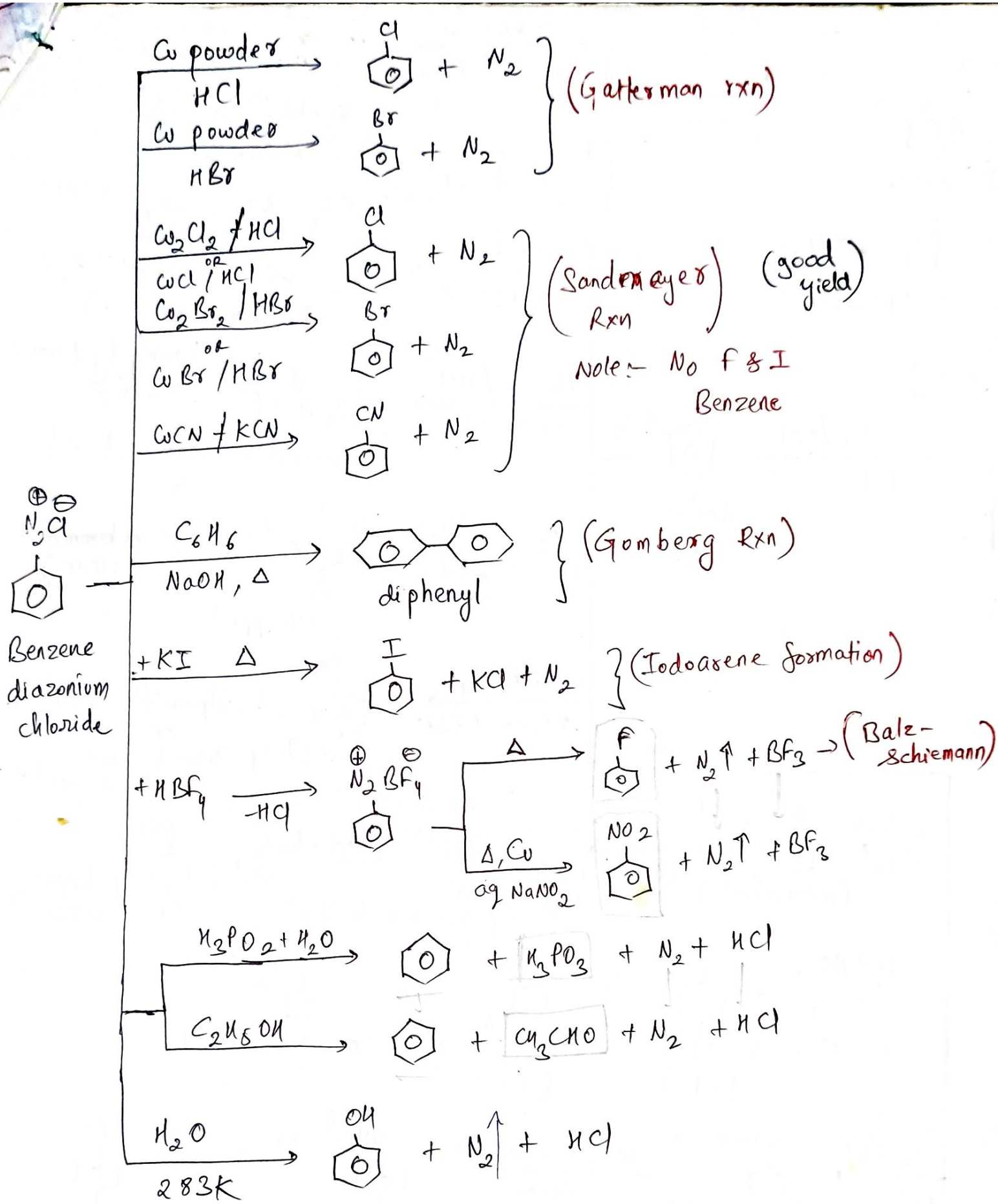
Preparation of amines:

1) By ammonolysis of alkyl halides:
2) Reduction of nitro compounds
3) Reduction of alkyl cyanide (Mendius Reduction)
4) Reduction of amides
5) Gabriel phthalimide synthesis → (only 1° amine)
6) Hoffmann degradation
7) Curtius Rxn

Chemical Properties

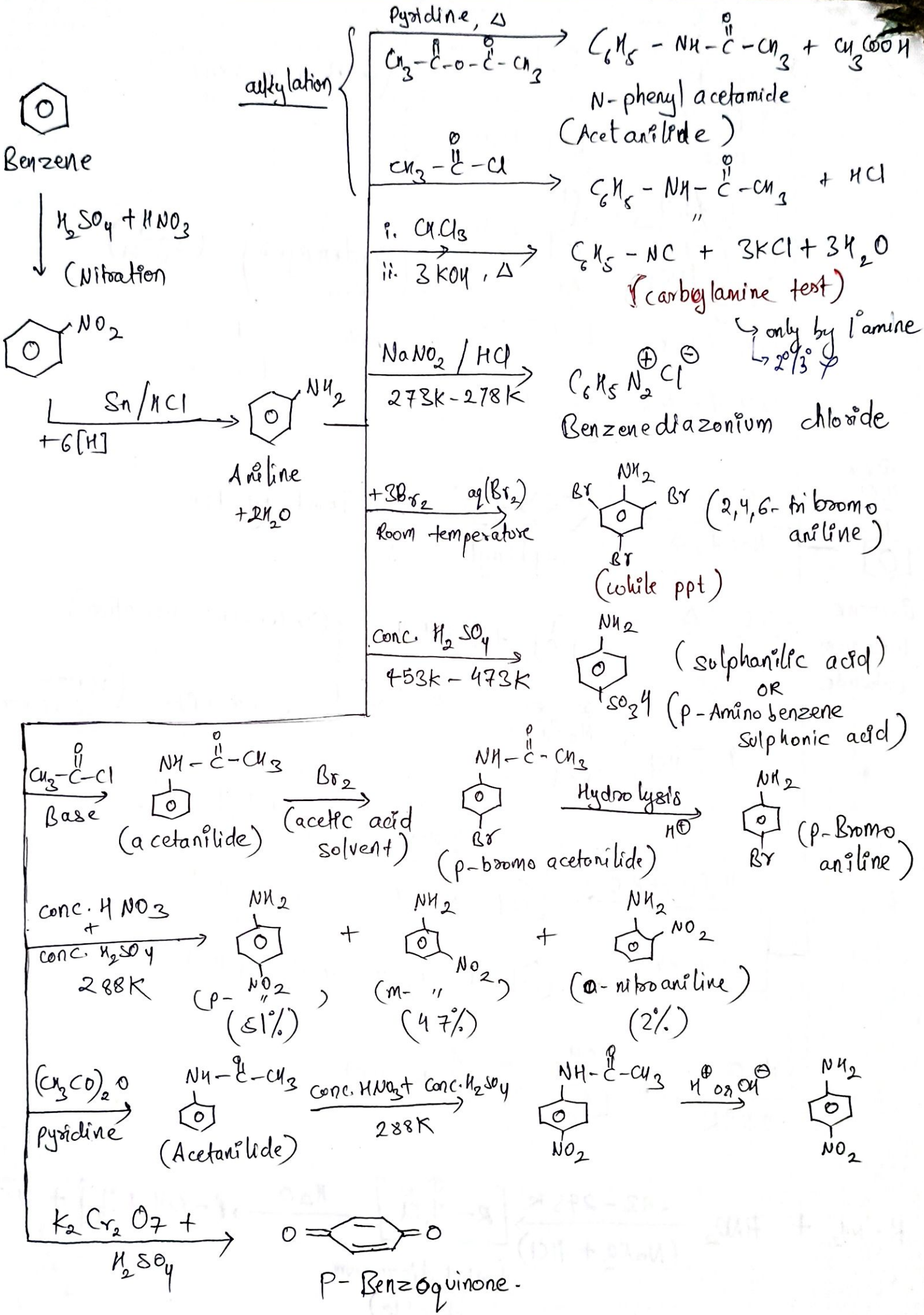
1) Laboratory test for amines
   - Test for amines as the base
   - Diazotization reaction / orange dye test.

