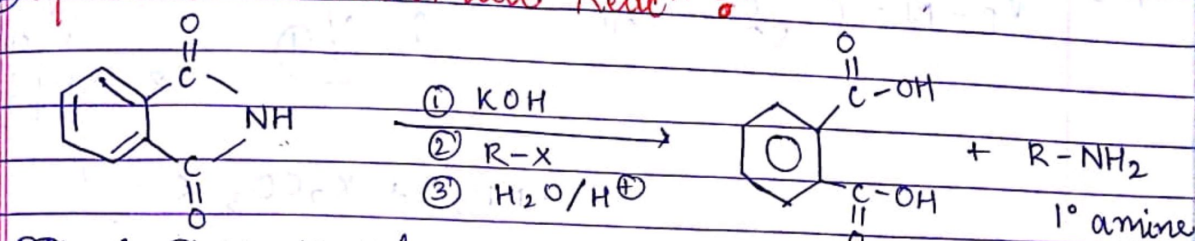
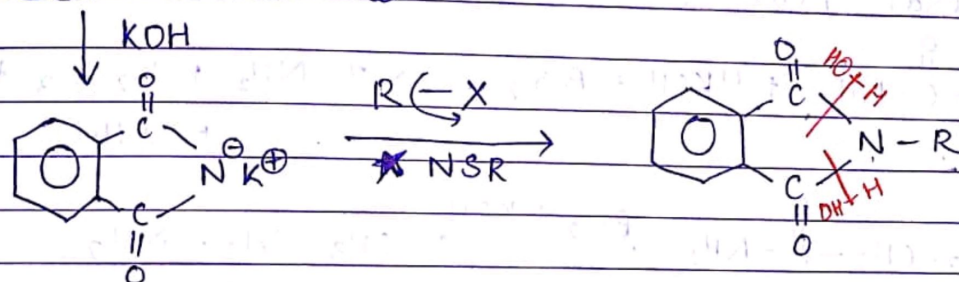


V.V. Smol
Gabriel Phthalimide Reacⁿ :-

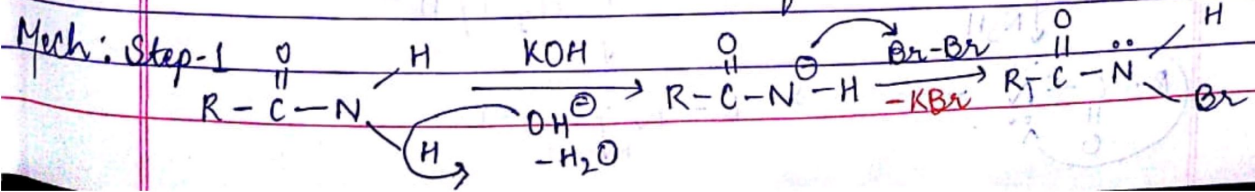
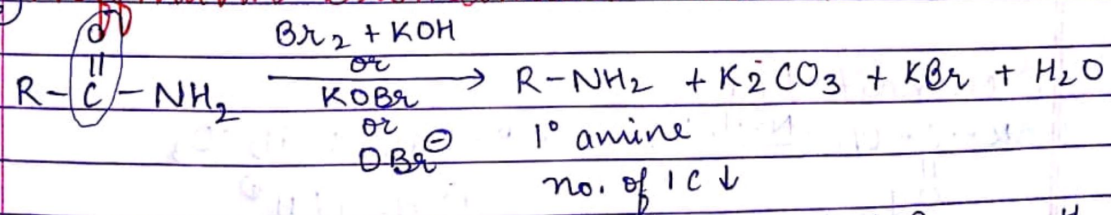


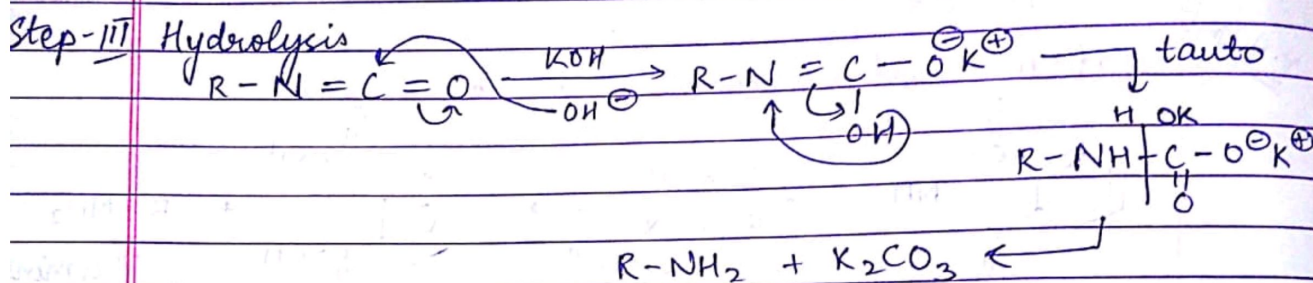
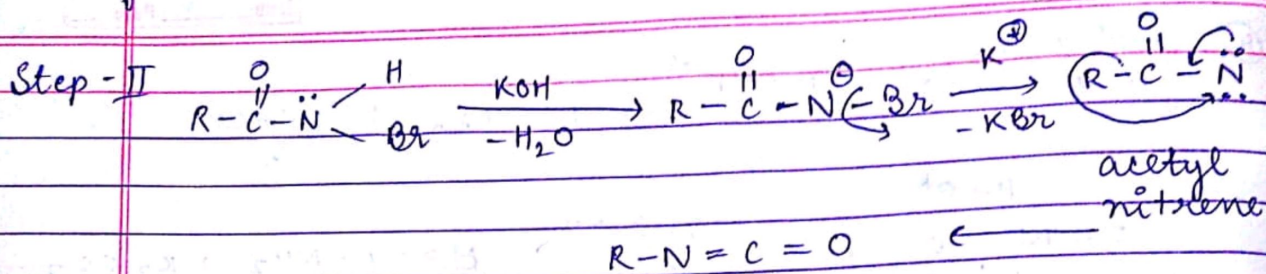
~~Phthal~~ Phthalimide



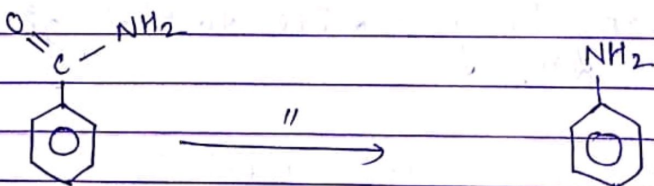
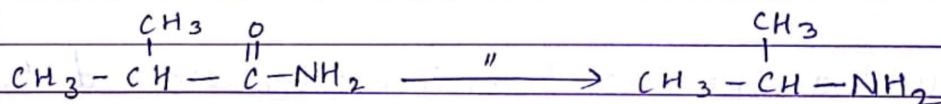
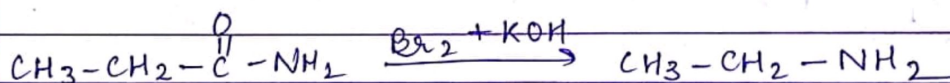
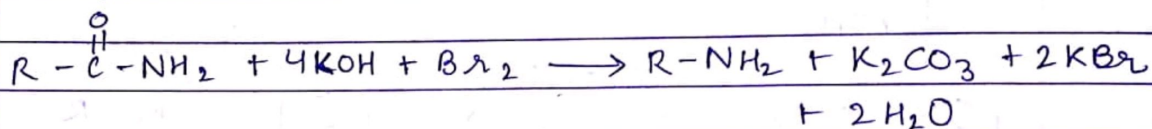
Note Only 1° amine except aniline are formed by this reacⁿ becoz aryl halide do not give NSR in Normal condⁿ.

V.V. Smol
Hoffmann Bromamide Reacⁿ :-

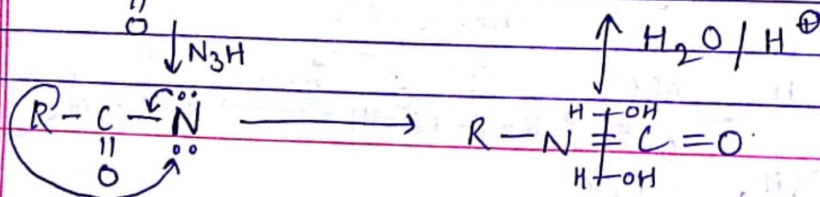
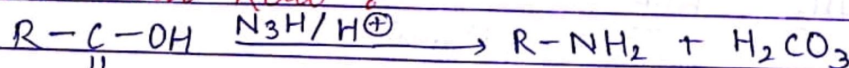




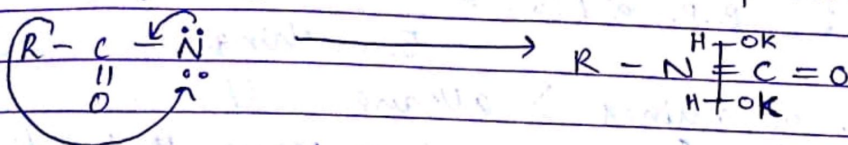
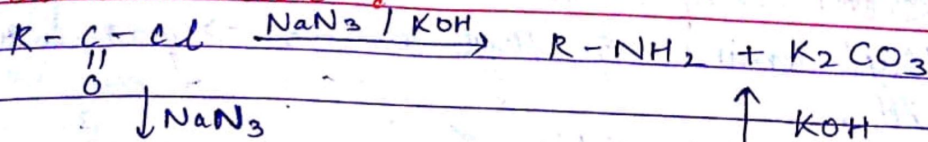
Overall Reacⁿ :-



