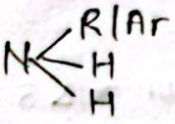
Amines

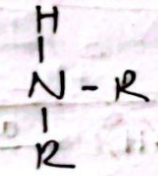
- Alkyl / Aryl derivative of ammonia.



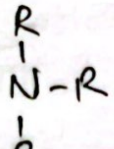
R-NH₂ (amine)

Ar-NH₂

1° amine

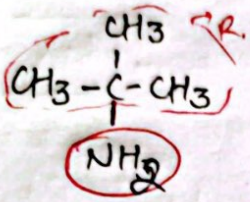


2° amine



3° amine

- $R-NH_2$ (1° Amine)
- R_2NH (2° amine)
- R_3N → (3° amine)



1° amine

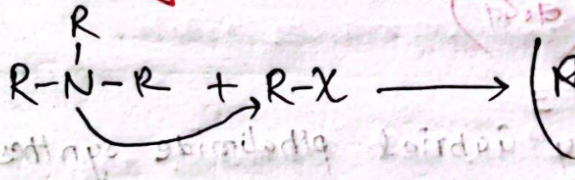


sp³ hybridization

- Tetrahedral geometry
- pyramidal shape

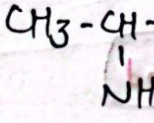
General Formula → $C_nH_{2n+3}N$.

Quaternary salt

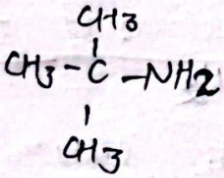


Quaternary ammonium salt

* Secondary butyl amine → 1° amine



* Tert. butyl amine → 1° amine



Abhishek

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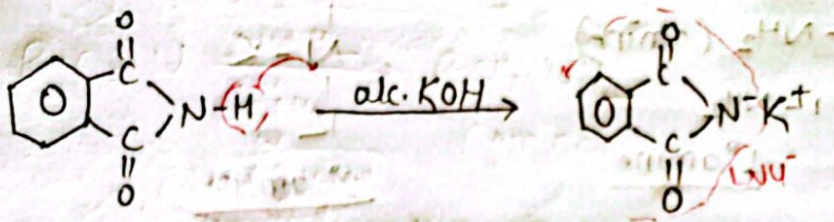
General Method of Preparation

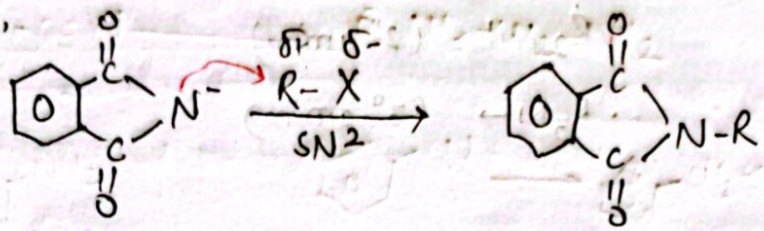
① By Gabriel pthalimide synthesis rxn



pthalimide

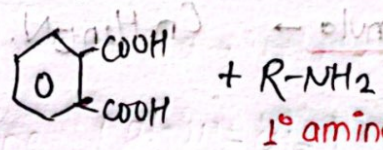
salt

then,

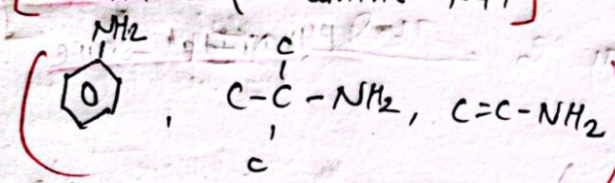


$SN^2 \rightarrow$ 3° haloalkane, $CH_2=CH-X$, (O-X या हुईन)

H^+/H_2O



[2° amine & 3° amine बन्दैन]



(बन्दैन)

