Nitrogen-Containing Compounds :-
& Amines :-

$R-NH_2$ — 1° amine

$R-NH-R$ — 2° Amine

$R-\underset{\underset{R}{|}}{N}-R$ — 3° Amine

$R_4N^{\oplus}$ — Quaternary amine

G.M.P. :-

① From alkyl Halide :-

$$R-X + \underset{\text{excess}}{NH_3} \xrightarrow{\Delta} R-NH_2$$

$$R-X + NH_3 \text{ (excess)} \xrightarrow{\Delta} R-NH_2 \xrightarrow{R-X} R-NH-R \xrightarrow{R-X} R-\underset{\underset{R}{|}}{N}-R \xrightarrow{R-X} R_4N^{\oplus}$$

② From Alcohol

$$R-OH + \underset{\text{excess}}{NH_3} \xrightarrow{Al_2O_3} R-NH_2 + H_2O$$

$$R-OH + \underset{\text{excess}}{NH_3} \xrightarrow[\text{dehydrating agent}]{Al_2O_3} R-NH_2 \longrightarrow R-NH-R \longrightarrow R-\underset{\underset{R}{|}}{N}-R \xrightarrow{X}$$

③ Reduction

$$R-C\equiv N \xrightarrow{LiAlH_4 / H^{\oplus}} R-CH_2-NH_2$$

$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{\quad " \quad} R-CH_2-NH_2$$

$$R-CH=N-OH \xrightarrow{\quad " \quad} R-CH_2-NH_2$$

$$R-CH_2-NO_2 \xrightarrow{Sn + HCl} R-CH_2-NH_2$$

$$R-NC \xrightarrow{LiAlH_4 / H^{\oplus}} \underset{2^{\circ}}{R-NH-CH_3}$$

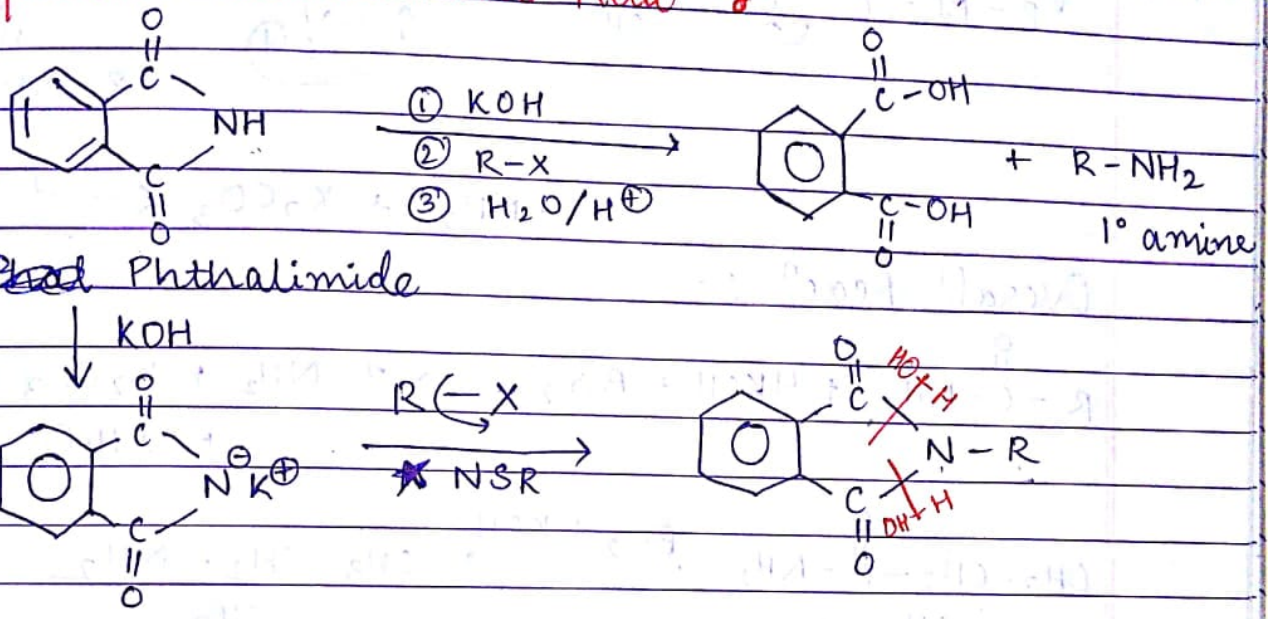
④ Hydrolysis

$$R-N\equiv C \xrightarrow{H_2O/H^{\oplus}} K-NH_2 + HC(=O)-OH$$

$$R-N\neq C(-OK)(-OK) \xrightarrow{aq.\ KOH} R-NH_2 + K_2CO_3$$

V.V. Imp

⑤ Gabriel Phthalimide Reacⁿ :-



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

V.V. Imp

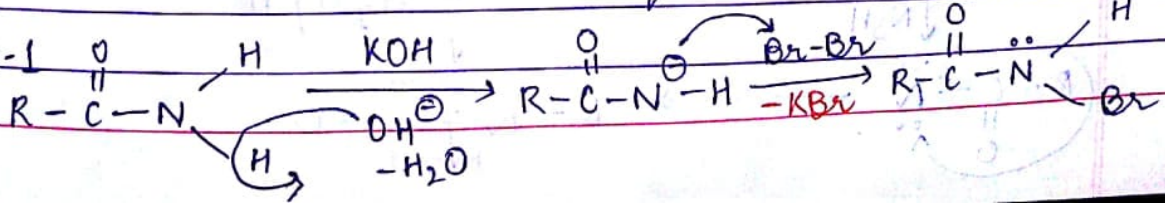
⑥ Hoffmann Bromamide Reacⁿ :-

$$R-CONH_2 \xrightarrow[\text{or } KOBr \text{ or } OBr^{\ominus}]{Br_2 + KOH} R-NH_2 + K_2CO_3 + KBr + H_2O$$

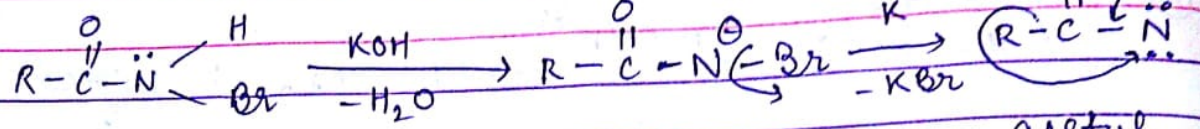
1° amine

no. of C ↓

Mech: Step-1

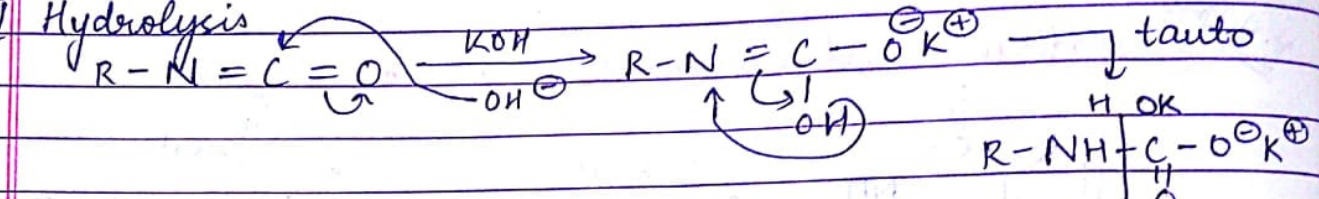


Step - II



$R-N=C=O$

Step - III Hydrolysis



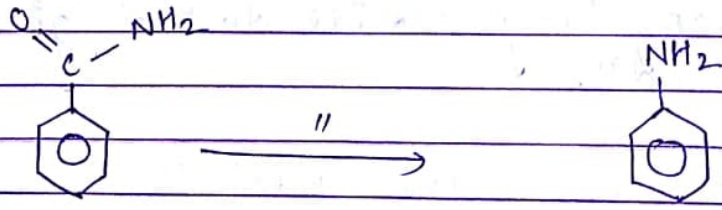
$R-NH_2 + K_2CO_3$

Overall Reac^n :-

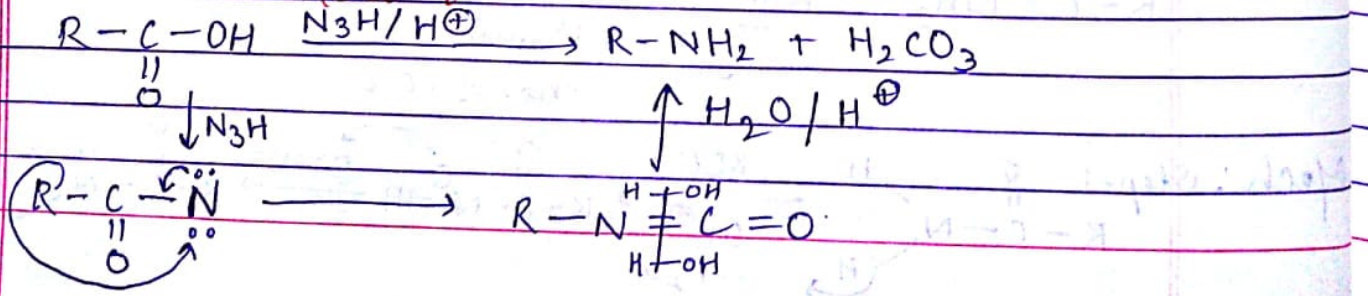
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + 4KOH + Br_2 \longrightarrow R-NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2 + KOH} CH_3-CH_2-NH_2$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{\quad} CH_3-\underset{\underset{CH_3}{|}}{CH}-NH_2$$