2) Alkylation of amines : Hoffman's exhaustive alkylation
3) Hofmann elimination
4) Acylation of amines
5) Carbylamine reaction
6) Reaction with nitrous acid
7) Rxn of arene diazonium salts:
   - Reactions involving displacement of diazo group
     - Gatterman reaction
     - Sandmeyer Rxn → No F & I Benzene
     - Gombeg Rxn
     - Iodoarene formation
     - Reaction with fluoroboric acid
     - Mild Reduction
     - Phenol formation
   - Coupling Rxn
     - Phenol "orange"
     - Anitine "Yellow"
     - Nepthol "Red"
8) Rxn with benzenesulfonyl chloride (Hinsberg's test)



$$R-NH_2 + HNO_2 \xrightarrow[(NaNO_2 + HCl)]{273-278\,K} \left[R-\overset{\oplus}{N_2}\overset{\ominus}{Cl}\right] \xrightarrow{H_2O} R-OH + N_2\uparrow + HCl$$

(alkyl diazonium chloride)


Benzene
alkylation
Pyridine, Δ
$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
$C_6H_5-NH-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$
N-phenyl acetamide
(Acetanilide)
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$
$C_6H_5-NH-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$
i. $CHCl_3$
ii. 3KOH, Δ
$C_6H_5-NC + 3KCl + 3H_2O$
(carbylamine test)
only by 1° amine
2°/3° ✗
$H_2SO_4 + HNO_3$
(Nitration
NO_2
Sn/HCl
+6[H]
NH_2
Aniline
$+2H_2O$
$NaNO_2$ / HCl
273K - 278K
$C_6H_5N_2^{\oplus}Cl^{\ominus}$
Benzenediazonium chloride
$+3Br_2$ aq(Br_2)
Room temperature
(2,4,6- tribromo aniline)
(white ppt)
Conc. H_2SO_4
453K - 473K
SO_3H
(sulphanilic acid)
OR
(p-Amino benzene Sulphonic acid)
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$
Base
(acetanilide)
Br_2
(acetic acid solvent)
(p-bromo acetanilide)
Hydrolysis
$H^{\oplus}$
(p-Bromo aniline)
conc. HNO_3 + conc. H_2SO_4
288K
(p- 17%)
(m- 47%)
(o- 2%)
(o-nitroaniline)
$(CH_3CO)_2O$
Pyridine
(Acetanilide)
conc. HNO_3 + conc. H_2SO_4
288K
$H^{\oplus}$ or $OH^{\ominus}$
$K_2Cr_2O_7 + H_2SO_4$
P- Benzoquinone.

Preparation of amines:

1) Ammonolysis of Alkyl halide:

$$R-X + \ddot{N}H_3 \xrightarrow{\Delta} R-\overset{\oplus}{N}H_2\,X^{\ominus} \xrightarrow[-NaX\ -H_2O]{\overset{+}{Na}\overset{-}{O}H} R-\ddot{N}H_2 \quad (1^\circ \text{ amine})$$

$$R-\ddot{N}H_2 + R-X \longrightarrow \left[R-\overset{\oplus}{N}H-R\right] X^{\ominus} \xrightarrow[-NaX\ -H_2O]{NaOH} R-\ddot{N}H-R \quad (2^\circ \text{ amine})$$

$$R-\ddot{N}H-R + R-X \longrightarrow \left[R-\overset{\oplus}{N}(R)-R\right] X^{\ominus} \xrightarrow[-NaX\ -H_2O]{NaOH} R-\ddot{N}(R)-R \quad (3^\circ \text{ amine})$$

$$R-\ddot{N}(R)-R + R-X \longrightarrow \left[R-\overset{\oplus}{N}(R)(R)-R\right] X^{\ominus} \xrightarrow{NaOH} R-\overset{+}{N}(R)(R)-R$$

quaternary ammonium salt.