Q. Which amine cannot be prepared by Gabriel pthalimide synthesis rxn ?

(a) $CH_3-NH-CH_3$ (b) $C_2H_5-NH_2$ (c) $C_6H_5-NH_2$ (d) $C_6H_5-CH_2-NH_2$

(e) $CH_3-C(CH_3)_2-NH_2$ (f) $C_2H_5-N(CH_3)-CH_3$ (g) $CH_2=CH-NH_2$

(h) CH_3-NH_2

b, d, h – can be prepared

② By hydrolysis of isocyanide

$$R-\overset{H}{\underset{H}{N}}\equiv\overset{OH}{\underset{OH}{C}} \xrightarrow{H_2O} R-NH_2 + HCOOH$$

e.g. $$CH_3-\overset{H}{\underset{H}{N}}\equiv\overset{OH}{\underset{OH}{C}} \xrightarrow{H_2O} CH_3-NH_2 + HCOOH$$

③ By reductive amination of ald/ketone

$$\underset{\text{ald/ket}}{\begin{matrix}R\\H/R\end{matrix}\!\!>C=\boxed{O} + \boxed{H_2}N-H} \xrightarrow[-H_2O]{} \begin{matrix}R\\R/H\end{matrix}\!\!>C=N-H \xrightarrow[\text{or } H_2/Ni]{LiAlH_4} \begin{matrix}R\\R/H\end{matrix}\!\!>CH-NH_2$$

1° amine

e.g. $$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=\boxed{O} + \boxed{H_2}N-H \xrightarrow[-H_2O]{} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=N-H \xrightarrow[\text{or } H_2/Ni]{LiAlH_4} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-NH_2$$

1° amine

④ Reduction of nitro compound

→ Both aliphatic & aromatic 1° amine.

(a) catalytic redn :- H_2 + Ni/pt/pd.

$$R/Ar-NO_2 \xrightarrow{H_2/Ni} R/Ar-NH_2$$

(b) Fe/Sn/Zn + conc HCL

$$R/Ar-NO_2 \xrightarrow{Sn/HCL} R/Ar-NH_2$$

(c) $LiAlH_4$

$$R-NO_2 \xrightarrow{LiAlH_4} R-NH_2$$

Note

$$Ar-NO_2 \xrightarrow{LiAlH_4} C_6H_5-N=N-C_6H_5$$

azobenzene

⑤ Cyanide / Isocyanide

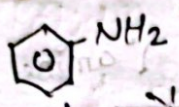
(i) Ni/pt/Pd + H_2 (ii) $LiAlH_4$ (iii) Na/C_2H_5OH

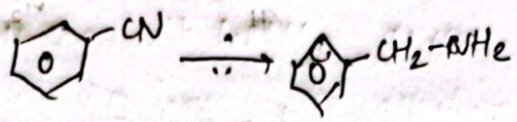
$R-C\equiv N \xrightarrow[\text{or } LiAlH_4 \text{ or } Na+C_2H_5OH]{Ni+H_2} R-CH_2-NH_2$ 1° amine

2° amine & 3° amine → can't form

Na + C_2H_5OH → mendius rxn

$CH_3-C\equiv N \xrightarrow[\because]{''} CH_3-CH_2-NH_2$

•  → बन्दैन

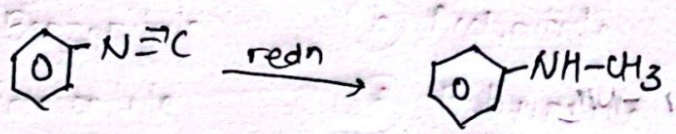


CH_3-N-CH_3 (H) → बन्दैन

→ $R-N\equiv C$ (H, 3H) $\xrightarrow{Red^n}$ 2° amine ($R-NH-CH_3$)

e.g. $CH_3-N\equiv C$ (H, 3H) $\xrightarrow{red^n} CH_3-NH-CH_3$

$C_2H_5-N\equiv C \xrightarrow{red^n} C_2H_5-NH-CH_3$



⑥ By reduction of amide

$R-\overset{O}{\overset{\|}{C}}-NH_2$ (CH_2) $\xrightarrow[\text{or } Na+C_2H_5OH]{LiAlH_4} R-CH_2-NH_2$