Schmidt Reac^n :-



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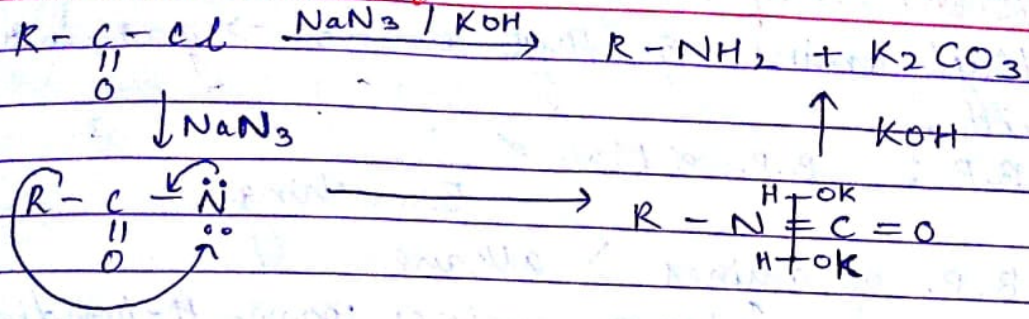
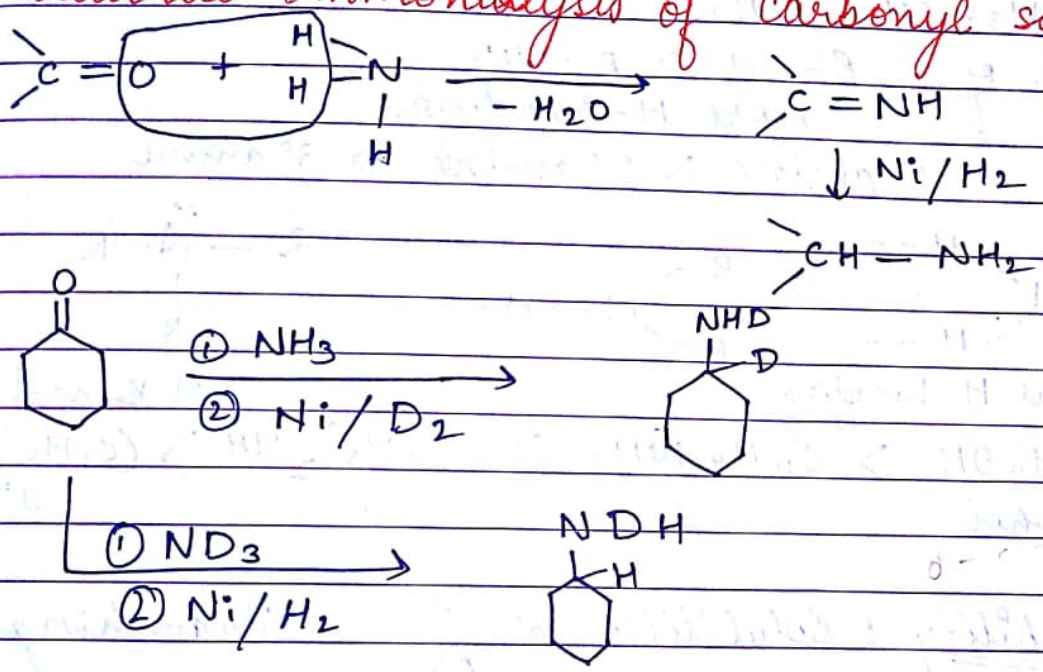
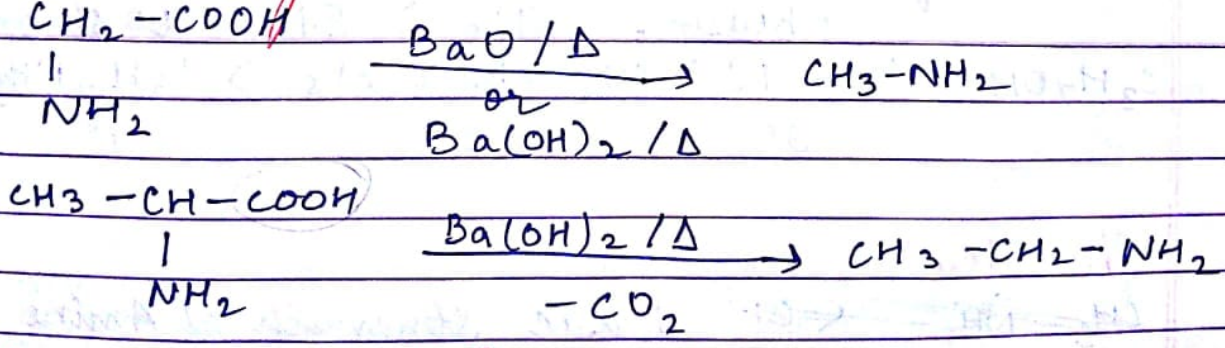
Curtius Reac^ :-



Reductive ammonialysis of carbonyl substance



Decarboxylation α-amino acid



By Grignard Reagent

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Physical Properties :-

1. Methyl amine & ethyl amine → gas & rest are liquid.
2. B.P. : B.P. $\propto$ Mw. $\propto \frac{1}{\text{Branching}}$

B.P. of amines > alkane

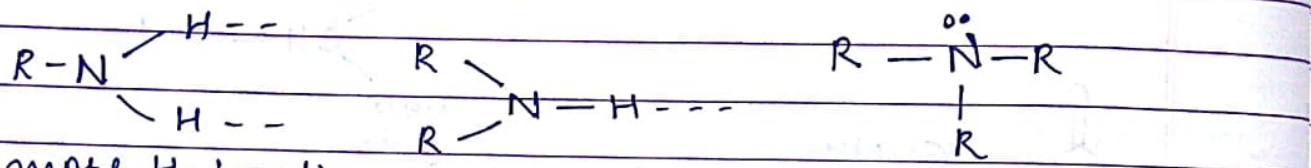
↑ Becoz amines form H-bonding

$CH_3-CH_2-NH_2 > CH_3-CH_2-CH_3$

B.P. of $R-OH > R-NH_2$

more H-Bonding

B.P. : 1° amine > 2° amine > 3° amine



more H-bonding

H Bond ✗

$C_4H_9OH > C_4H_9NH_2 > (C_2H_5)_2NH > (C_2H_5)N(CH_3)_2$

alcohol 1° 2° 3°

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

Solubility of $R-OH > R-NH_2$

Reason EN° > E.N.N so strong H-bond

$C_3H_7OH > (CH_3)_3N > CH_3-NH-C_2H_5 > C_3H_7NH_2$

3° 2° 1°

Chemical Properties :-

~~$CH_3-\ddot{N}H_2$ ← EF~~ Basic strength of Amine :-

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

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$CH_3-NH_2 < CH_3-CH_2-NH_2 < CH_3-\underset{CH_3}{CH}-\ddot{N}H_2$

In gaseous state B.S. of amine $3^\circ > 2^\circ > 1^\circ > \ddot{N}H_3$

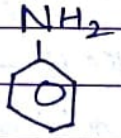
In aq. state B.S. of amines :-

$R = -CH_3$ $\quad 2^\circ > 1^\circ > 3^\circ > \ddot{N}H_3$

$CH_3-NH-CH_3 \quad CH_3-NH_2 \quad (CH_3)_3-N$

$R = -CH_2-CH_3 \quad 2^\circ > 3^\circ > 1^\circ > NH_3$

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > \ddot{N}H_3$

$R-\ddot{N}H_2 >$ 

$(C_2H_5)_2NH > C_2H_5NH_2 > \ddot{N}H_3 > C_6H_5-\ddot{N}H_2$

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

Reac^n due to basic nature :-

$R-NH_2 + HCl \longrightarrow R-NH_3^{\oplus}Cl^{\ominus}$

~~$R-NH_2 + H_2SO_4$~~ salt

$R-NH_2 + H_2SO_4 \longrightarrow R-NH_3^{\oplus})_2\, SO_4^{2-}$

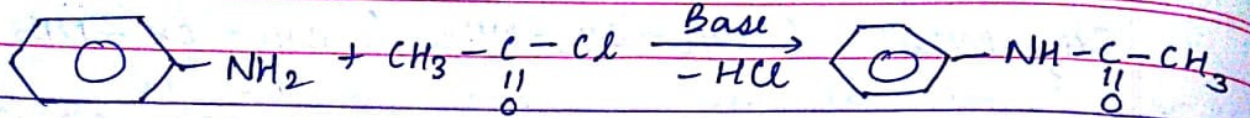
Acylation :-

$C_2H_5-\ddot{N}H_2 + CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Base} C_2H_5-\overset{\oplus}{\underset{H}{N}}-\underset{O^{\ominus}}{\overset{CH_3}{C}}-Cl$