Order of Reactivity of Halo Alkyl

$$R-I > R-Br > R-Cl$$

Note :-

$$CH_3-\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + NH_3(alc) \xrightarrow{-Br^{\ominus}} \left[CH_3-\overset{CH_2-H}{\underset{\oplus}{\overset{|}{C}}}-CH_3\right] \xrightarrow{-H^{\oplus}}$$

Tert-Butyl Bromide

$$CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + HBr$$

(isobutylene)

2-methyl prop-1-ene

Elimination rxn > Nu- substitution rxn.

Because, stable carbocation.

(2) Reduction of nitro compounds:

$$R-NO_2 + 6[H] \xrightarrow[\text{(2) Fe/HCl}]{\text{(1) Sn/HCl}} R-NH_2 + 2H_2O$$

(3) Zn/HCl

(4) H_2/Ni

(5) Pt or Pd

(6) $LiAlH_4$ / ethers

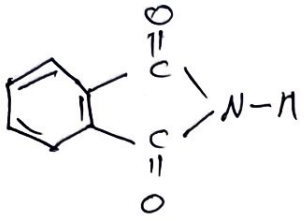
③ Reduction of Nitrile: (Mendius Reduction)

$$R-C\equiv N + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} R-CH_2-NH_2$$

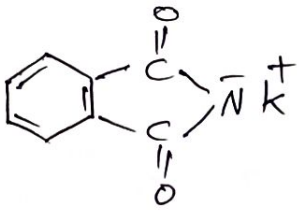
$$CH_3-I + KCN \longrightarrow CH_3-CN + KI$$

④ Gabriel Phthalimide Synthesis:

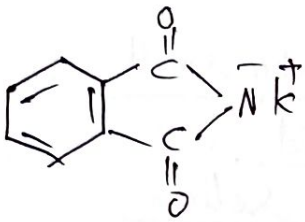
→ we can only form 1° alkyl amine & No aryl amine.

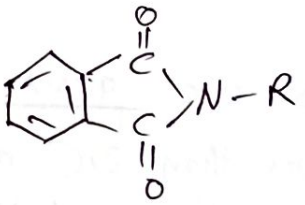


phthalimide

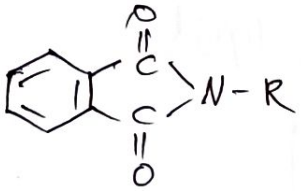


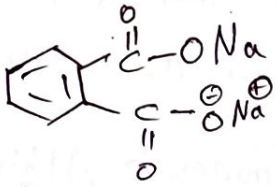
(potassium salt of phthalimide)





(N-alkyl phthalimide)





+ $R-NH_2$ 1° amine

(Sodium phthalate)

⑤ Reduction of amides:

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + 4[H] \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4/\text{ether}} CH_3-CH_2-NH_2$$

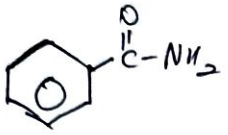
(amine)

(Benzyl amine)

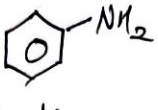
⑥ Hoffmann - degradation / Hoffmann Bromamide degradation

↳No 3° amine ✗

$$R-\underset{\text{amide}}{\overset{O}{\overset{\|}{C}}-NH_2} + 1Br_2 + 4NaOH_{(aq)} \xrightarrow{\Delta} \underset{(1^\circ \text{ amine})}{R-NH_2} + Na_2CO_3 + 2H_2O + 2NaBr$$



$$+ Br_2 + 4NaOH \xrightarrow{\Delta}$$



$$+ 2H_2O + 2NaBr + Na_2CO_3$$

(Benzamide) Aniline

⑦ Curtius Reaction :

$$CH_3-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow[ii)\ H_2O]{i)\ \Delta} CH_3-NH_2 + CO_2\uparrow$$

Physical Properties:

① Lower aliphatic amines are gases, smell → fishy smell
② Middle member or more than 3C amines → Liquid.
③ Higher member or more than 8 to 10C amines → Solids
④ Aniline & other arylamines are usually colourless liquid

[2] Solubility :- Alcohol > Amines > Alkanes → (AAA)

[3] Boiling. P :- 1°amine > 2° amine > 3° amine

Carboxylic acid > Alcohols > Amines > alkane.