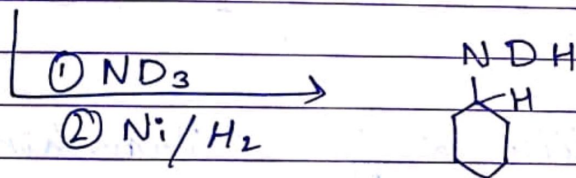
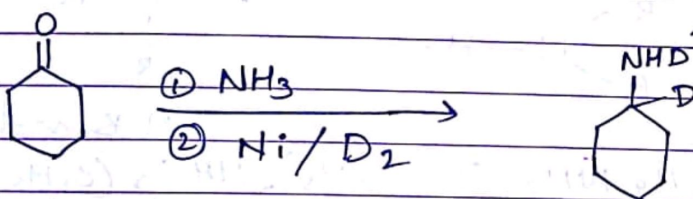
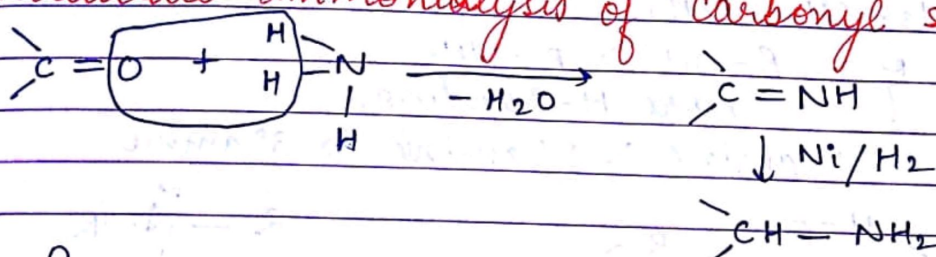
Schmidt Reacⁿ :-



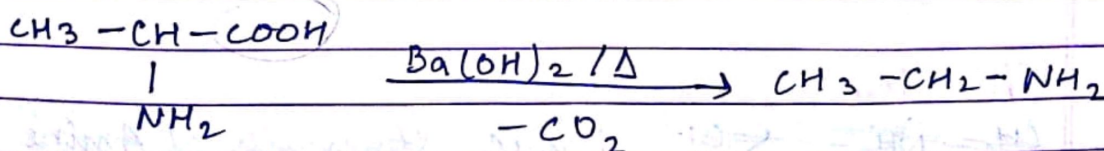
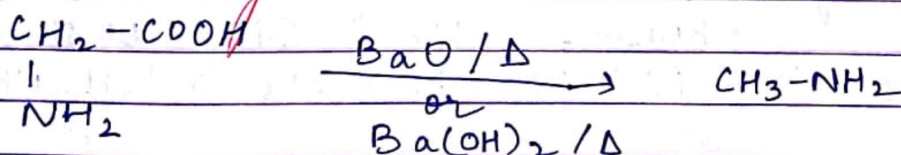
Curtius Reacⁿ :-



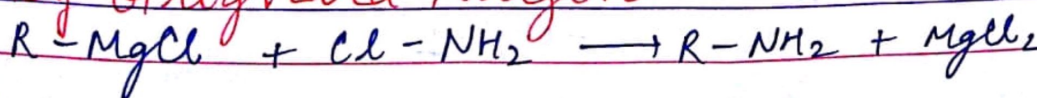
Reductive ammonialysis of carbonyl substance



Decarbonylation of amino acid



By Grignard Reagent



Physical Properties :-

1. Methyl amine & ethyl amine \rightarrow gas & rest are liquid.

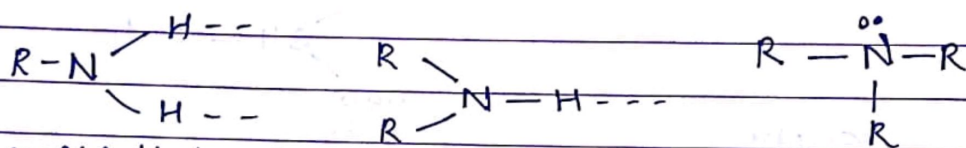
2. B.P. : B.P. \propto Mw. \propto $\frac{1}{\text{Branching}}$

B.P. of amines $>$ alkane

\uparrow Reason amines form H-bonding
 $\text{CH}_3\text{-CH}_2\text{-NH}_2 > \text{CH}_3\text{-CH}_2\text{-CH}_3$

B.P. of $\text{R-OH} > \text{R-NH}_2$
 more H-bonding

B.P. : $1^\circ \text{ amine} > 2^\circ \text{ amine} > 3^\circ \text{ amine}$



more H-bonding

H Bond \times

$\text{C}_4\text{H}_9\text{OH} > \text{C}_4\text{H}_9\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)\text{N}(\text{CH}_3)_2$
 alcohol 1° 2° 3°

3. Solubility : Solubility $\propto \frac{1}{\text{Mw}}$ \propto Branching

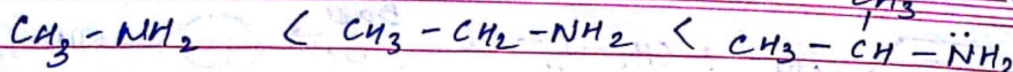
Solubility of $\text{R-OH} > \text{R-NH}_2$

Reason $\text{EN}_\text{O} > \text{E.N.N}$ so strong H-bond
 $\text{C}_3\text{H}_7\text{OH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{-NH-C}_2\text{H}_5 > \text{C}_3\text{H}_7\text{NH}_2$
 3° 2° 1°

Chemical Properties :-

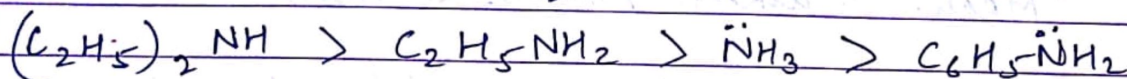
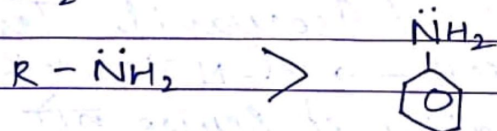
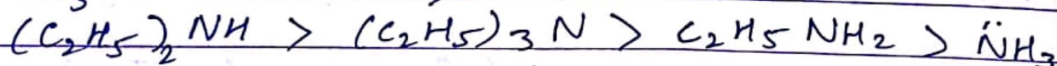
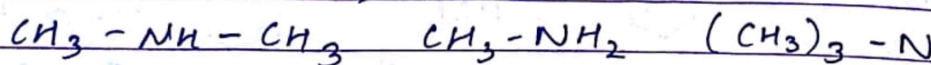
~~$\text{CH}_3\text{-NH}_2$~~ $\leftarrow \text{EF}$ Basic strength of Amine :-

B.S. \propto $\frac{+M}{+I}$
 $\frac{-M}{-I}$



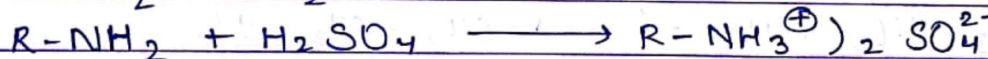
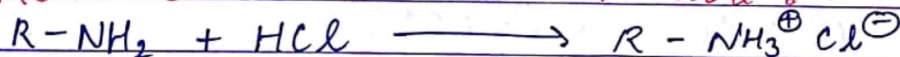
In gaseous state B.S. of amine $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$

In aq. state B.S. of amines ..