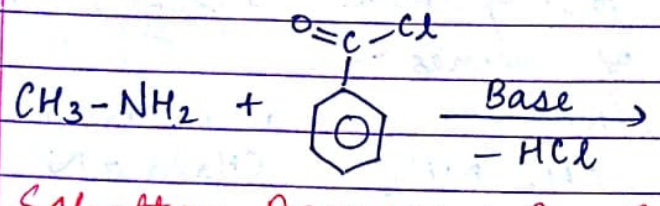
$\downarrow$

$C_2H_5-NH-\underset{\underset{O}{\|}}{C}-CH_3 + HCl$

$C_2H_5-\underset{C_2H_5}{N}-H + Cl-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[-HCl]{Base} C_2H_5-\underset{C_2H_5}{N}-\underset{\underset{O}{\|}}{C}-CH_3$



N-Phenyl ethanamide



N-methyl Benzamide

Schotten Baumann Reac^n

Carbyl amine Reac^n : / Isocyanide Test

$R-NH_2 + CHCl_3 + KOH \longrightarrow R-N\equiv C + KCl + H_2O$

Mech. → alkyl halide ⇄ Reuse ⇄

Reac^n ~~with~~ due to acidic H :–

$R-NH_2 + Na \longrightarrow R-NH^{\ominus}Na + H_2\uparrow$

Reac^n with Tildane :–

$R-NH_2 \xrightarrow{\text{Tildane}} R-Cl + N_2 + H_2O$

N O Cl ~~CCl~~ NOCl

IIT

$CH_3-CH_2-NH_2 \xrightarrow{NOCl} CH_3-CH_2-Cl$

Reac^n with Aldehyde

$R-NH_2 + O=CH-R \longrightarrow R-N=CH-R$

Schiff Base

Reac^n with Nitrous Base (HNO_2)

$R-NH_2 \xrightarrow[\text{or } NaNO_2 + HCl \; 0^\circ C]{HNO_2} R-OH + N_2\uparrow + H_2O$

1° Amine

Except CH_3-NH_2

$CH_3-NH_2 \xrightarrow{\Delta} CH_3-O-CH_3$

$R_2N-H + HO-NO \longrightarrow R_2N-NO + H_2O$

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

↓ Phenol & few drop of conc. H_2SO_4

Red $\xleftarrow{NaOH}$ Blue

$R-\underset{\underset{R}{|}}{N}-R \xrightarrow{HNO_2} X$

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

Hoffmann Mustard Oil Reac^n :-

$R-NH_2 + S=C=S \longrightarrow R-\overset{H}{\overset{|}{\overset{+}{N}}}-C(=S)-S^{\ominus}$

(Mustard oil smell) $R-N=C=S \xleftarrow{HgCl_2} R-NH-C(=S)-SH$

$+ 2HCl + HgS$

$R_2NH + S=C=S \longrightarrow R-\underset{\underset{R}{|}}{N}-\underset{\underset{S}{||}}{C}-SH$

↓ $HgCl_2$

X

$R-\underset{\underset{R}{|}}{N}-R + S=C=S \longrightarrow X$

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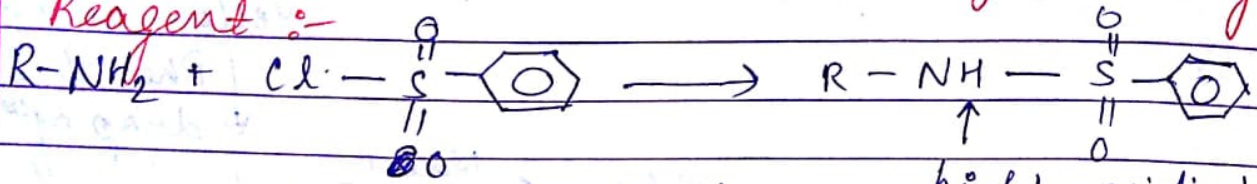
Only 1° amine will give mustard oil smell hence distinction b/w 1° amines can be separated from 2°/3° amine.

NCERT

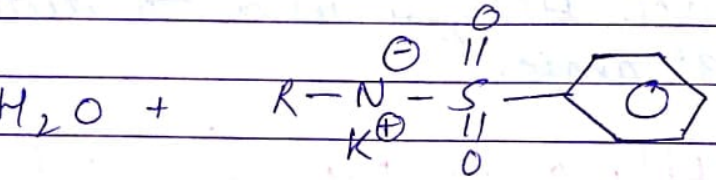
Distinction b/w 1°/2°/3° amine by Hinsberg Reagent :-



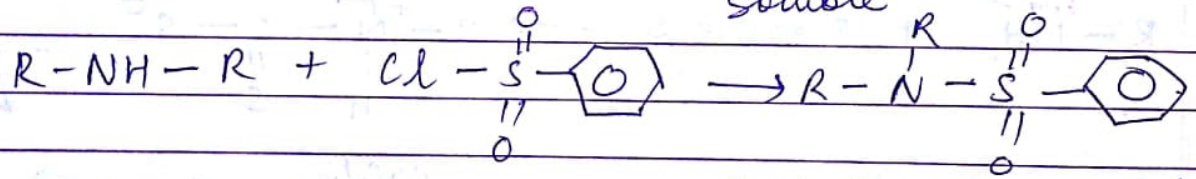
Benzene Sulphonyl Chloride (Hinsberg Reagent

