nucleophilic Substitution Reaction :

Nucleophile \rightarrow Nucleus loving species

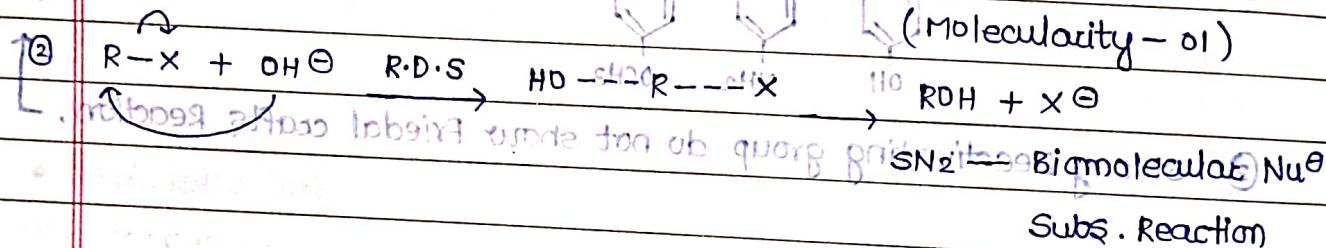
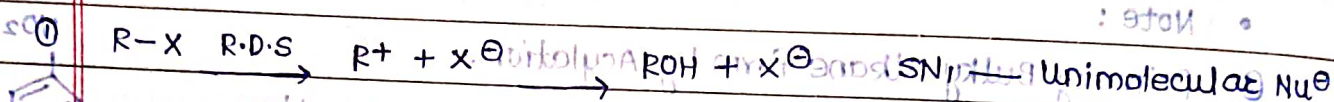
Condition \rightarrow ① Octet complete

② Minimum 1 lone pair.

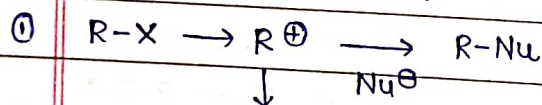
Ex: Cl^- , OH^- , SH^- , N^{3-} , H_2O , NH_3 , OH^- .



- Reaction in two- methods :

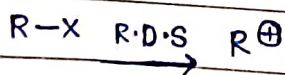


- SN1 Reaction



Carbocation (T.S)

- ② Kinetics.



a) 2-step rxn.

b) Intermediate step.

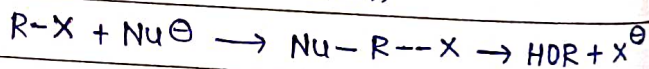
c) Rate = $k[\text{R}-\text{X}]^1$

d) Molecularity - 01

e) Order of Reaction - 01

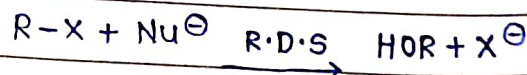
(Molecularity - 02)

SN2 Reaction



T.S

Kinetics



1-step reaction

Transition state

Rate = $k[\text{R}-\text{X}]^1[\text{Nu}^-]^1$

Elementary rxn.

M=2 ; Order of Reaction = 2.

SN1 Reaction

③ Rate of SN1 \propto stability of carbocation

④ Effect of Nucleophile
- No effect

⑤ Effect of Solvent

Favour polar protic solvent

- CH₃COOH

- H₂O

- C₂H₅OH

- etc.

SN2 Reaction

Rate of SN2 \propto Bulkness

Rate \propto strength of Nucleophile

① L \rightarrow R \rightarrow Nucleophilicity decreases

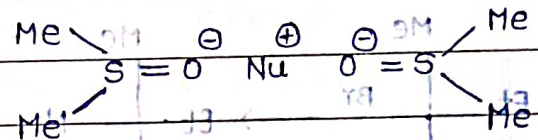
② Down the group \rightarrow Nu⁻ increases

③ Nu⁻ \propto Bulkness (same type ions)

Effect of Solvent

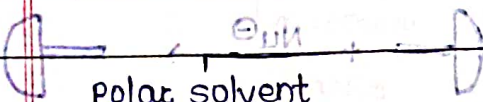
Favour polar aprotic solvent

DMSO \rightarrow Dimethyl sulphoxide.