Order of Basicity of amine :-

$OH^- \uparrow \quad K_b \uparrow \quad pK_b \downarrow \quad \text{Basic} \uparrow$

Aniline < NH_3 < Alkyl amine

a) R ⇒ (C_2H_5) b) R ⇔ (CH_3) } Aq. phase

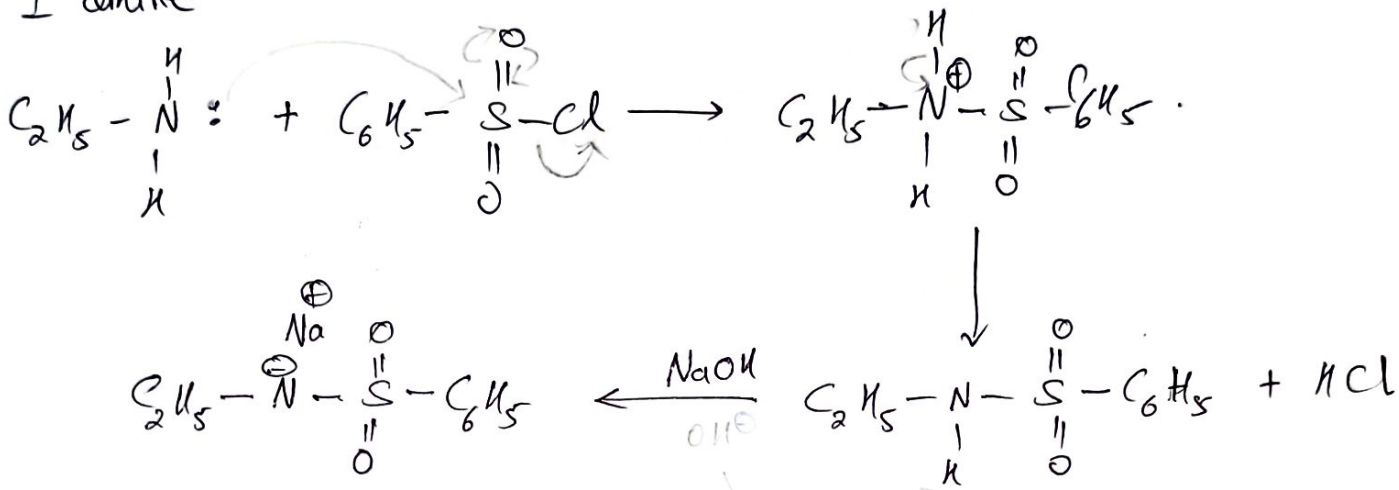
2° > 3° > 1° 2° > 1° > 3°

R-Me 3° > 2° > 1°
R-Et 3° > 2° > 1° } gas phase.