(7) Redn of oxime

$$R-CH=N-OH \xrightarrow{LiAlH_4} R-CH_2-NH_2 + H_2O$$

1° amine

$$CH_3-CH=N-OH \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2 + H_2O$$

(8) By decarboxylation of amino acids

$$R-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow[(Ba(OH)_2 + H_2O)\ \text{i.e. } Ba(OH)_2]{\text{Baryta water}} R-CH_2-NH_2 + CO_2$$

e.g. $CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow{Ba(OH)_2} CH_3-CH_2-NH_2 + CO_2$

alanine

$$H-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow{\upsilon} CH_3-NH_2 + CO_2$$

(9) Ammonolysis of alkyl halide

S_N2

$$NH_3 + R-X \longrightarrow R-NH_2 + H-X$$

excess

1° amine $+R-X$

$$R-\underset{H}{\underset{|}{N}}-R \xrightarrow{R-X} R-\underset{R}{\underset{|}{N}}-R \xrightarrow{R-X} R_4N^+X^-$$

2° amine — 3° amine — Q. salt

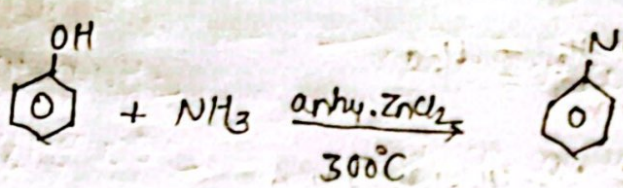
(10) Hoffmann Bromamide degration rxn

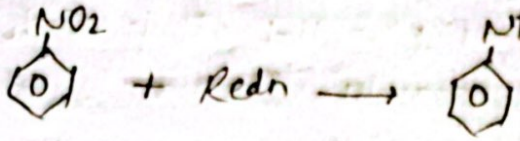
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br+KOH} R-NH_2$$

intermediate:- Acyl nitrene $R-\overset{O}{\overset{\|}{C}}-\ddot{N}:$

→ decreases the carbon no.

Aniline

(i) 

(ii) 

Chemical properties

Q. Reduction of nitroethane with LiAlH4 gives:-

(a) ethylhydroxylamine (b) Ethanol

(c) ethylamine (d) Ethanamide

$C_2H_5-NO_2 \xrightarrow{Redn} C_2H_5-NH_2$

Q. The major product formed when ammonia reacts with excess of ethyl iodide is:-

(a) Diethylamine (b) ethylamine (excess NH_3)