CH₃COCH₃

Solvent



polar solvent

($\mu \neq 0$)

Non-polar solvent

* Hydrocarbon

* CCl₄, CS₂

Polar protic solvent \leftarrow

- O-H

- S-H

- N-H

- F-H

Polar aprotic solvent

absence of

- O-H

- S-H

- F-H

Bond

SN₁ Reaction

① Effect of leaving group

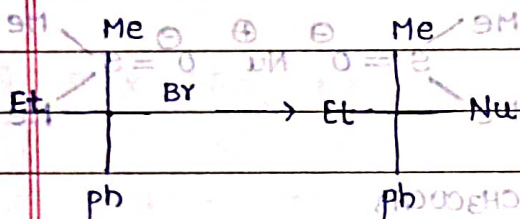
Good leaving group.

Rule ①: Neutral molecules are good leaving molecule.

Rule ②: Weak Base are good leaving group.

② Stereochemistry of SN₁

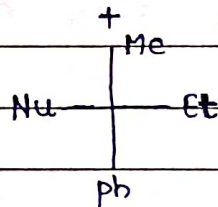
Both side attack is possible



- enantiomers

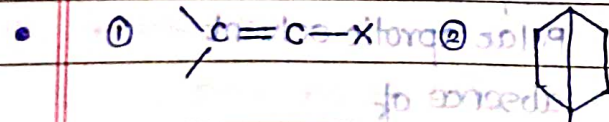
- Racemic

mixture.

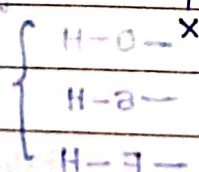


③ Effect of substrate

α Bulky group.

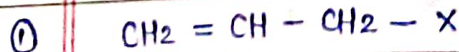


Molecule



SN₁

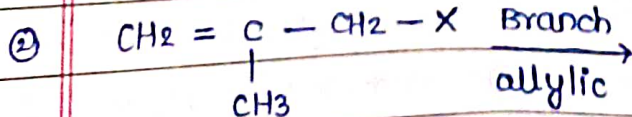
SN₂



Yes

<

Yes



Yes

>

Yes

allylic Condition

SN₂ Reaction

Effect of leaving group

Good leaving group.

Rule ②: Down the group leaving group tendency increases.

Rule ④: leaving tendency × stability of leaving ion

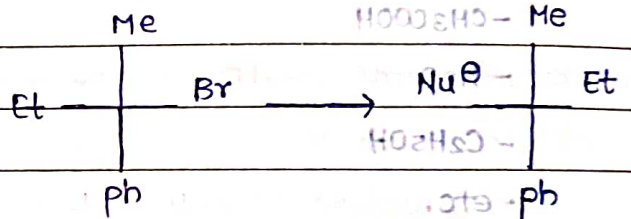


poor

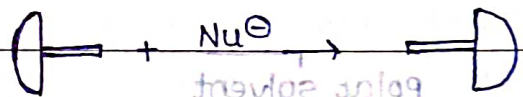
good leaving group

Stereochemistry of SN₂

- Only Back attack is possible.



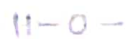
Walden Inversion



Effect of substrate

α small group.

→ do not show SN₁ and SN₂

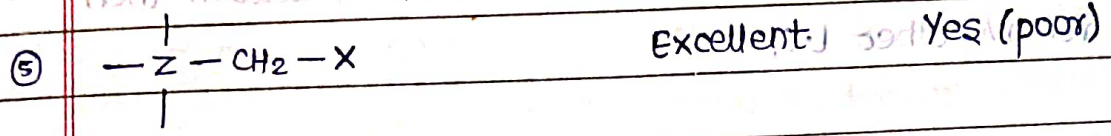
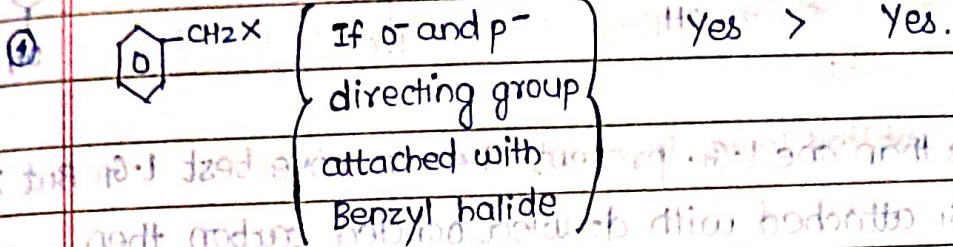
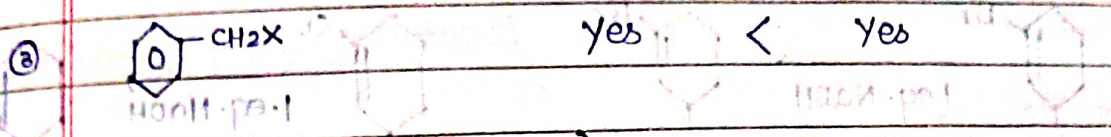