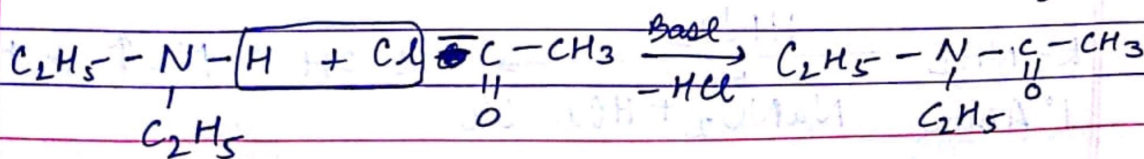
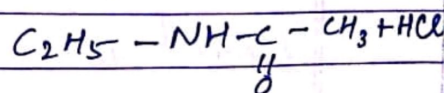
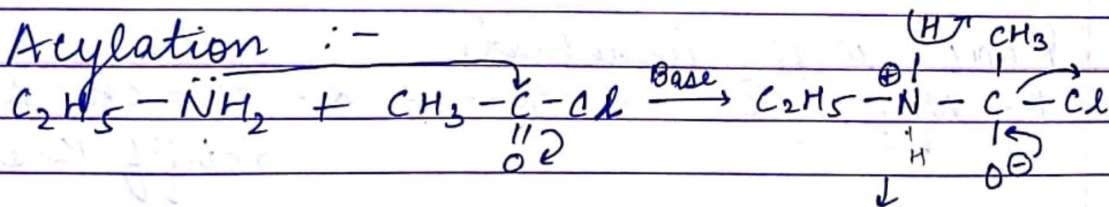


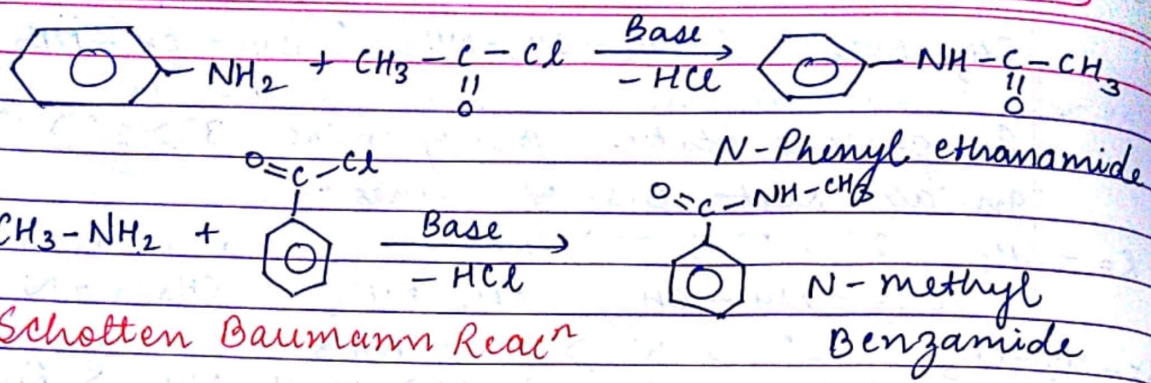
Amines can turn red litmus into blue.
Amines can form salt with acid

Reacⁿ due to basic nature :-



Acylation :-





Carbyl amine Reacⁿ : / Isocyanide Test

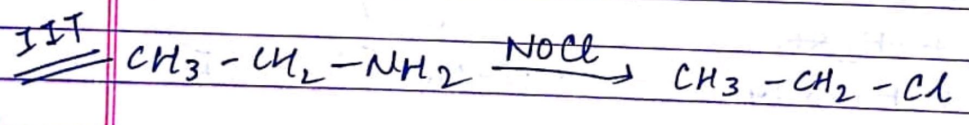
$$\text{R-NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow \text{R-N}\equiv\text{C} + \text{KCl} + \text{H}_2\text{O}$$

Mech. \rightarrow alkyl halide \uparrow Reine \rightarrow RT

Reacⁿ with due to acidic H :-

$$\text{R-NH}_2 + \text{Na} \rightarrow \text{R-NH}^\ominus\text{Na} + \text{H}_2 \uparrow$$

Reacⁿ with Tildane :-

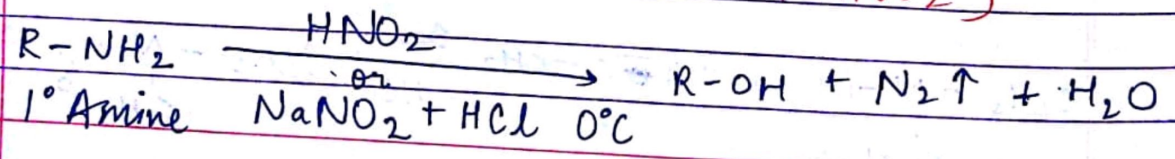
$$\text{R-NH}_2 \xrightarrow[\text{NOCl}]{\text{Tildane}} \text{R-Cl} + \text{N}_2 + \text{H}_2\text{O}$$


Reacⁿ with Aldehyde

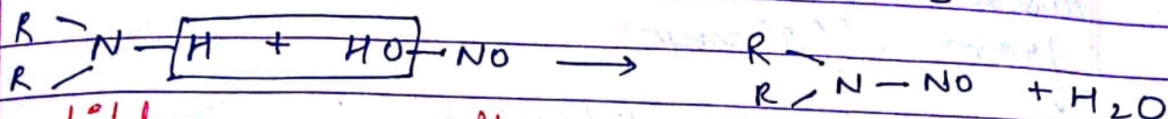
$$\text{R-NH}_2 + \text{O}=\text{CH-R} \rightarrow \text{R-N}=\text{CH-R}$$

Schiff Base

Reacⁿ with Nitrous Base (HNO₂)

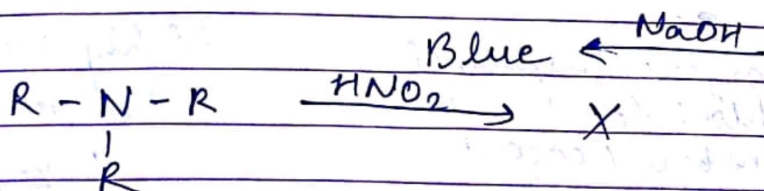


Except $\text{CH}_3 - \text{NH}_2$



Libbermann nitroso Test Dialkyl nitroso amine
(Yellow oily liq.)

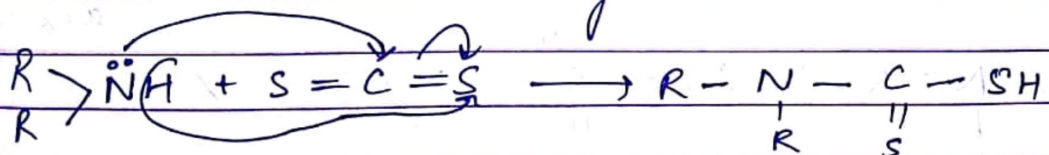
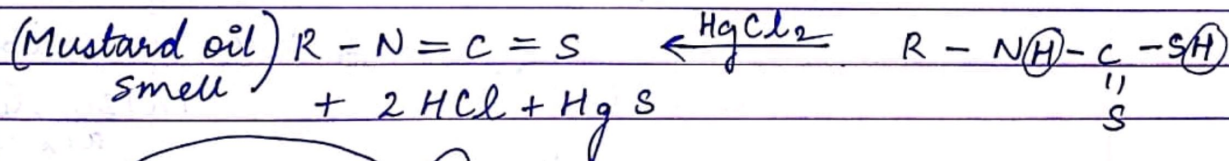
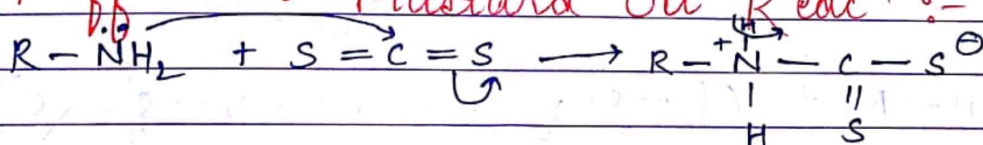
↓ Phenol & few
drop of H_2SO_4



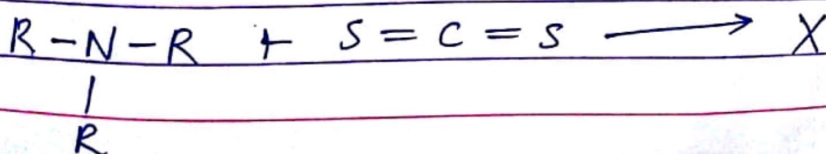
Red

Hence HNO_2 is used to distinguish b/w 1°, 2°, 3° amine

Hoffmann Mustard Oil Reacⁿ :-



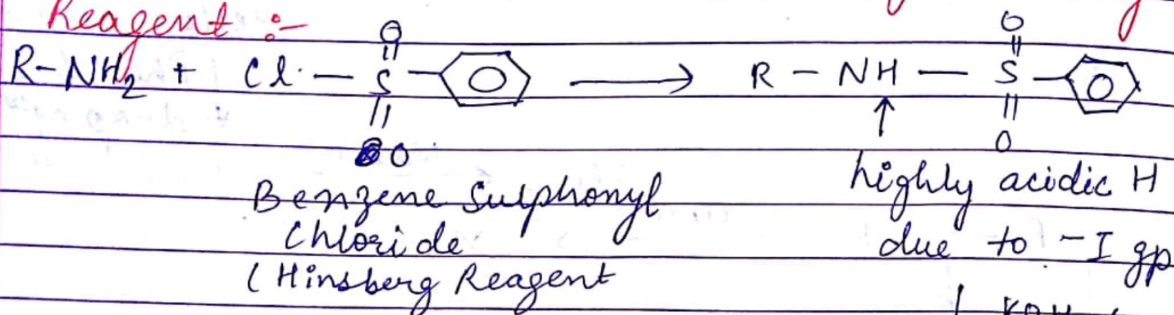
↓ HgCl_2
X



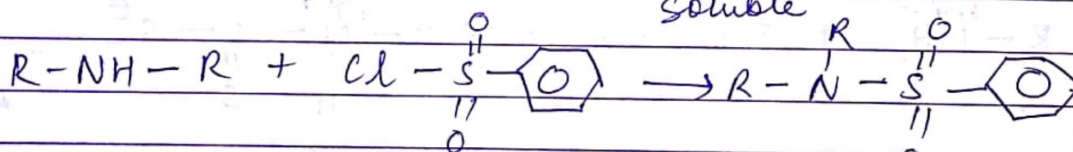
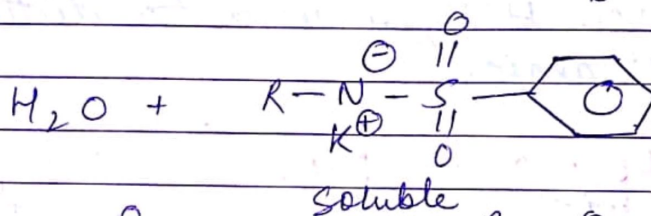
Only 1° amine will give mustard oil smell hence distinction b/w 1° amines can be separated from 2°/3° amine.