(c) Triethylamine (d) Tetraethylammonium iodide

Q. Which of the following on reduction with hydrogen and Raney Nickel gives benzylamine? 

(a) Benzonitrile (b) Acetonitrile

(c) Propionitrile (d) Butyronitrile

Q. Which one of the following is produced by reduction of RCN in sodium and alcohol? Mendius rxn.

(a) $RCONH_2$ (b) $RCOO^-NH_4^+$

(c) RCH_2NH_2 (d) $(RCH_2)_3N$

Q. Which of the following compounds gives a secondary amine on r

(a) Nitromethane (b) Nitroethane (c) Methyl cyanide (d) Methyl isocyan

Q. Which of the following gives primary amine on redn?

(a) $CH_3CH_2NO_2$ (b) $CH_3CH_2-O-N=O$

(c) $C_2H_5N=NC_6H_5$ (d) CH_3CH_2NC

Q. Aldoximes on redn with $LiAlH_4$ or Na/C_2H_5OH gives:-

(a) 1° amines (b) 2° amines (c) 3° amine (d) Quaternary salt

$R-CH=N-OH \xrightarrow[-H_2O]{} R-CH_2-NH_2$

Q. Acetone oxime on redn with Na/C_2H_5OH would give:-

(a) Isopropylamine (b) n-propylamine

(c) ethylaminemethylamine (d) Diethylamine

$(CH_3)_2C=N-OH \longrightarrow (CH_3)_2CH-NH_2 + H_2O$

Q. Which of the following rxn doesn't yield amine?

(a) $R-X + NH_3 \longrightarrow$

(b) $R-CH=NOH + [H] \xrightarrow{Na/C_2H_5OH}$

(c) $R-CN + H_2O \xrightarrow{H^+}$ C. acid

(d) $R-CONH_2 \xrightarrow{LiAlH_4}$

Q. The rxn by which a primary amine is formed from a 1° amide is called:-

(a) Hoffmann bromamide rxn. (b) Gabriel phthalimide rxn

(c) Carbylamine rxn (d) Liebermann nitrosoamine rxn

Q. Indicate which of the following compounds amongst the following undergo Hoffman rxn, i.e. rxtion with Br_2 & strong KOH to give 1° amine

(a) $R-CO-NHCH_3$ (b) $R-CO-ONH_4$

(c) $R-CO-NH_2$ (d) $R-CO-NHOH$

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Q. Which of the following amides not undergo Hoffman bromamide rxn?

(a) CH_3CONH_2 (b) $CH_3CH_2CONH_2$

(c) $C_6H_5CONH_2$ (d) $CH_3CONHCH_3$ (2° amide)

Q. Which of the following reagents can be used to convert 1° amides into 1° amine containing same no. of C atoms?

(a) $Br_2 + NaOH$ (b) $LiAlH_4$ (c) $Sn + HCl$ (d) $Na + C_2H_5OH$

Q. Which of the following amines can't be prepared by Gabriel phthalimide rxn?

(a) Benzylamine (b) Aniline (c) ethylamine (d) Methylamine

Q. In $(CH_3)_3N$, the state of hybridization of N-atom & the spatial arrangement of methyl groups around it are respectively:-

(a) sp^3, pyramidal (b) sp^3, tetrahedral

(c) sp^2, trigonal planar (d) sp^3, trigonal planar

Q. The end product of the rxn seq:-

$$C_6H_5NH_2 \xrightarrow[\Delta]{CHCl_3, KOH} A \xrightarrow[(ii)\ H_2O]{LiAlH_4} B$$

A = C_6H_5NC, B = $C_6H_5-NH-CH_3$

(a) $C_6H_5NHCH_3$ (b) $C_6H_5CH_2NH_2$

(c) C_6H_5NHCHO (d) C_6H_5NC

Q. Methane is produced when CH_3MgBr reacts with:-

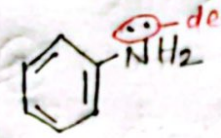
(a) $CH_3CH_2NH_2$ (b) $(CH_3CH_2)_2NH$ (c) CH_3CH_2OH

(d) all of above

II Chemical properties

① Basic strength:-

$$\boxed{B.S. \propto K_b \propto \frac{1}{pK_b}}$$



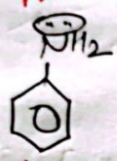
deloaglized. resonance भाग < R-$\ddot{N}H_2$ localized.

$$\boxed{\text{Basic strength} \propto \frac{EDG\,|+I|+R}{EWG\,|-I|-R}}$$

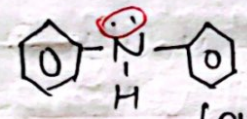
→ $R-NH_2$ > $H-NH_2$

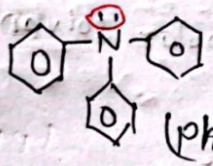
amine ammonia

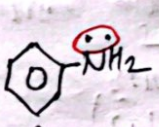
more basic.

–  < $R-\ddot{N}H_3$ < $R-\ddot{N}H_2$

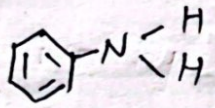
least basic ↳ more basic

(i)  $(Ph)_2-NH$

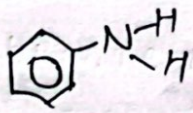
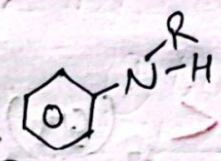
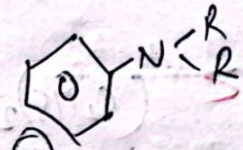
(ii)  $(Ph)_3-N$

(iii)  $(Ph)-NH_2$

basicity:- iii > ii > i

Q.  → H remove गरेर C_6H_5 ring जोड्यो भने B.S ↓es

R↑ → B.S ↑es.