highly acidic H due to -I gp

KOH so soluble in alkali

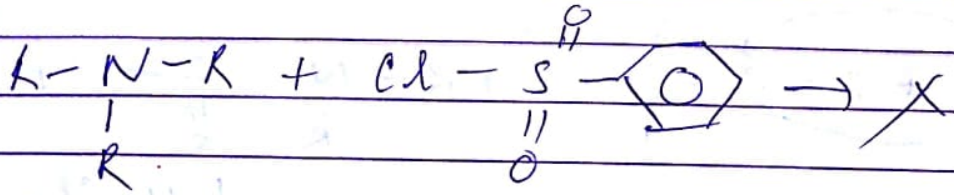


Soluble

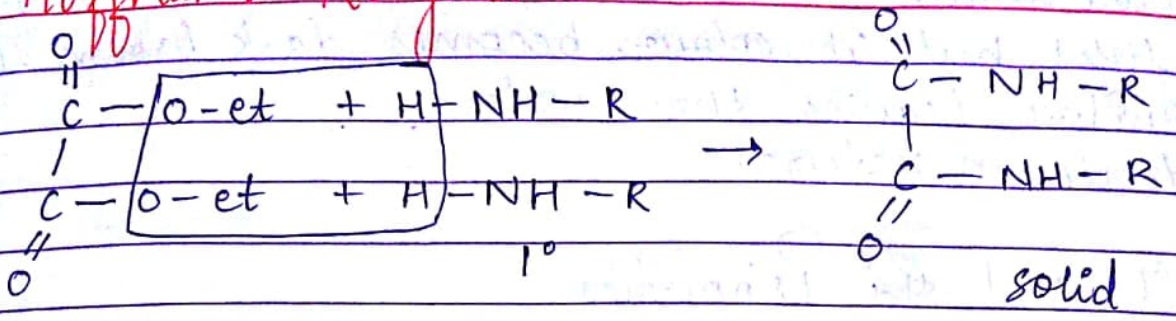


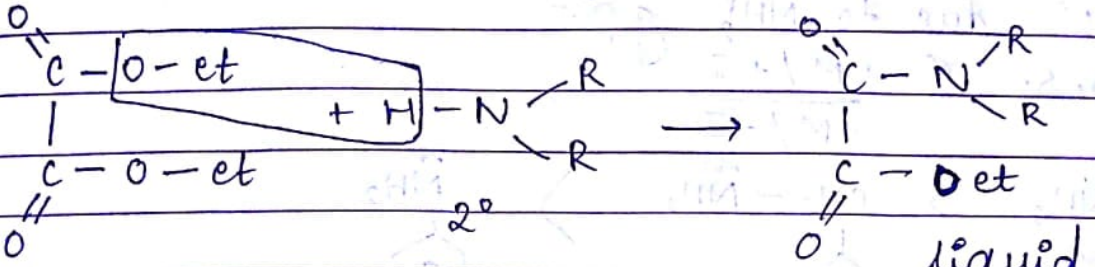
insoluble ← ~~insoluble~~ KOH

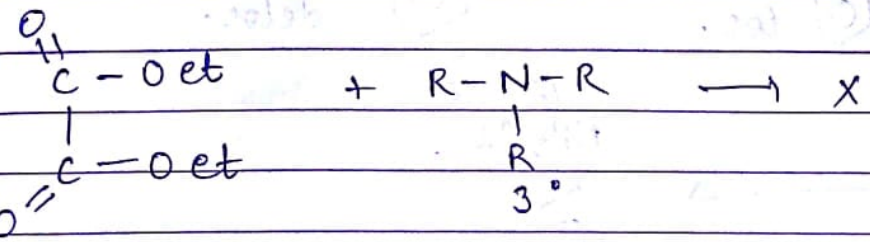
no acidic H insoluble in alkali



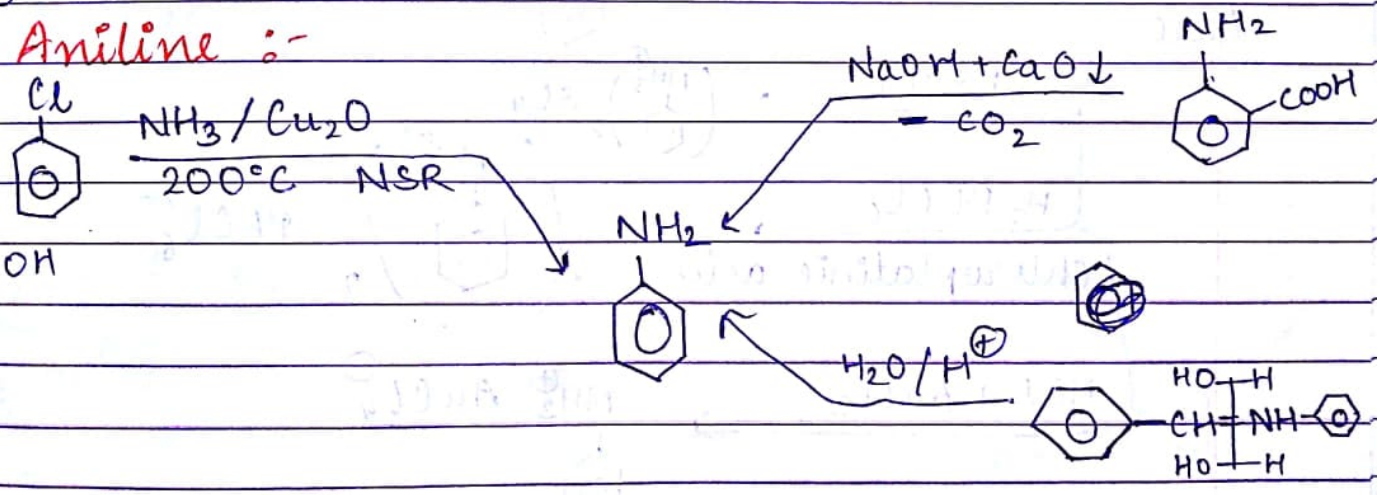
Hoffmann Reagent :-







Aniline :-



AGHA

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Pure aniline → colourless liq. but in ⁺nce of air & light but it colour becomes dark brown. (B.P. 183°C)

Aniline heavier than water.

toxic in nature.

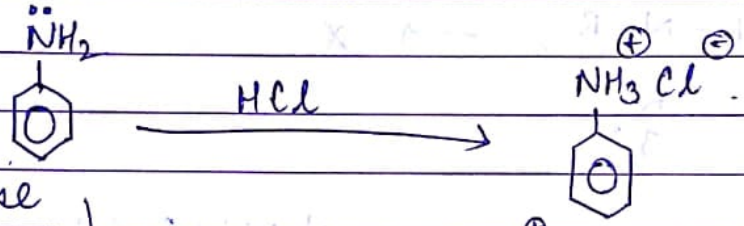
Chemical Properties

Reac^{n} due to NH_2 gp:-

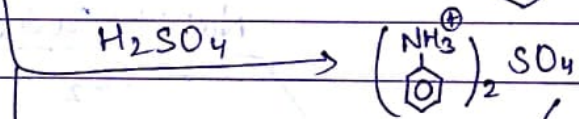
B.S. $\propto \frac{+M/+I}{-M/-I}$

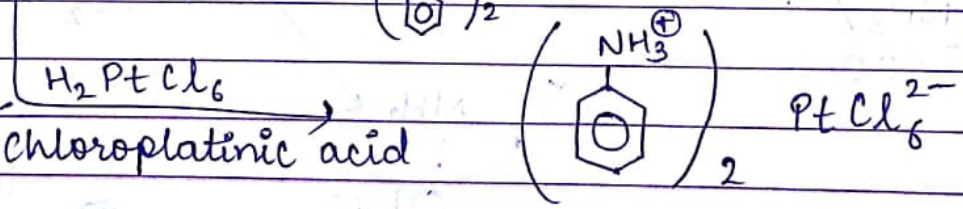
$R-\ddot{N}H_2 > CH_2-\ddot{N}H_2 > \ddot{N}H_2$

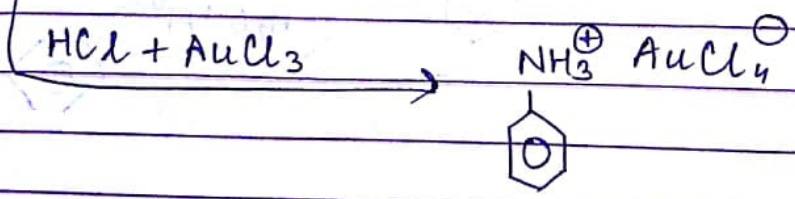
loc. loc. deloc.