SN₂

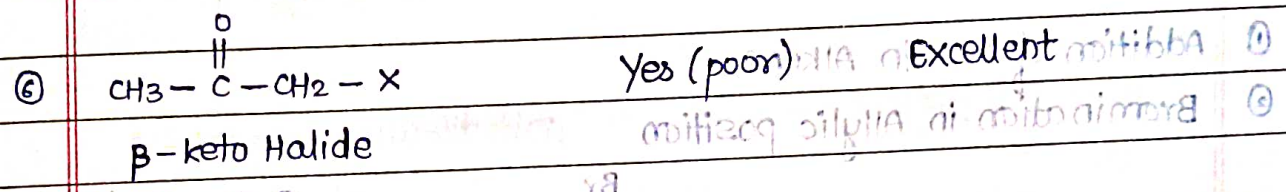


Yes

Yes



(where $\rightarrow Z = \ddot{O}, \ddot{N}^+$)



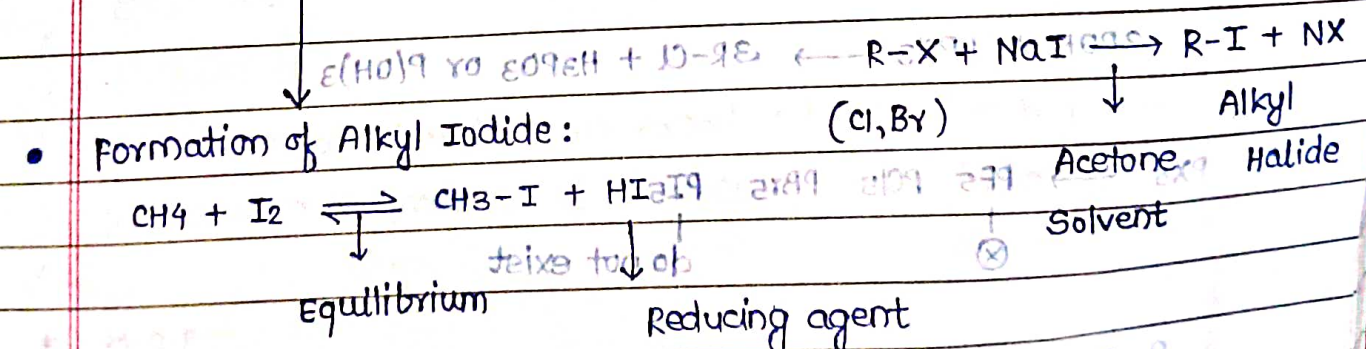
• Swarts Reaction:

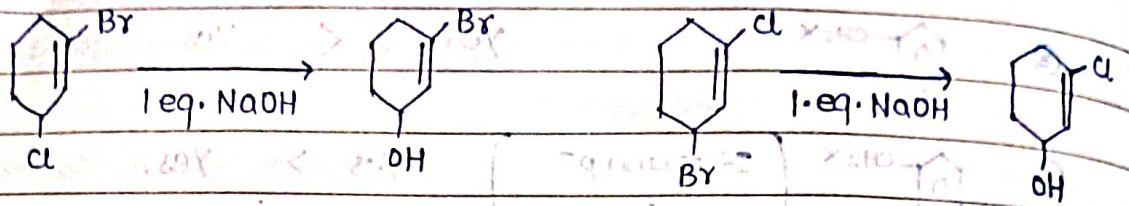
2.2.11 Alkyl Fluoride Formation

$CH_4 + F_2 \rightarrow \text{carbon} + \text{High Black energy}$

R-X	\xrightarrow{NaOH}	$R-OH$
	$\xrightarrow{NaOCH_3}$	$R-OCH_3$
	\xrightarrow{NaSH}	$R-SH$
	$\xrightarrow{CH_3COONa}$	$R-OOCCH_3$
	$\xrightarrow{NaNO_2}$	$R-NO_2$
	$\xrightarrow{AgNO_2}$	$R-ONO_2$
	\xrightarrow{KCN}	$R-CN$
	\xrightarrow{AgCN}	$R-NC$