NCERT

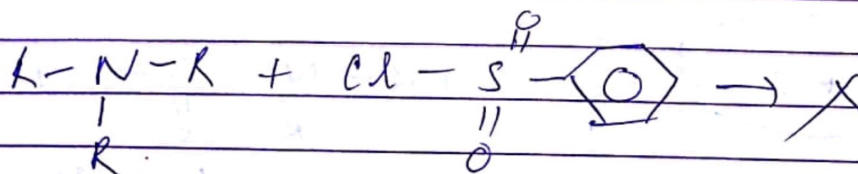
Distinction b/w 1°/2°/3° amine by Hinsberg Reagent :-



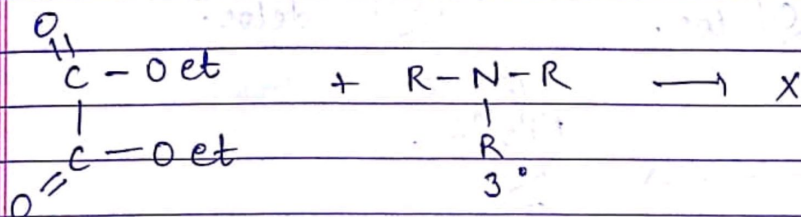
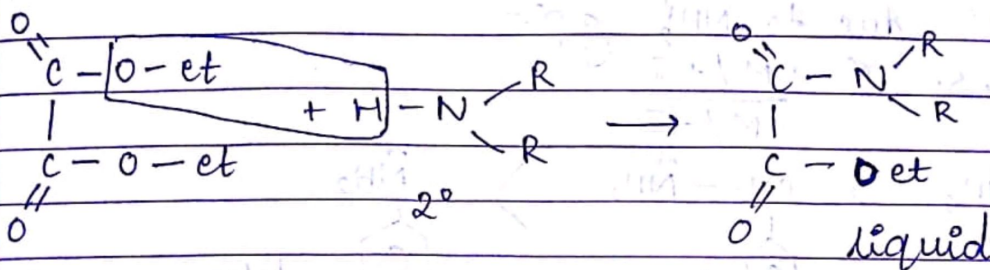
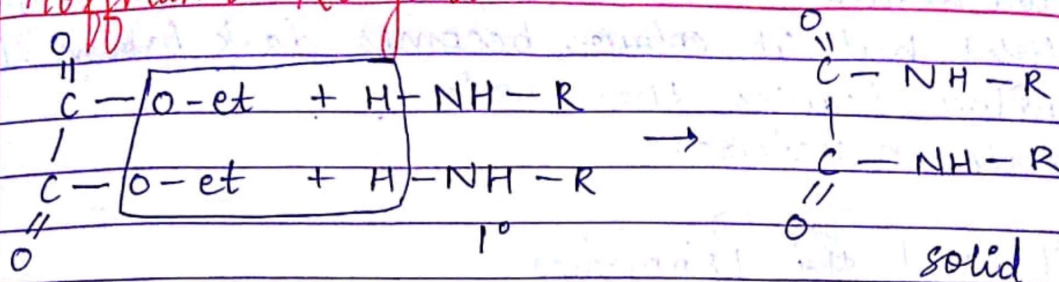
KOH so soluble in alkali



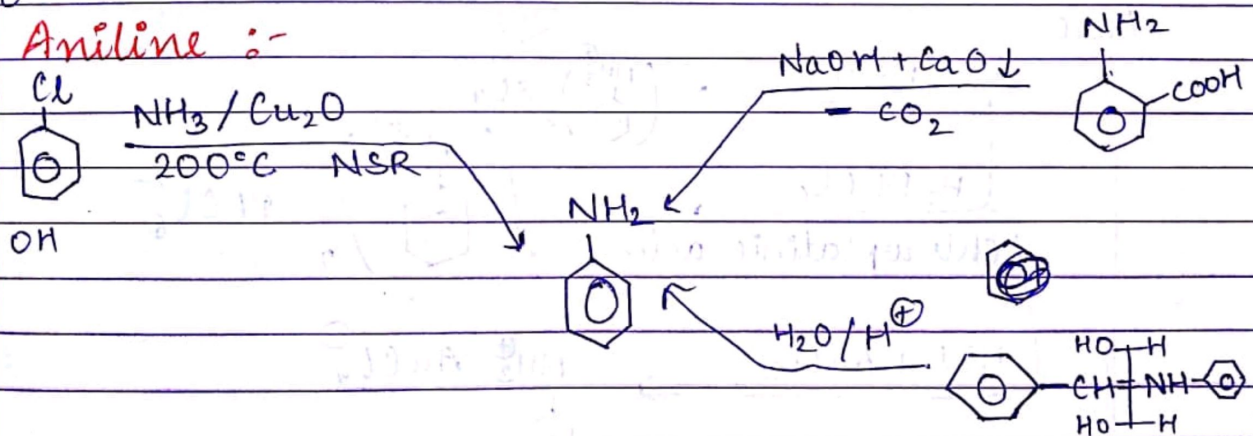
insoluble ← ~~insoluble~~ KOH no acidic H insoluble in alkali



Hoffmann Reagent :-



Aniline :-

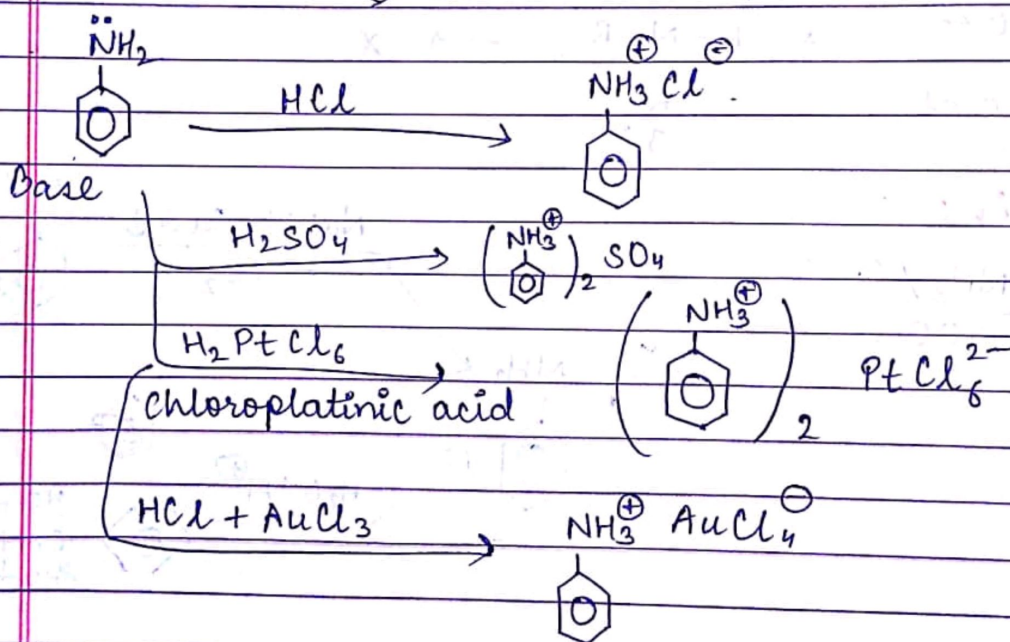
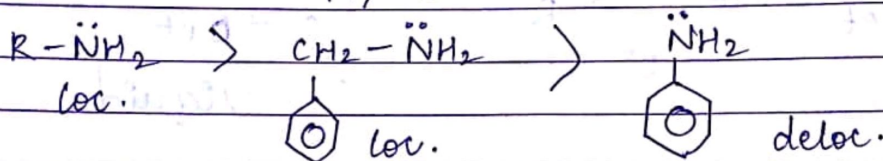


Pure aniline \rightarrow colourless liq. but in +nce of air & light but its colour becomes dark brown (B.P. ~~183~~¹⁸³ $^{\circ}$)
Aniline heavier than water
toxic in nature.