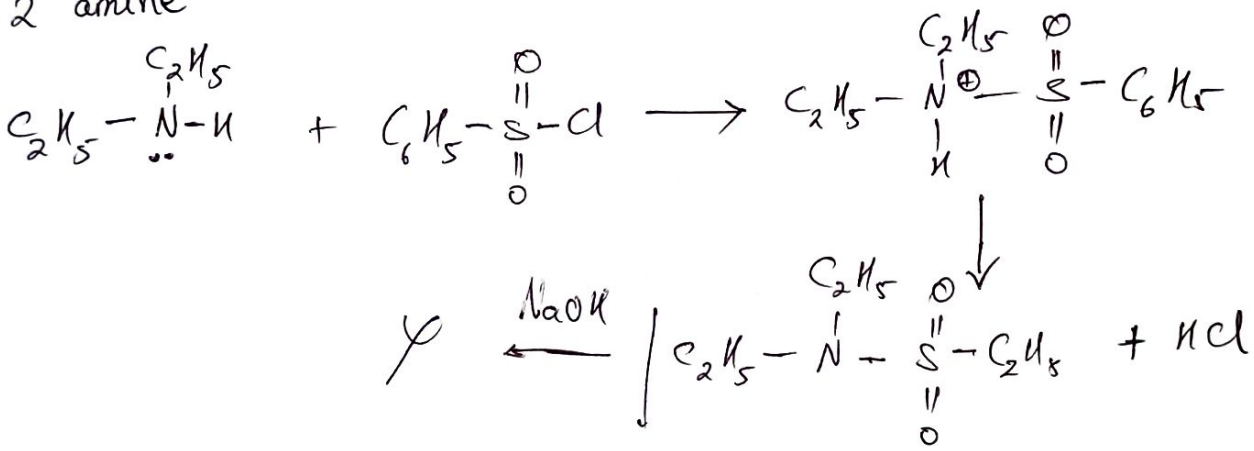
Hinsberg's Reaction : ($C_6H_5SO_2Cl$)

- 1° amine $\xrightarrow{H.R}$ ✓ $\xrightarrow{NaOH}$ soluble in alkali
- 2° amine $\xrightarrow{H.R}$ ✓ $\xrightarrow{NaOH}$ ✗ Insoluble
- 3° amine $\xrightarrow{H.R}$ ✗

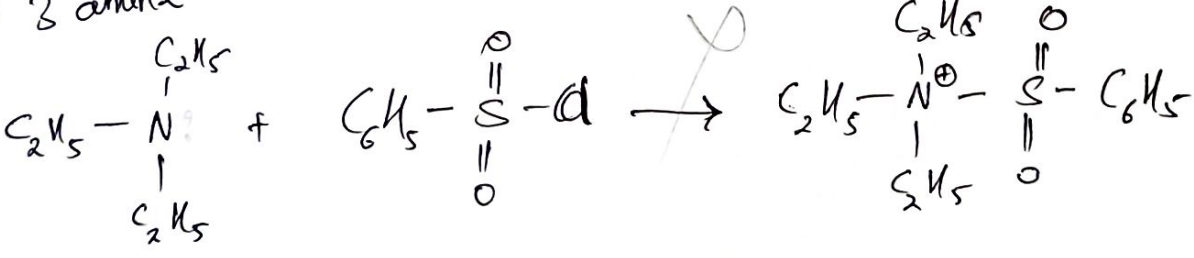
1) 1° amine



2) 2° amine



3) 3° amine



Homologous Series	General formula
Alkane	C_nH_{2n+2}
Alkene & cycloalkane	C_nH_{2n}
Alkyne / Alkadiene & cycloalkene	C_nH_{2n-2}
Alkyl Halide	$C_nH_{2n+1}X$
Alcohol & Ether	$C_nH_{2n+2}O$
Aldehyde & ketone	$C_nH_{2n}O$
Amide, Oximes & Nitroso Compounds	$C_nH_{2n+1}NO$
Carboxylic acid & ester	$C_nH_{2n}O_2$
Cyanides & Isocyanides	$C_nH_{2n+1}N$
Nitro & Nitrite	$C_nH_{2n+1}NO_2$

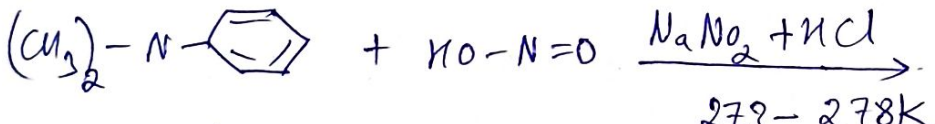
Paraffins → alkane

Olefins → ~~alkene~~ alkene

In Hoffmann elimination, the major product is

Least substituted alkene

Action of nitrous acid (HNO_2)



N,N-dimethyl aniline