$R-X + AgF \rightarrow R-F + AgX$
(Cl, Br, I)
(Metal Fluoride)
 SbF_3, Hg_2F_2 etc.

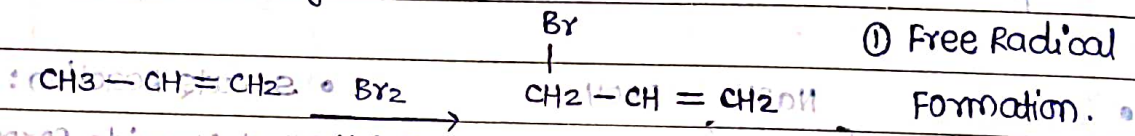




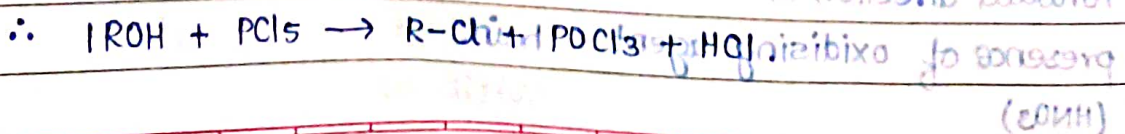
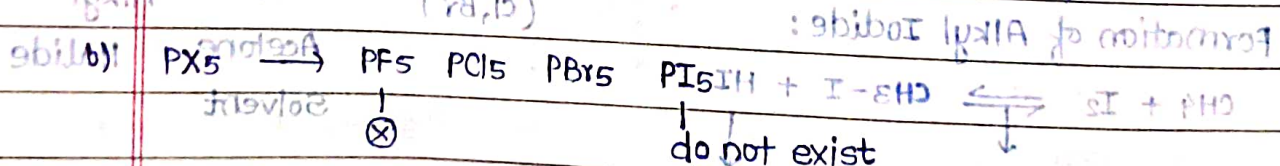
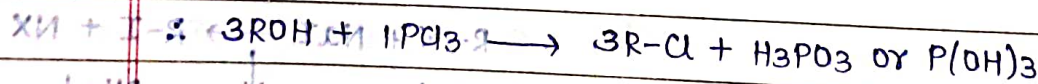
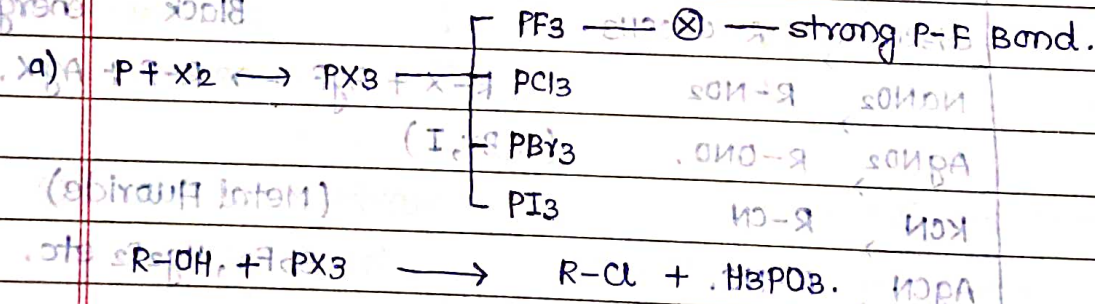
Note: If more than one L.G. present then remove best L.G. But X Best L.G. attached with double bonded carbon then remove other L.G.