Base







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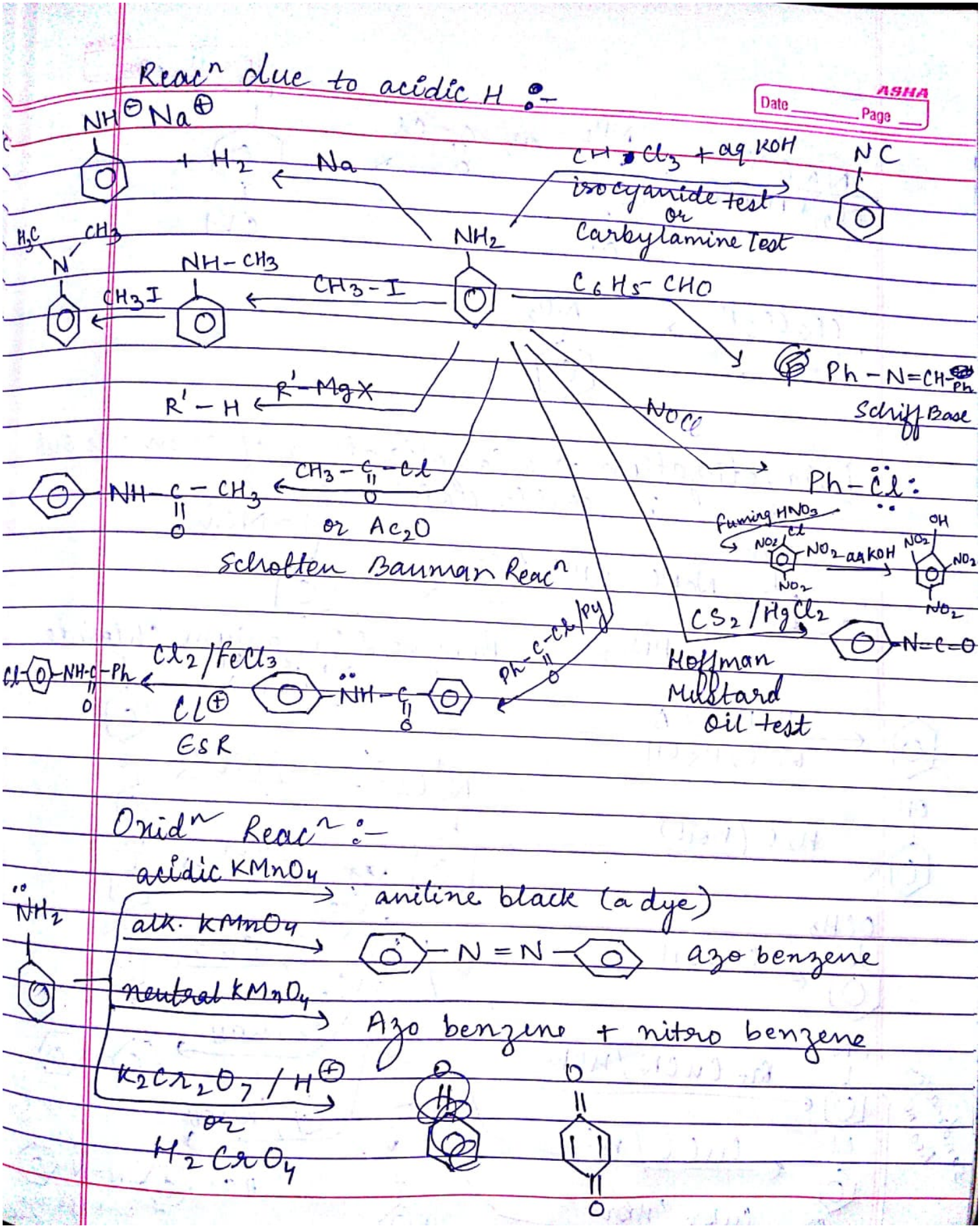
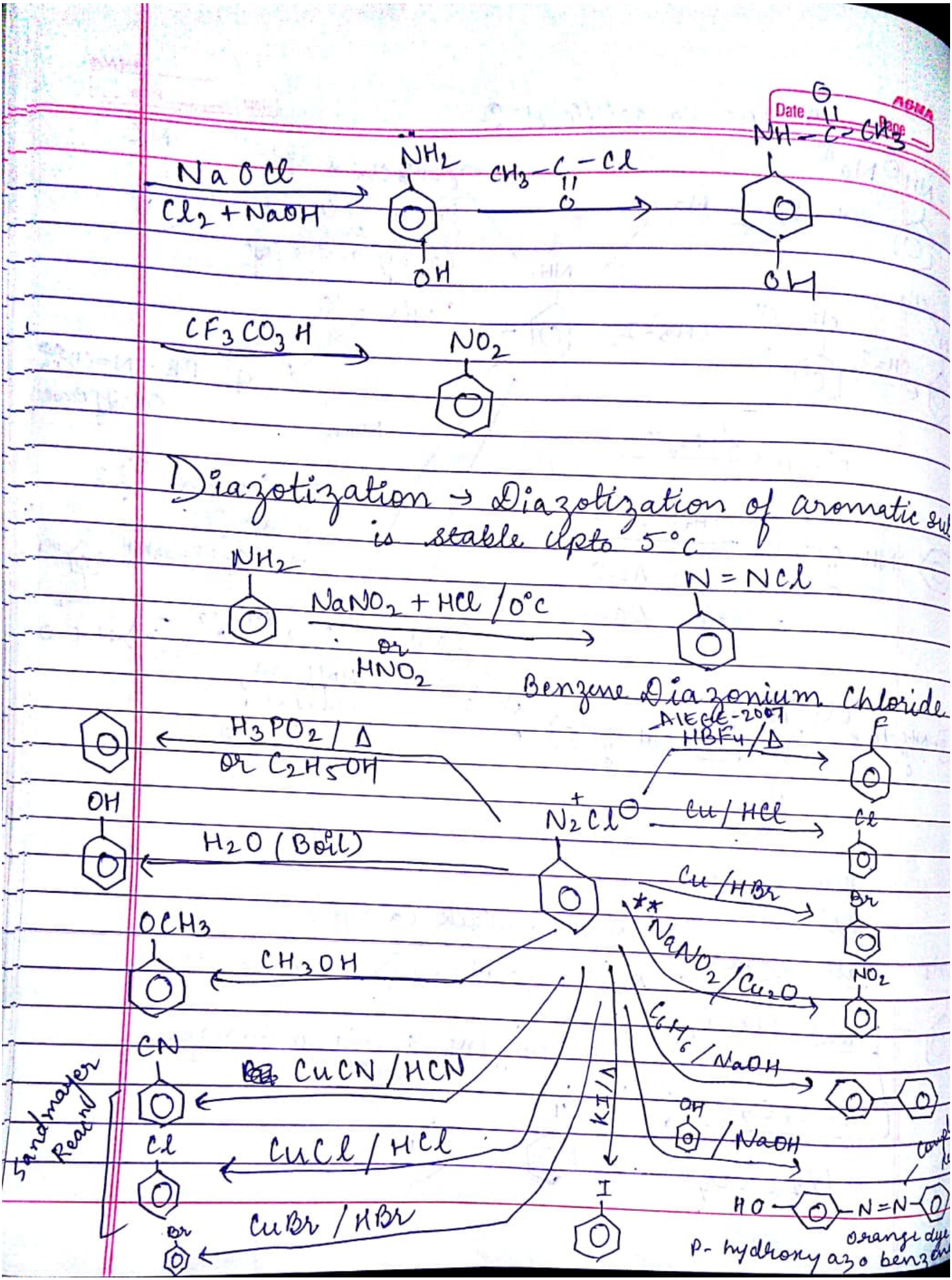
Reacⁿ due to acidic H :-

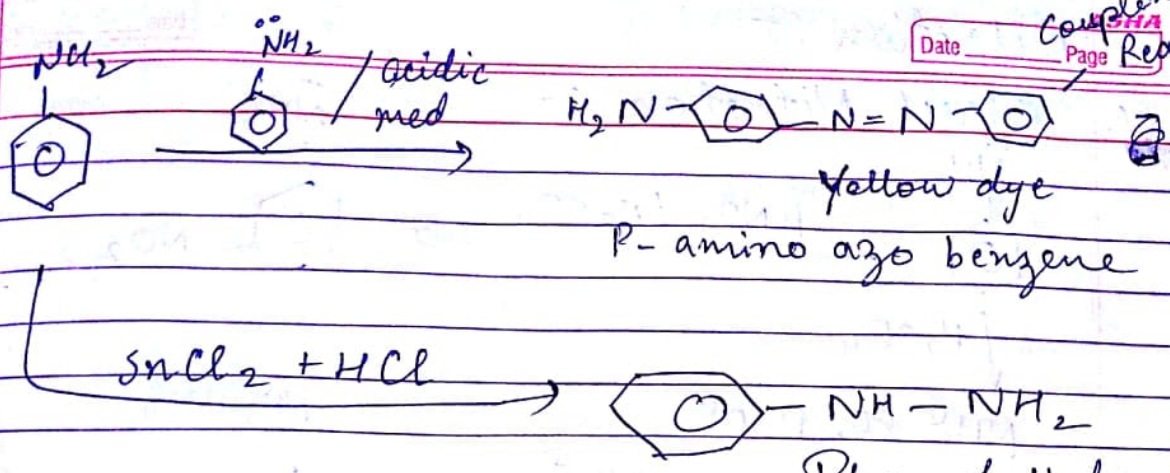


Oxidⁿ Reacⁿ :-

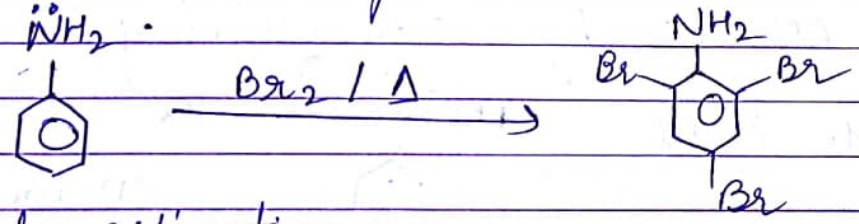


Diazotization → Diazotization of aromatic amines is stable upto 5°C

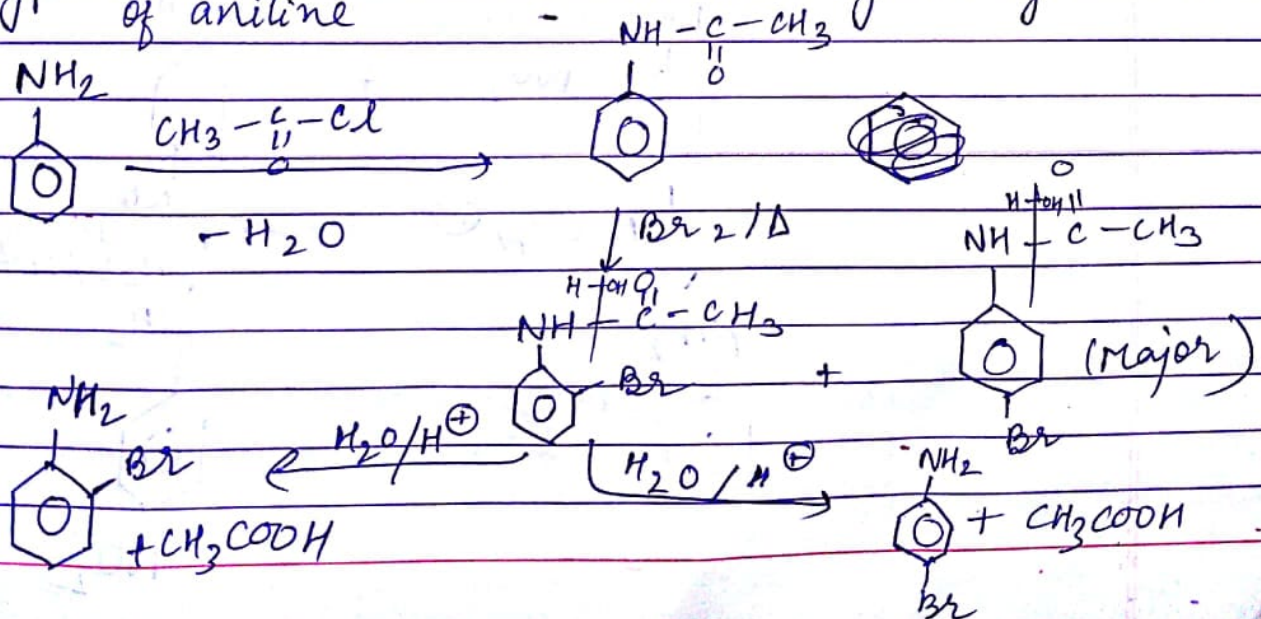
Benzene Diazonium Chloride



3. [B] Reac^n due to benzene Ring :— Halogenation since $-NH_2$ gp is +M gp i.e. activating so ESR takes place