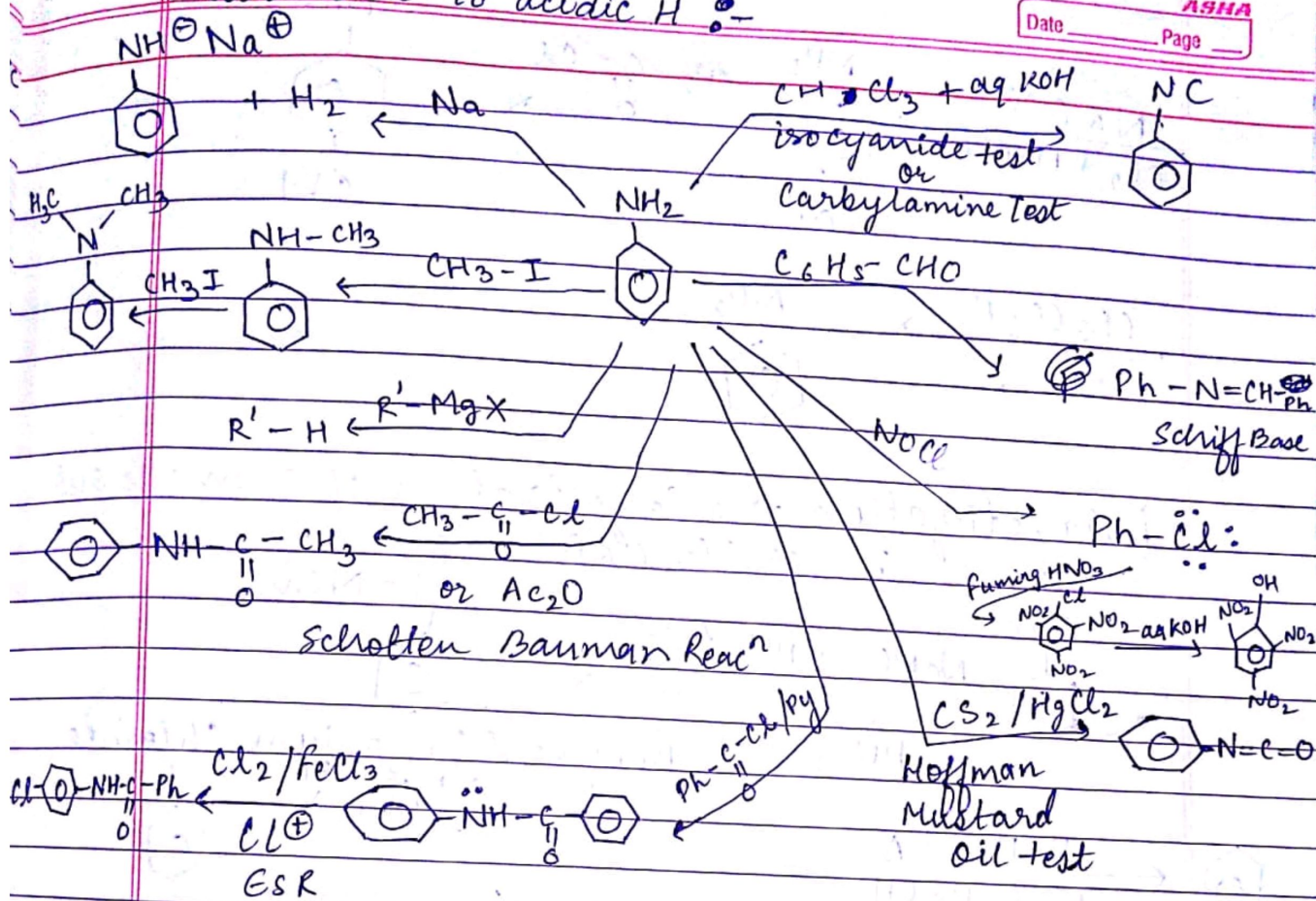
Chemical Properties

Reacⁿ due to NH_2 gp:-

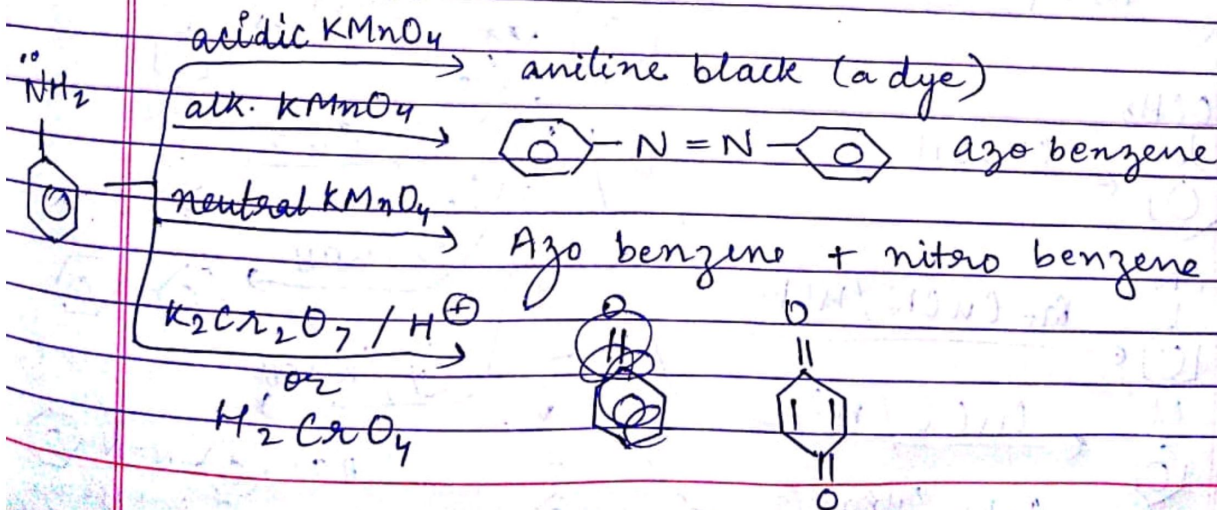
B.S. $\propto \frac{+M/+I}{-M/-I}$

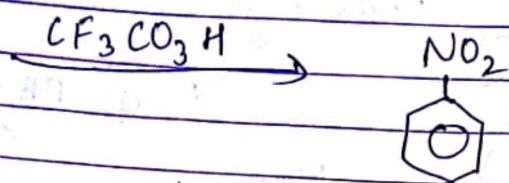
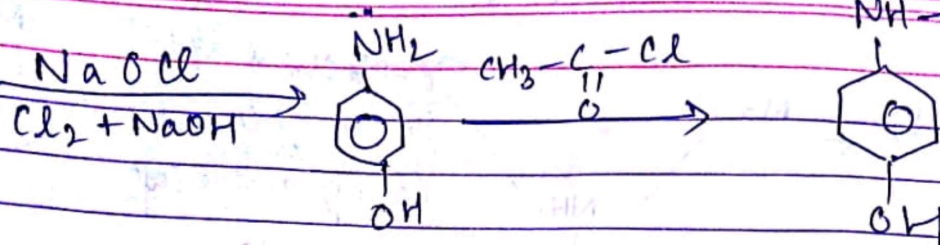


Reacⁿ due to acidic H :-

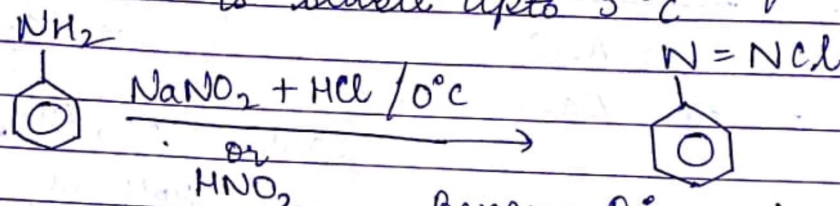


Oxidⁿ Reacⁿ :-

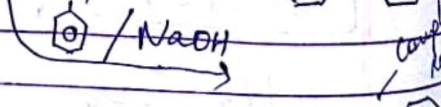
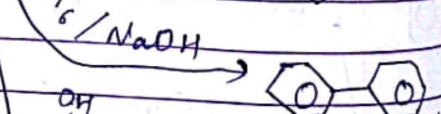
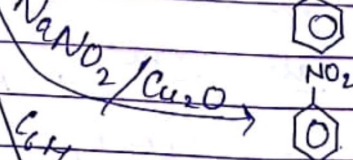
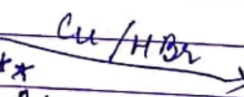
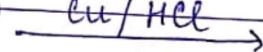
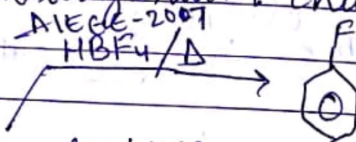
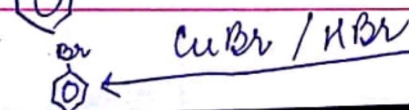
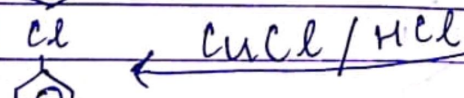
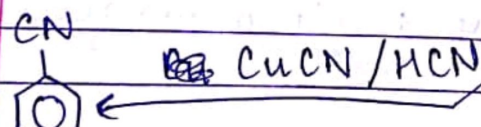
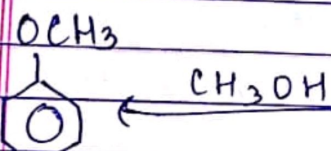
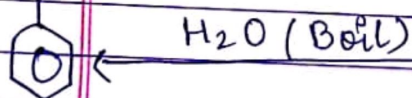
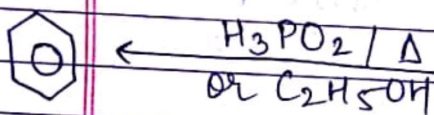