Method of preparation \rightarrow Alkyl Halide: $= \text{X} - \text{C} - \text{R}$

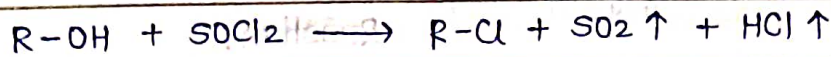
- ① Addition of HBr in Alkene
- ② Bromination in Allylic position



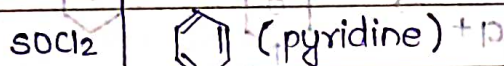
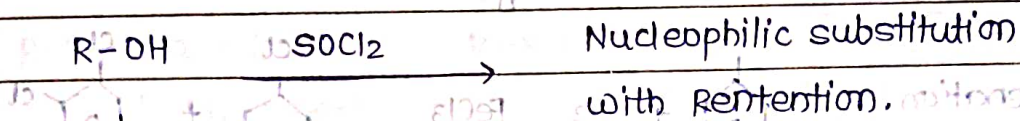
By alcohol: $\text{R-OH} + \text{PX}_3 \rightarrow \text{R-X} + \text{H}_3\text{PO}_3$



(c) SOCl_2 (Darzen Method)

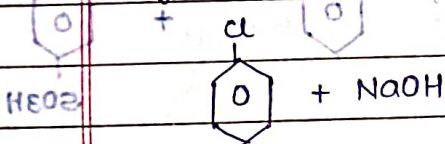


Best method for preparation of Alkyl halide.

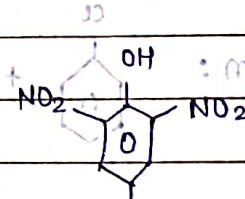
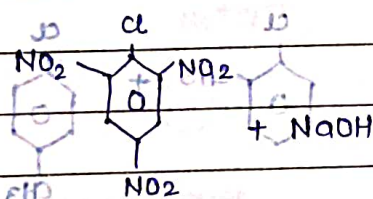


Nucleophilic substitution
with inversion.

Aryl halides:

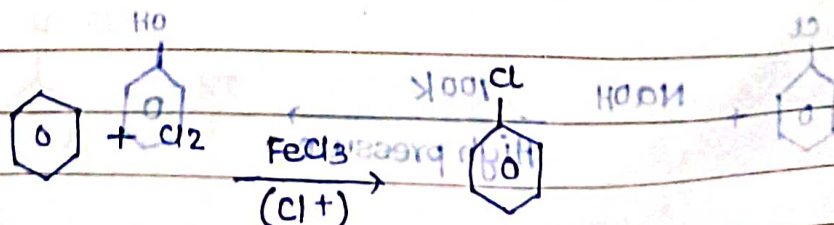


High Temp.
High pressure

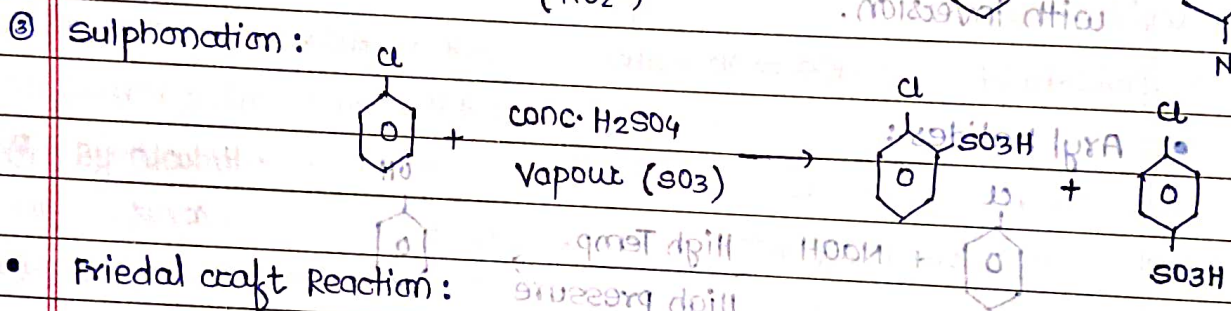
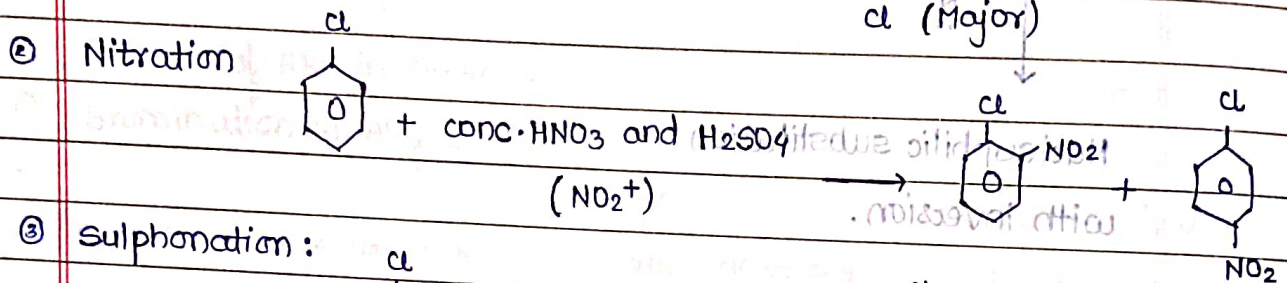
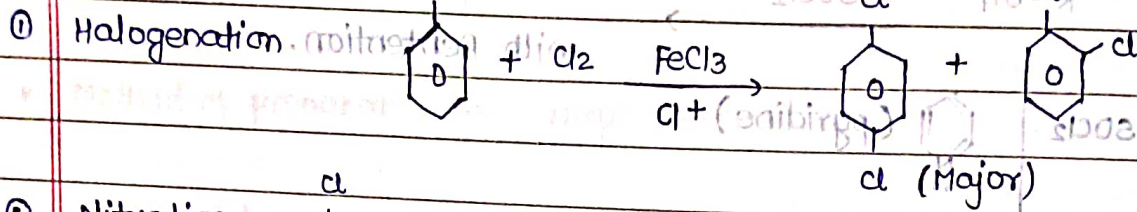
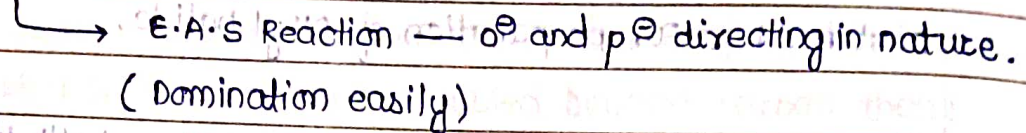
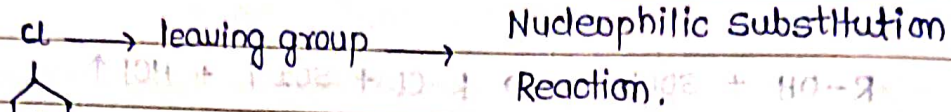


Note: Aromatic halides gives ArSN^1 and ArSN^2 at high temp and pressure or in presence of number of meta directing group.

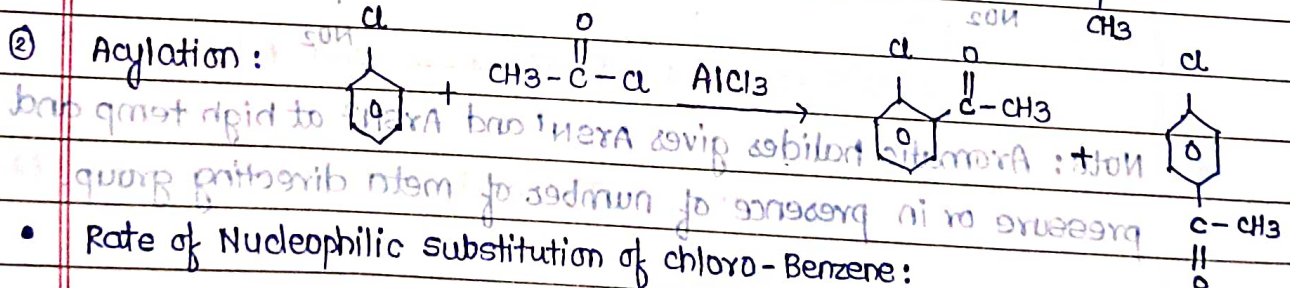
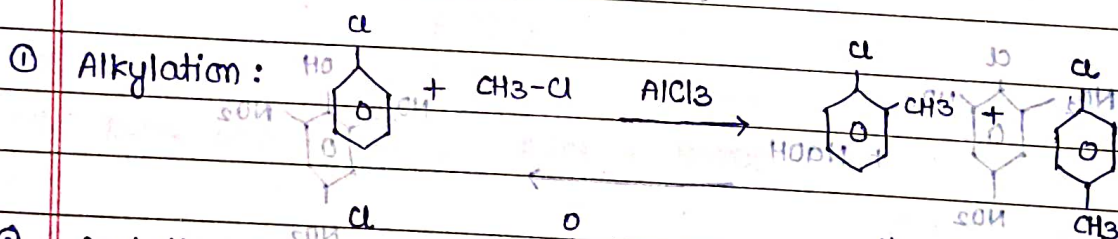
M.O.P:



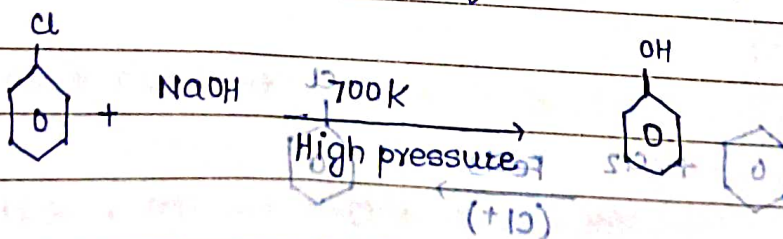
Chemical properties:

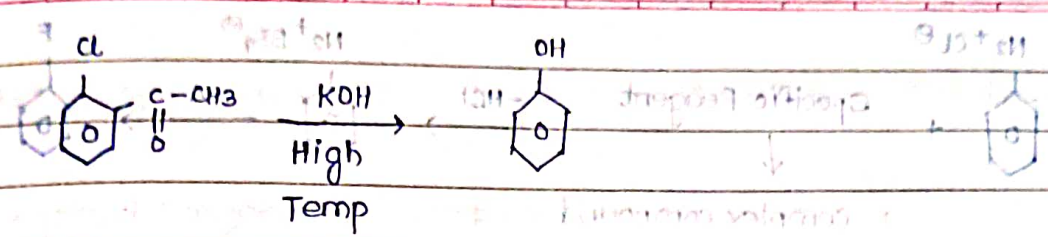


Friedel craft Reaction:



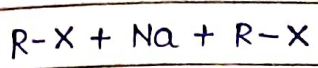
Rate of Nucleophilic Substitution of chloro-Benzene:



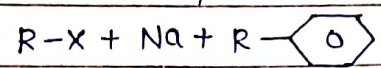
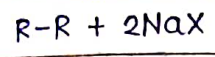


Wurtz Reaction
(Both aliphatic)

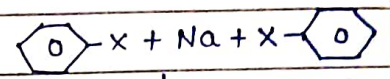
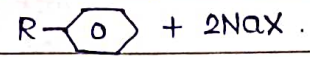
Wurtz-Fittig Rxn / Fittig Reaction
(one aromatic and one aliphatic)



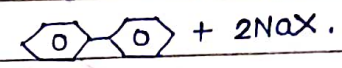
↓ (dry ether)



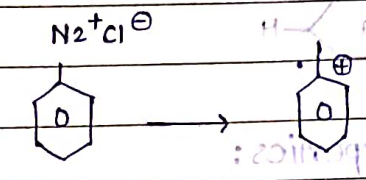
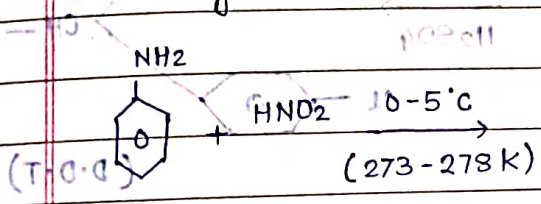
↓ (dry ether)



↓ (dry ether)



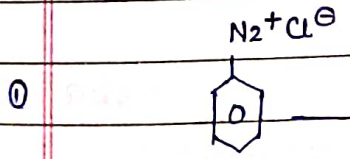
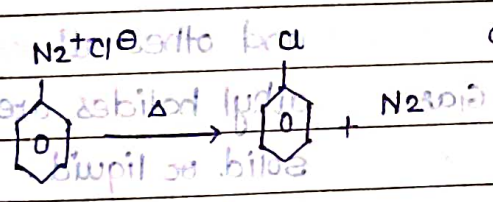
Sandmeyer Reaction:



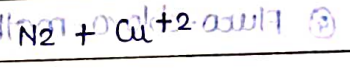
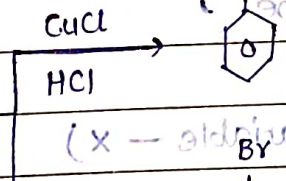
Free Radical or carbocation.