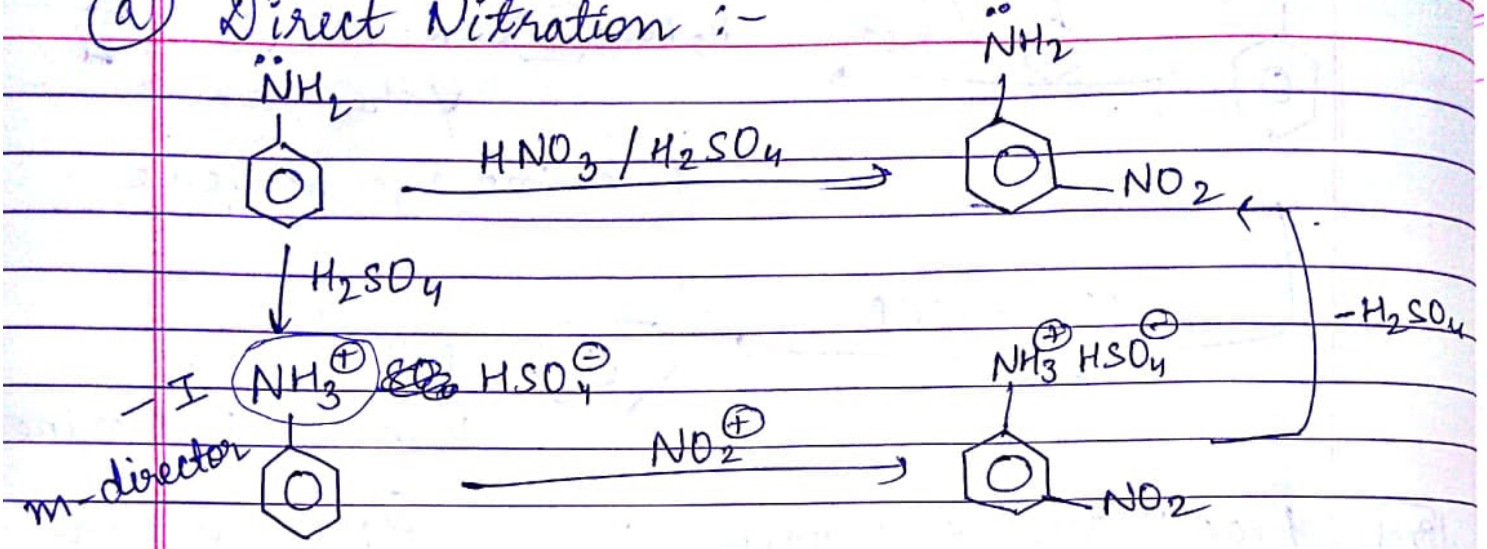


$\ddot{N}H_2$ highly activating gp to form O/P ~~director~~ isomer reactivity of $\ddot{N}H_2$ gp. is reduced towards ESR by acetylation of aniline