Diazotization \rightarrow Diazotization of aromatic sul is stable upto 5°C

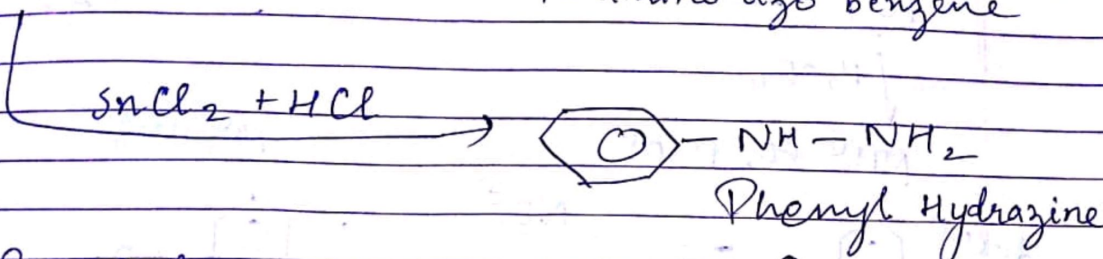
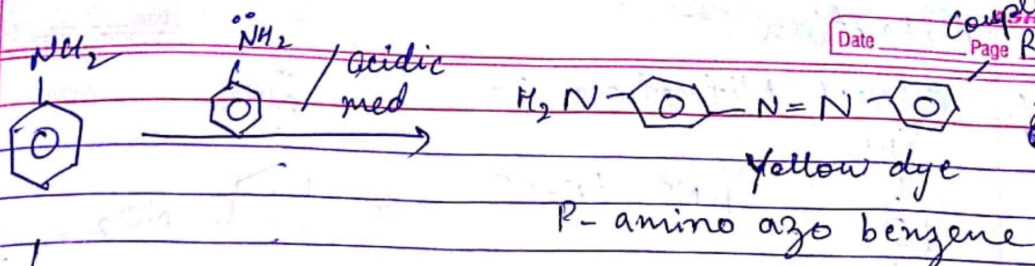


Benzene Diazonium Chloride

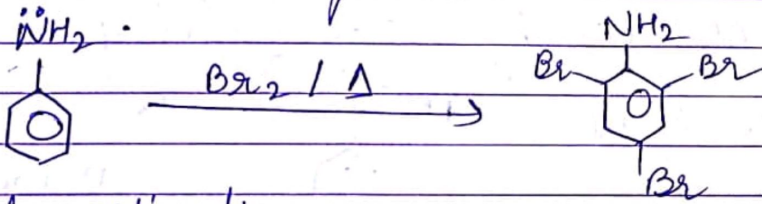


p-hydroxy azo benzene
orange dye

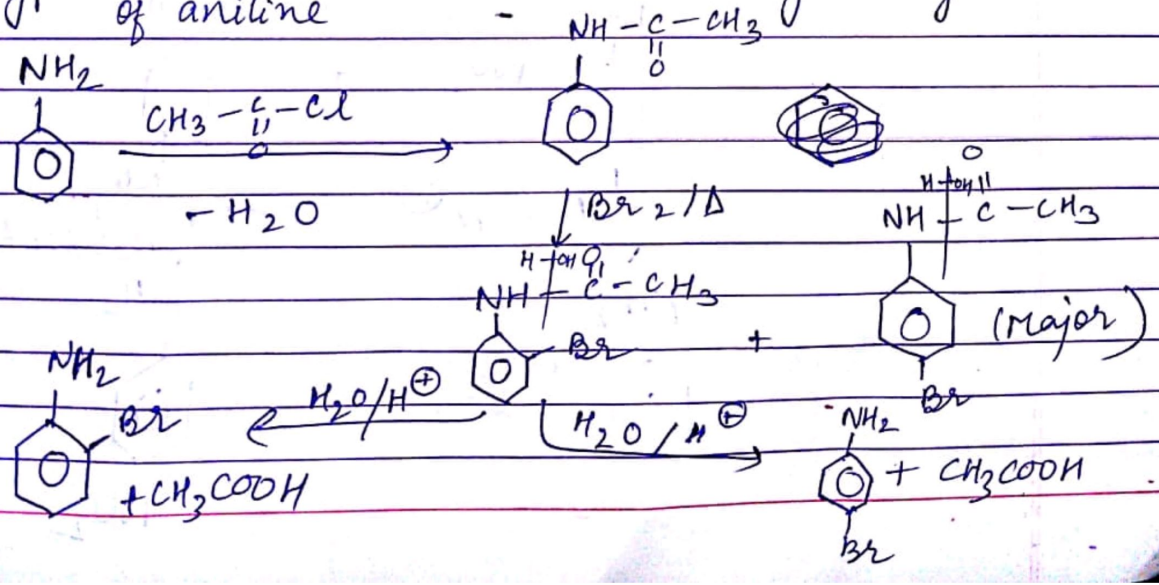
Sandmeyer
Reaction



b. [B] Reacⁿ due to benzene Ring :- \ominus Halogenation since -NH₂ gp is +M gp i.e. activating so ESR takes place

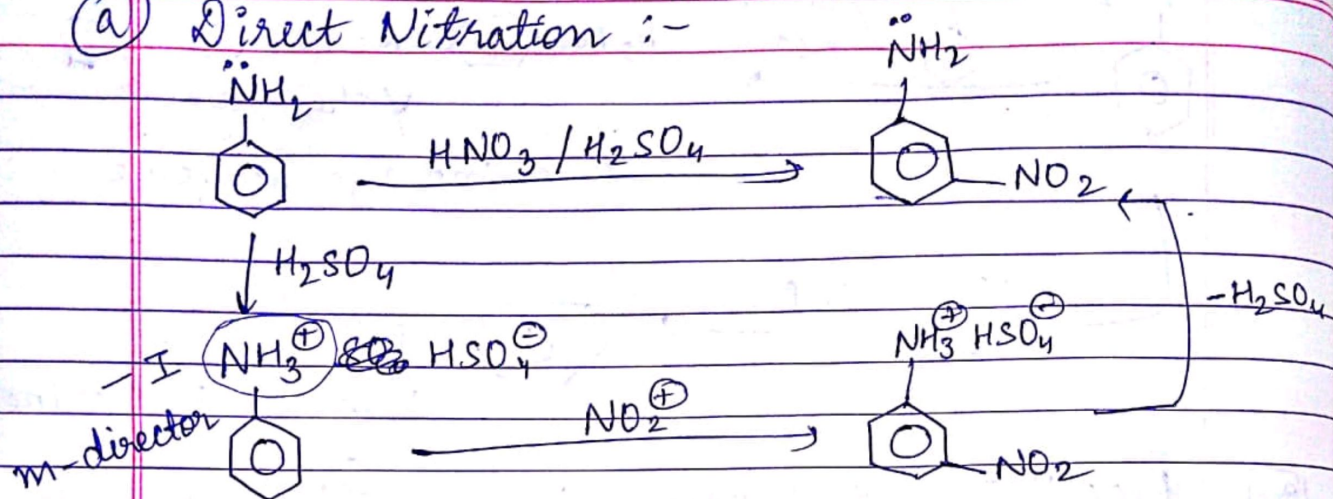


NH₂ highly activating gp to form O/P director isomer reactivity of NH₂ gp. is reduced towards ESR by acetylation of aniline