Benzene Diazonium

Nucleophile add
dikar dena.

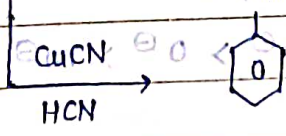


(Sandmeyer Reactions)

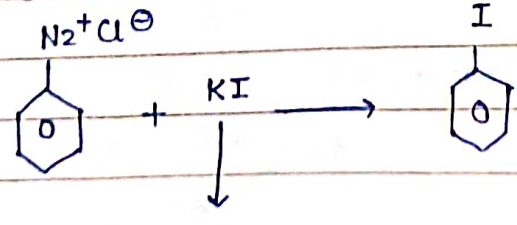


Note: CuX

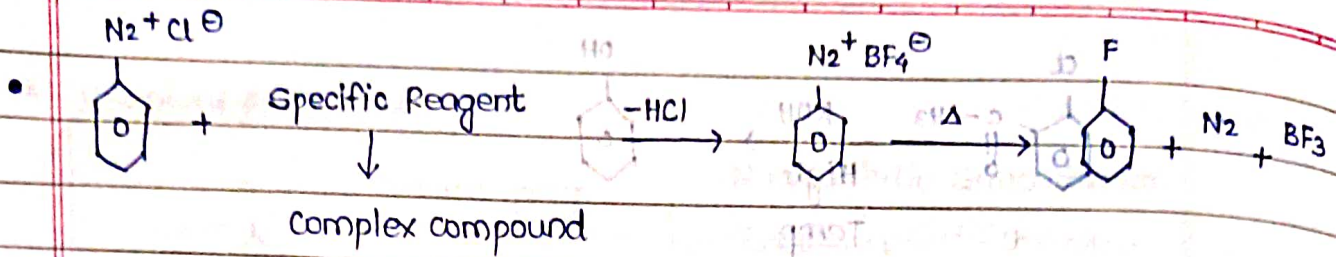
Reducing agent



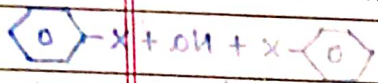
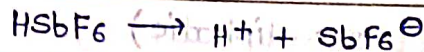
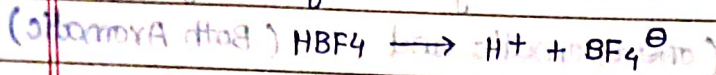
Note:



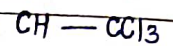
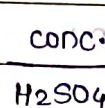
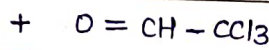
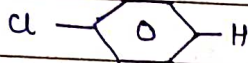
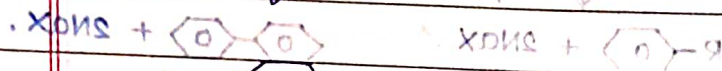
(I^- - self mein Reducing agent ka kaam karta hai)



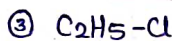
of Fluoride



Formation of DDT



Physical properties:



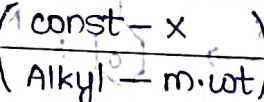
Gas

and other alkyl halides are solid or liquid.

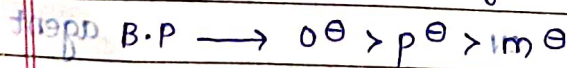
Bolling point \propto M.wt (Variable - x)



Branch

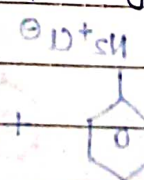
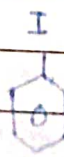


Reducing



Melting point \propto M.P \propto P $>$ O $>$ M — due to

packing in solid state.



(Iodine is a strong oxidizing agent for many organic compounds)