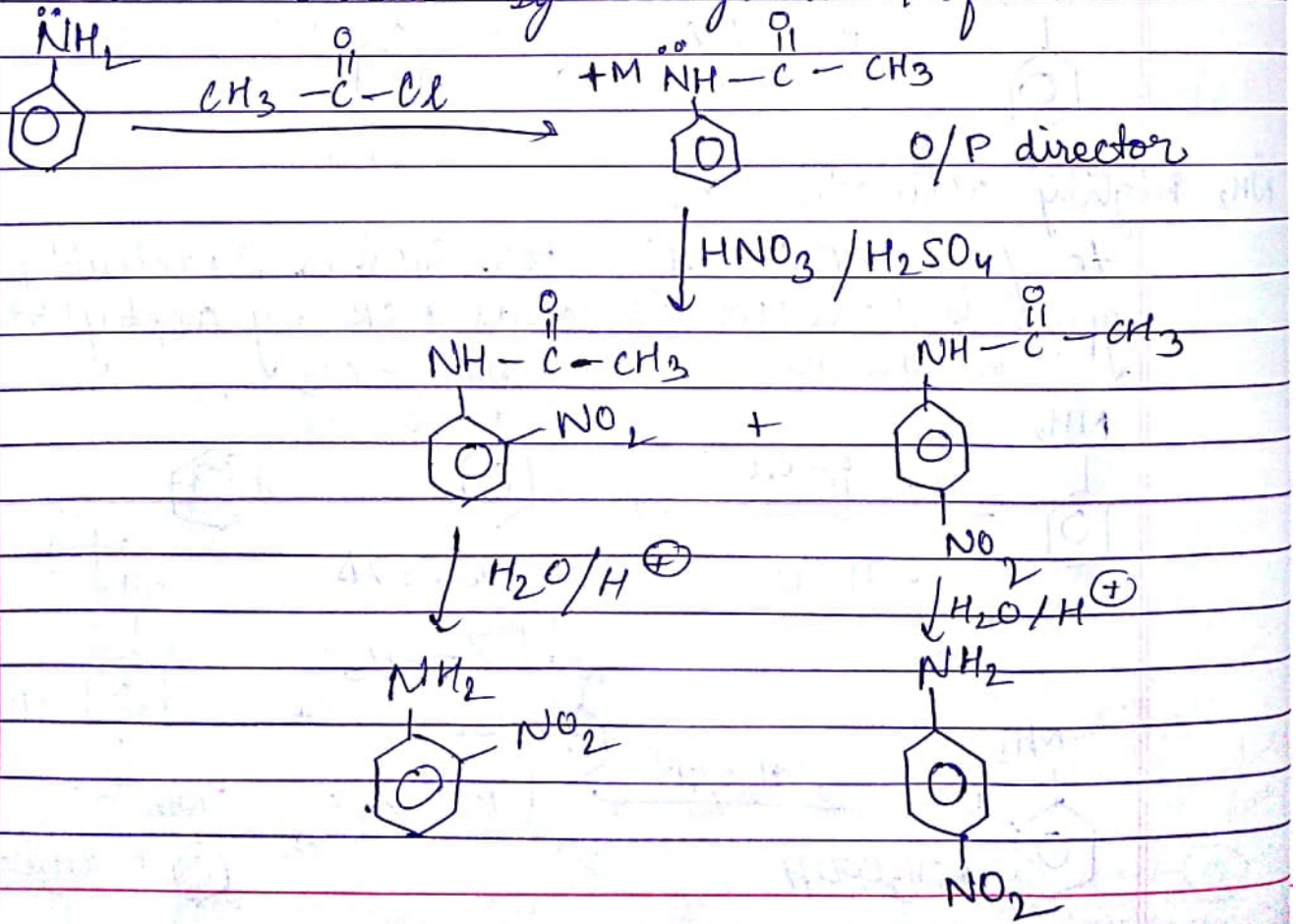
Nitration :-

(a) Direct Nitration :-

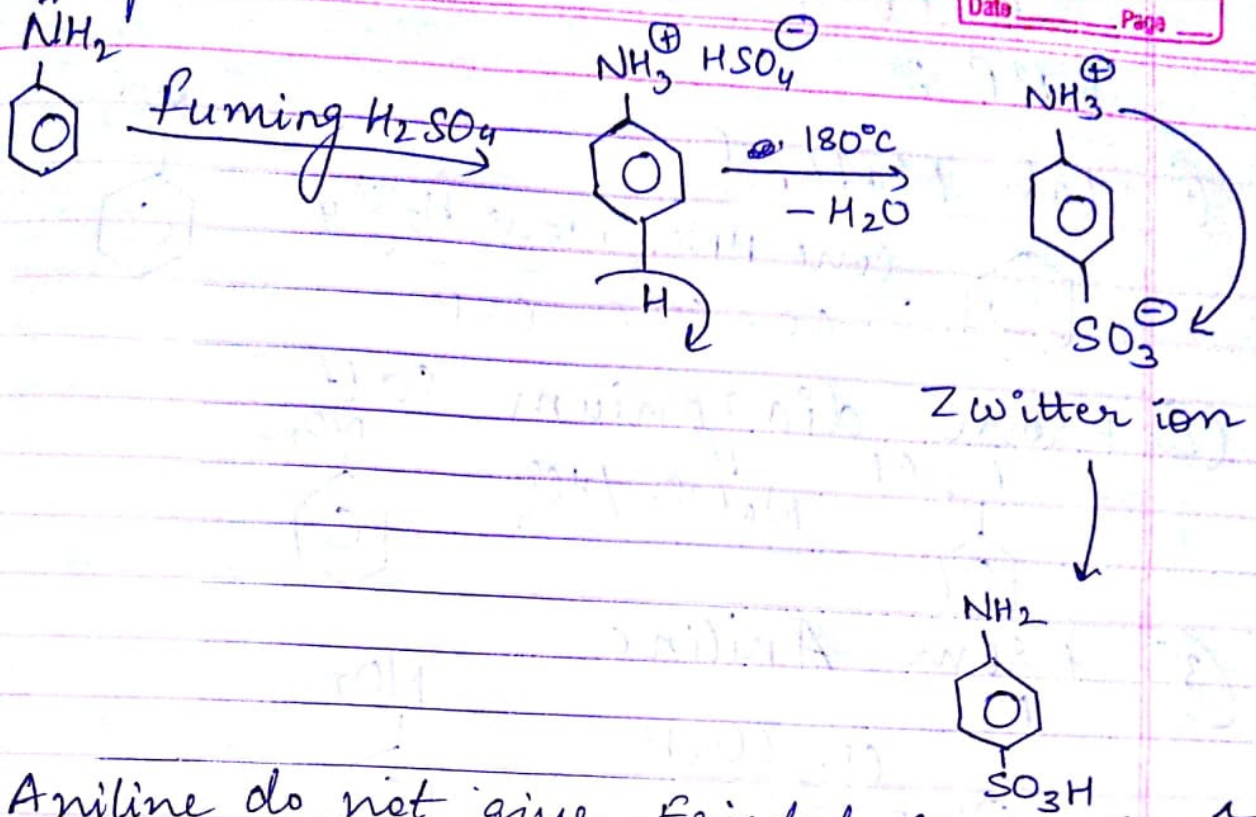


(b) Indirect Nitration :-

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

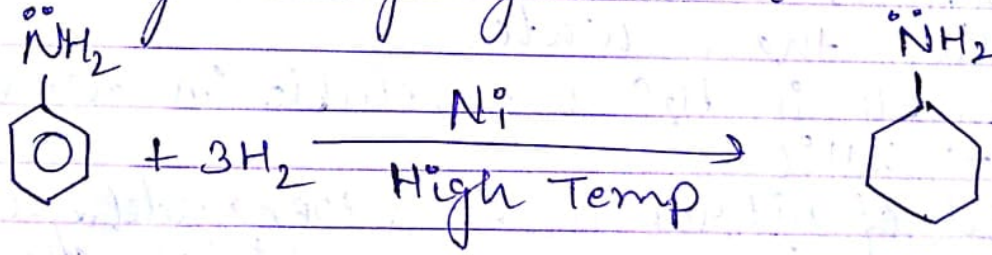


Sulphonation :-



Note Aniline do not give Friedal Craft Reac~~tion~~ because lewis acid form coordinate bond with $-\ddot{N}H_2$ gp.

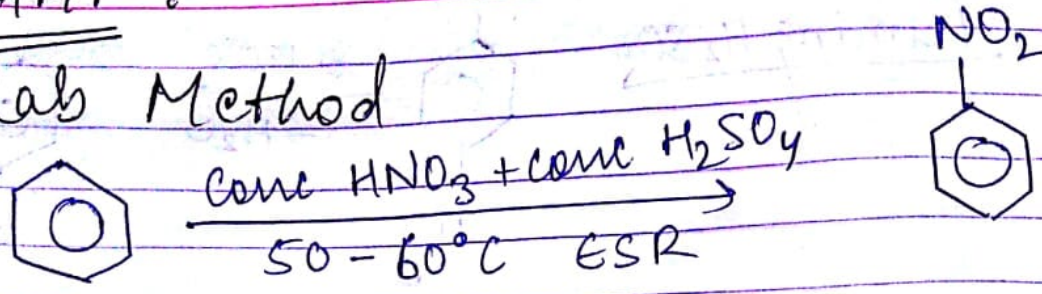
Catalytic Hydrogenation :-



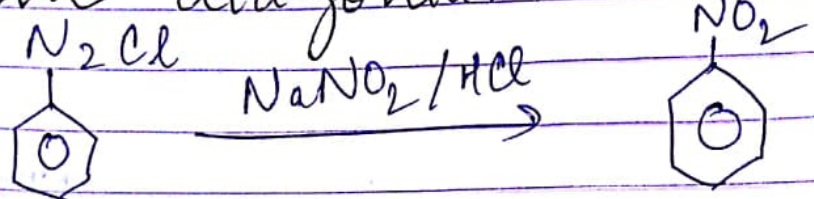
Nitrobenzene :-

GMP :-

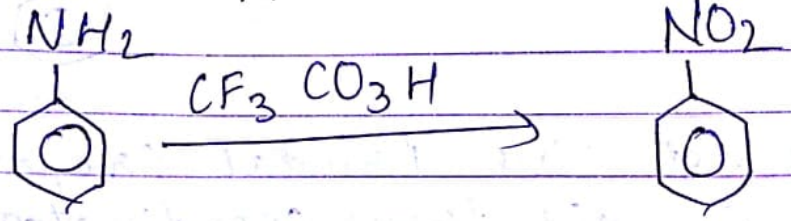
① Lab Method



② From diazonium salt



③ From Aniline



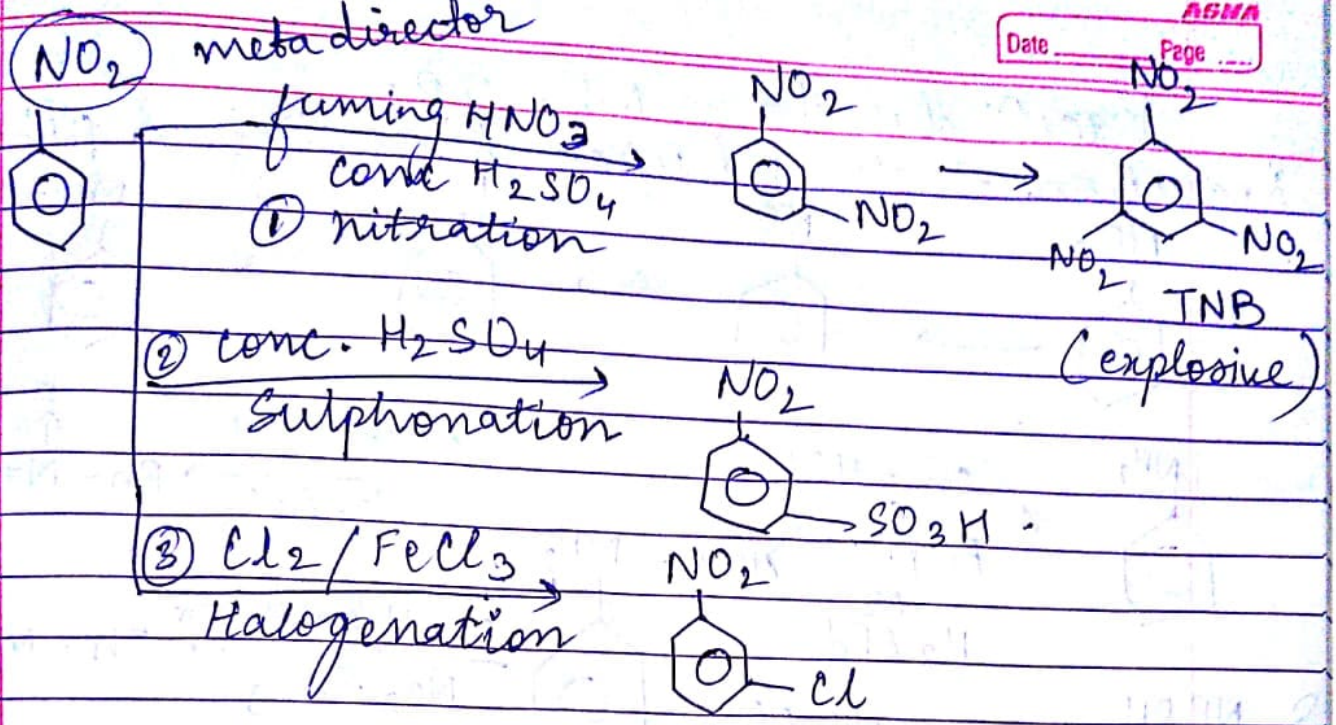
Physical Properties of nitro benzene :-

1. Yellow Oily liquid
2. Poisonous in nature
3. heavier than water
4. Insoluble in H_2O but soluble in alcohol & ether
5. BP → 211°C
6. Smell of nitrobenzene & Benzaldehyde is same i.e. smell of bitter almond.