Q.  ①  ② >  ③

Basicity → 3>2>1.

Q. (1) $CH_2=CH-\ddot{N}H_2$ ② $CH_2=CH-\overset{H}{N}-CH=CH_2$ ③ $CH_2=CH-\ddot{N}(CH=CH_2)-CH=CH_2$

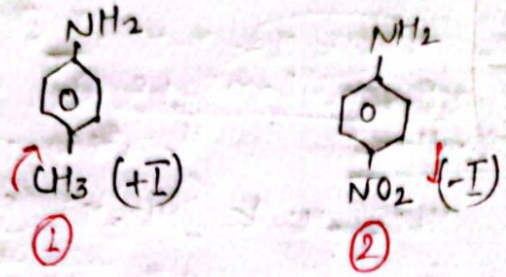
basicity → 1>2>3



K_b > K_b

pK_b < pK_b

Q.



basicity → 1 > 3 > 2

1° / 2° / 3° amines

Gaseous medium (non polar) — e.g. benzene, cyclohexane also

aq. medium (polar solvent)

→ $R-NH_2$ R_2NH R_3N

Gaseous medi:- inductive plays role only.

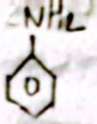
3° > 2° > 1°

Q. $C_6H_5-NH_2$ < $(C_2H_5)_2NH$ < $(C_2H_5)_3N$

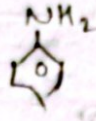
aqueous medium:- (polar solvent)

* Inductive
* solvation
* steric hinderence.

} plays role.

$2^\circ > 1^\circ > 3^\circ > NH_3 >$ 

$R \Rightarrow C_2H_5$

$2^\circ > 3^\circ > 1^\circ > NH_3 >$ 

Q. Basic strength order :-

(a) $C_2H_5-NH_2$ (b) $(C_2H_5)_2NH$ (c) $(C_2H_5)_3N$

basicity :- b > c > a

Note :- कुनै medium पछे दिएको छैन भने aq. medium बुझ्ने ।

* Basic str. order

(1) $R-NH_2$ (2) R_2NH (3) R_3N. ($R = CH_3$ मान्ने)

→ 2 > 1 > 3.

Q. What is the decreasing order of 1°, 2° & 3° & ammonia ?
ethylamine
med. भने छैन.

→ $2^\circ > 3^\circ > 1^\circ > NH_3$

Q. In chlorobenzene solutions, the basic strength of amines increases in order?
└non polar (gaseous)

(a) $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$

(b) $C_2H_5-NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$ 3 > 2 > 1

(c) $(C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3N$

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Q. Among NH_3, $C_2H_5NH_2$ and $C_6H_5NH_2$, the basic strength follows the order:- (aq. मांगो)

(a) $NH_3 > C_2H_5NH_2 > C_6H_5NH_2$

(b) $C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

(c) $C_6H_5NH_2 > C_2H_5NH_2 > NH_3$

(d) $C_2H_5NH_2 > C_6H_5NH_2 > NH_3$

2 > 1 > 3

Q. In aq. medium, the basic strength of amines decreases in the order:- (methyl group)

(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

(b) $(CH_3)_2NH > (CH_3)_3N > (CH_3)NH_2$

(c) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$

(d) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

Q. The correct sequence of increasing order of basicity in aq. soln is:

(a) $NH_3 < C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3N$ (ethyl. 2 > 3 > 1 > NH_3 > 6)