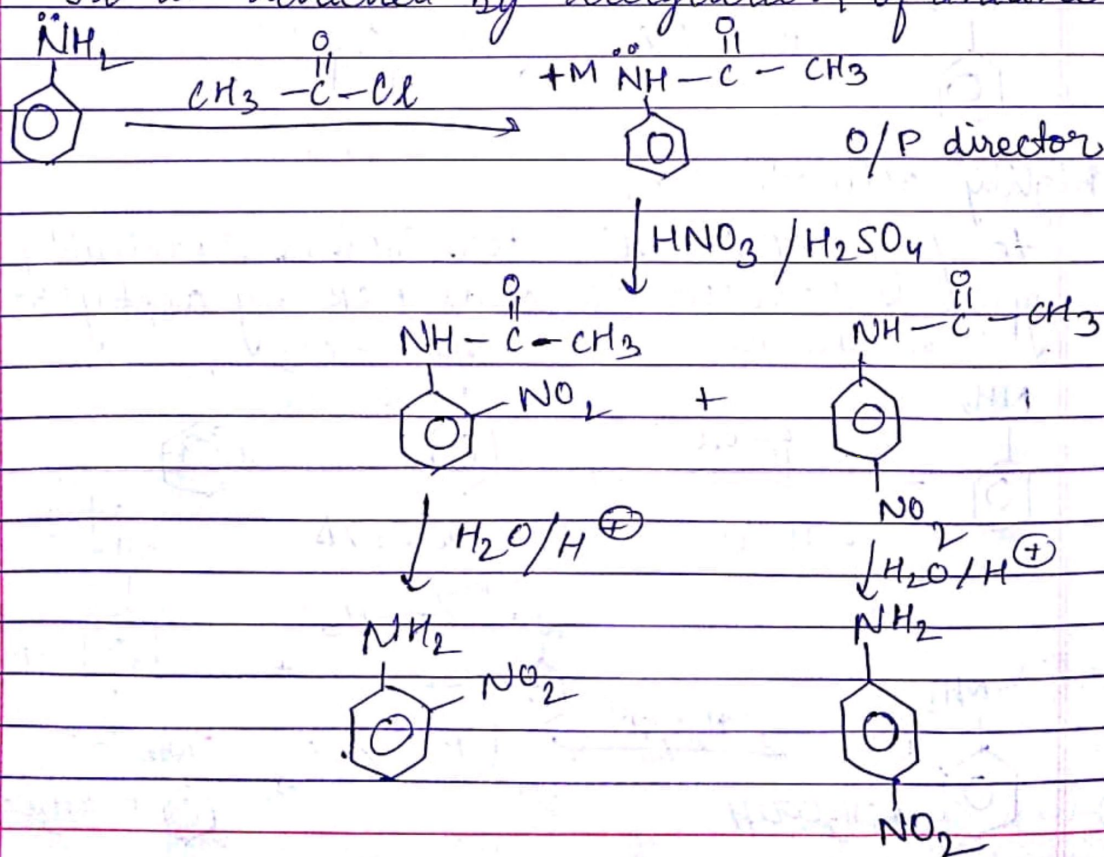
Nitration :-

(a) Direct Nitration :-

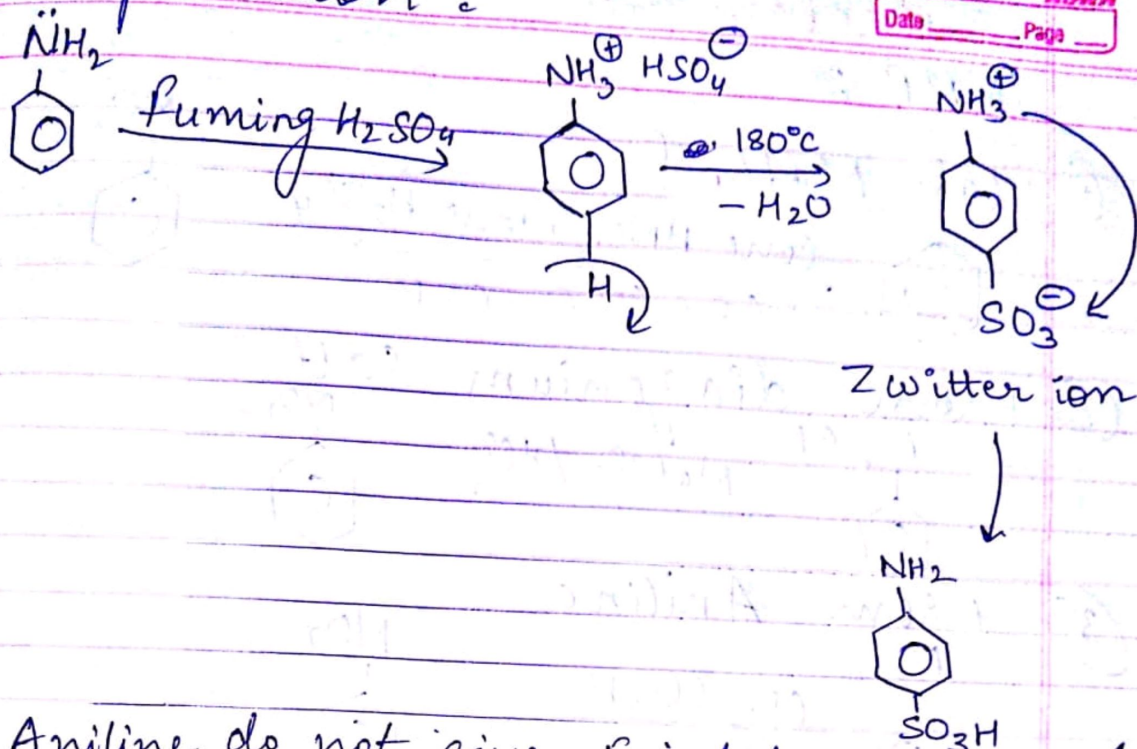


(b) Indirect Nitration :-

nitration of aniline is done by protection
It is achieved by acetylation of aniline



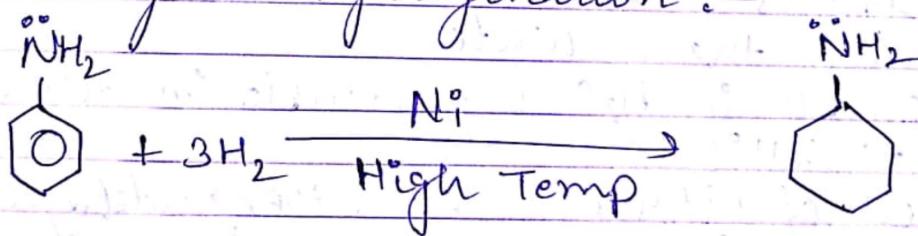
Sulphonation :-



Note

Aniline do not give Friedal Craft Reaction because Lewis acid form coordination bond with $-\ddot{\text{N}}\text{H}_2$ gp.

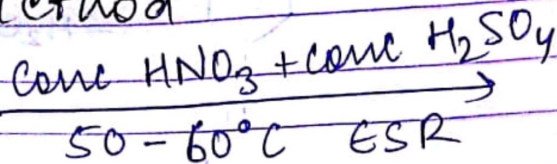
Catalytic Hydrogenation :-



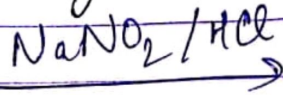
Nitrobenzene :-

GMP :-

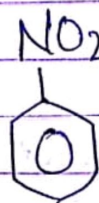
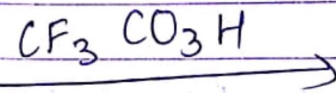
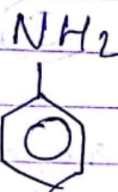
① Lab Method



② From diazonium salt



③ From Aniline



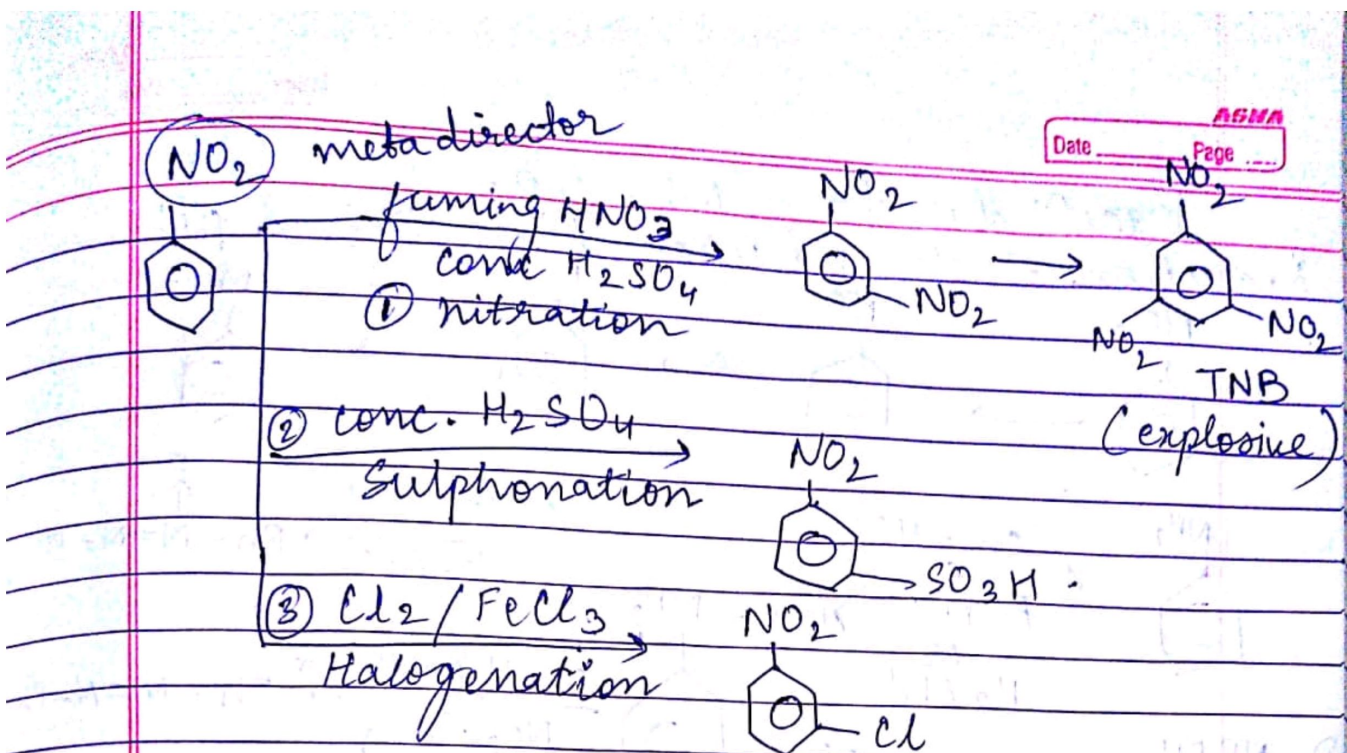
Physical Properties of nitro benzene :-

1. Yellow Oily liquid
2. Poisonous in nature
3. heavier than water
4. Insoluble in H_2O but soluble in alcohol & ether
5. BP $\rightarrow 211^\circ\text{C}$
6. Smell of nitrobenzene & Benzaldehyde is same i.e. smell of bitter almond.