Chemical Properties :-

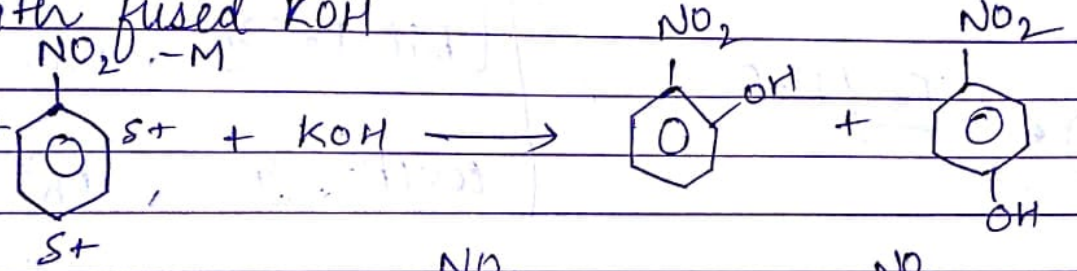
① Reac^n due to benzene ring → ESR
→ NSR

(a) ESR

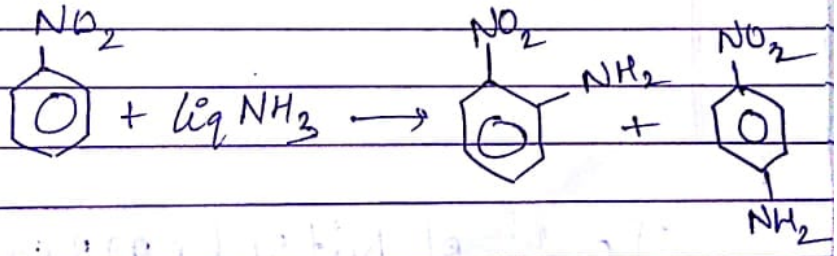


(B) NSR :-

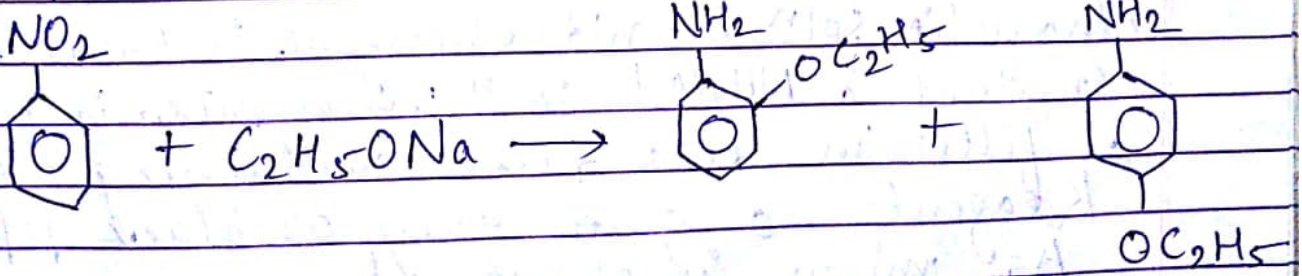
*(a) With fused KOH



(b) With liq. NH_3

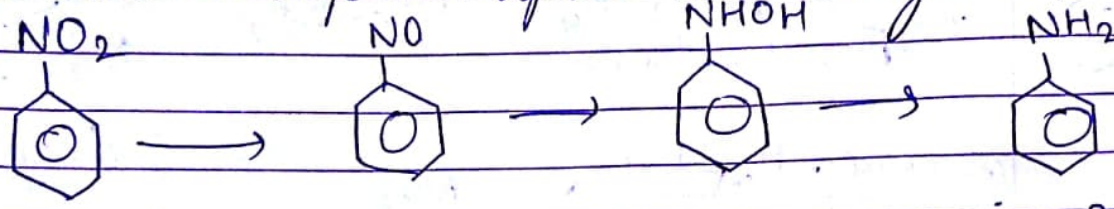


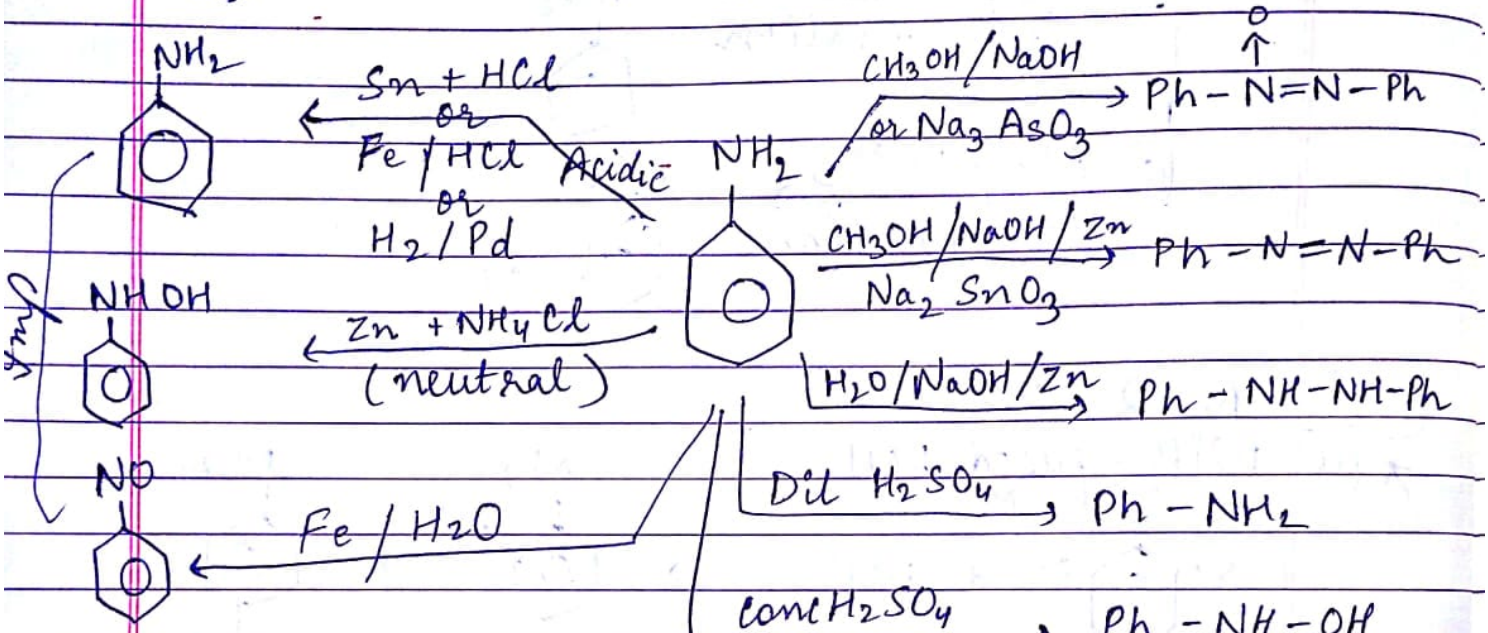
(c) With C_2H_5ONa



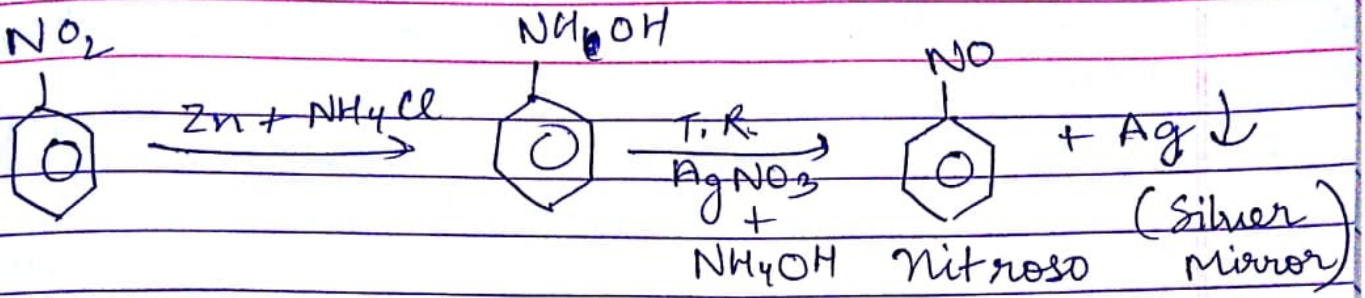
ASHA
Date Page

Reac^{n} duc to $-NO_2$ gp:
Reduction → depend upon Reducing & pH





Test of Nitrobenzene
Mulliken Barker Test
Ethanolic sol^{n} of nitrobenzene is treated with Zn dust & NH_4Cl sol^{n}. Then mix. is heated & filter in test tube containing Tollen's Reagent a grey or black ppt of Ag mirror is obtained.



Nitroso benzene

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