Chemical Properties :-

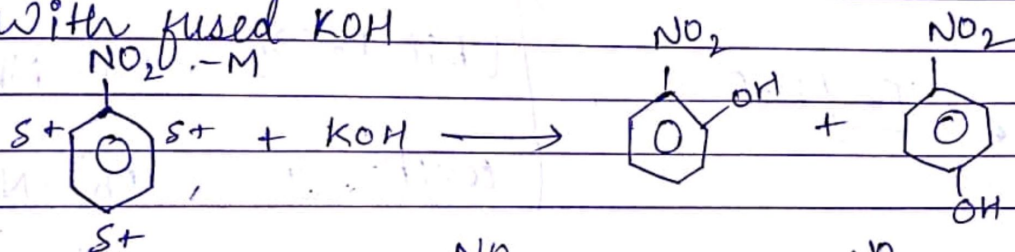
① Reacⁿ due to benzene ring $\begin{cases} \rightarrow \text{ESR} \\ \rightarrow \text{NSR} \end{cases}$

① a) ESR

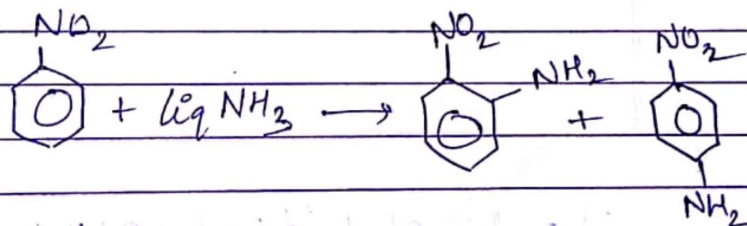


(B) NSP :-

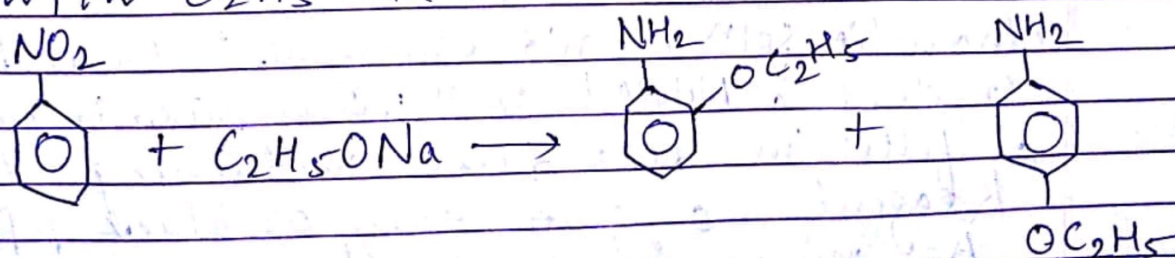
* (a) With fused KOH



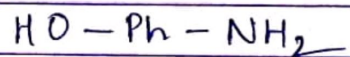
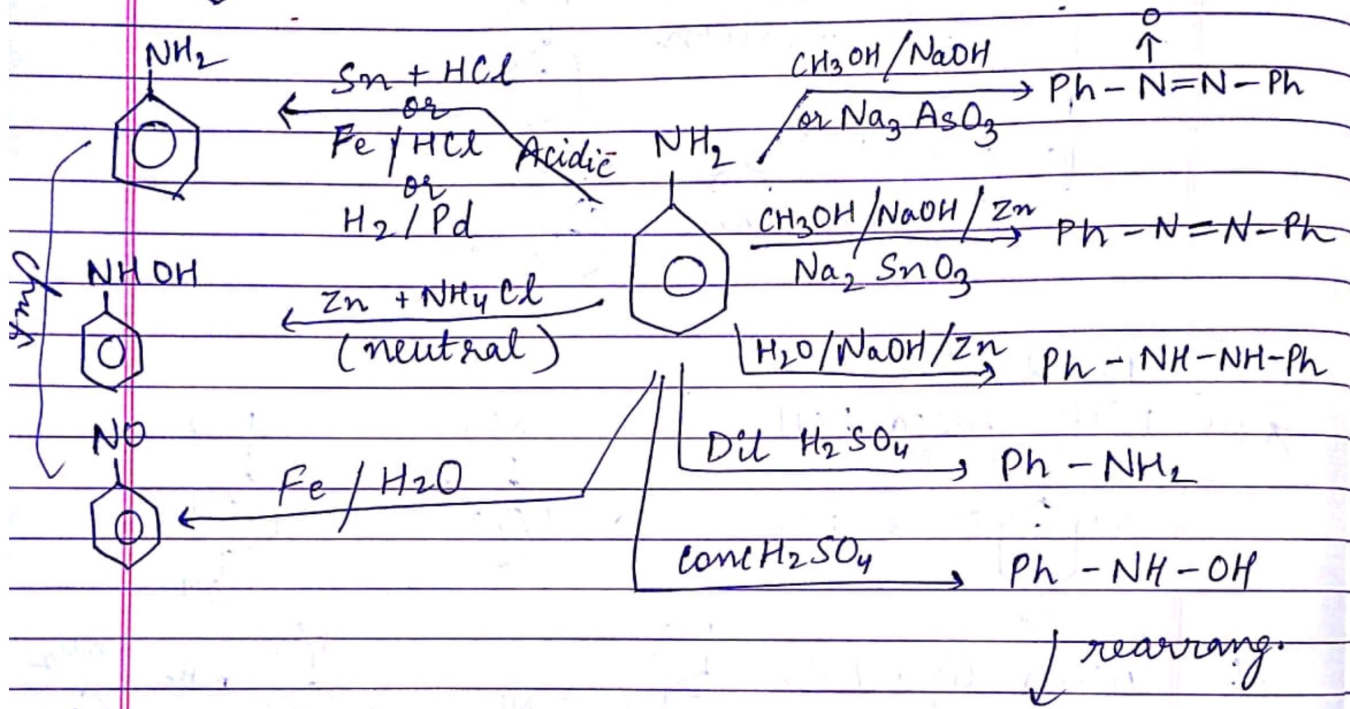
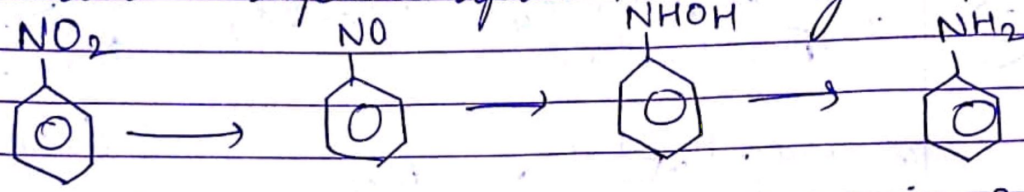
(b) With liq. NH₃



(c) With C₂H₅ONa

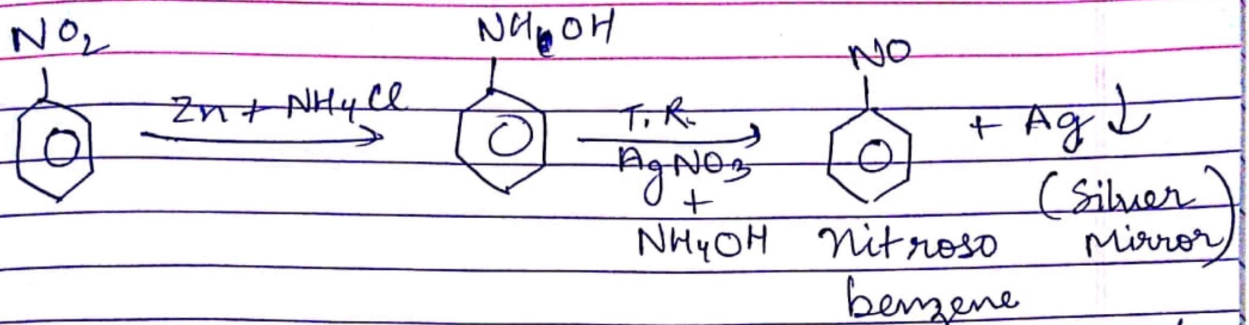


Reacⁿ due to -NO₂ gp.
Reduction → depend upon Reducing & pH



Test of Nitrobenzene
Mullikam Barker Test

Ethanollic solⁿ of nitrobenzene is treated with Zn dust & NH₄Cl solⁿ then mix. is heated & filter in test tube containing Tollen's Reagent a grey or black ppt of Ag mirror is obtained.



Uses :- (1) In manufacture of aniline & dye
(2) used as a solvent.