(b) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$

(c) $C_6H_5NH_2 < NH_3 < (C_2H_5)_2NH < (C_2H_5)_3N < (C_2H_5)_2NH$

(d) None

① Reaction with acids

$$R-NH_2 + HCl \longrightarrow RNH_3^{\oplus}Cl^{\ominus}$$

salt

② Rxn with water

$$R-NH_2 + H_2O \longrightarrow RNH_3^{\oplus}OH^{-}$$

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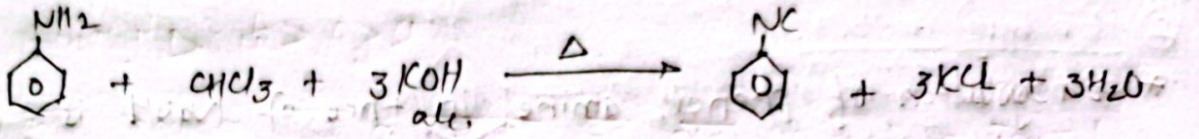
Carbylamine rxn (Rxn with chloroform)

- Aliphatic + aromic 1° amine ले दिन्छ

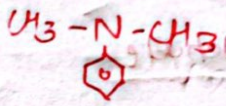
$+ CHCl_3 + alc.KOH \xrightarrow{\Delta}$ isocyanide
↳ Unpeasent order
1° amine test.
or isocyanide test

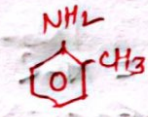
• Intermediate :— $:CCl_2$
dichlorocarbene (E^+)
↳ also in reimer tiemann rxn

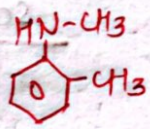
e.g. $C_2H_5NH_2 + CHCl_3 + 3KOH_{alc} \xrightarrow{\Delta} C_2H_5NC + 3KCl + 3H_2O$
1° amine — isocyanide.



Q. Which gives carbylamine rxn:-

(a) N,N-dimethyl aniline (3° amine) 

(b) O-methyl aniline 

(c) O-methyl-N-methyl aniline (2° amine) 

(d) None

(4) Rxn with acid chloride / acid anhydride with aliphatic amines

• $R-\overset{O}{\overset{\|}{C}}-Cl + H-NH-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH-R + HCl$
1° amine — amine

• $R-\overset{O}{\overset{\|}{C}}-Cl + H-N(R)_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-N(R)_2 + HCl$
2° amine

• $R-\overset{O}{\overset{\|}{C}}-Cl + R_3N \longrightarrow$ No rxn.
No-H
3° amine

with aniline

$C_6H_5-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl$

$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H-NH-C_6H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$

acetanilide

Q $C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H-NH-C_6H_5 \xrightarrow[\text{pyridine}]{NaOH} C_6H_5-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$

Benzoyl chloride, aniline, Benzanilide

* Benzoylation of phenol, amine in ^nce of NaOH is called Schotten Baumann reaction.

Reaction with aldehyde:

$R-CH=O + H_2-NR \longrightarrow R-CH=N-R + H_2O$

schiff's base or Anil

$C_6H_5-CHO + H_2N-C_6H_5 \rightarrow C_6H_5-CH=N-C_6H_5$

Rxn with Grignard reagent

$R-MgX + R-N(H)-H \longrightarrow R-H + Mg(X)(NHR)$

1° amine

$R-MgX + R-\overset{R}{N}-H \longrightarrow R-H + Mg(X)(NR_2)$

2° amine

$R-MgX + R-\overset{R}{N}-R \longrightarrow$ No rxn.

3° amine

Rxn with Nitrous acid — HNO_2 or HONO (Imp)
($NaNO_2$ + HCl).

→ $R-NH_2$ (OH, N, O) $\xrightarrow{HNO_2}$ $R-OH + N_2 + H_2O$
1° amine

intermediate: R^+

→ R_2N-H (2° amine) $\xrightarrow[-H_2O]{HO-NO}$ $R_2N-N=O$ (Nitroso amine (yellow oily liq.))

→ R_3N (3° amine) $\xrightarrow{HONO}$ No rxn. (due to absence of acidic H).

· [CH_3NH_2 + HONO $\longrightarrow$ $CH_3-O-N=O$ + CH_3-O-CH_3] exception.
Methyl nitrite

Hoffman's mustard oil rxn (imp)

→ $R-NH_2$ (1° amine) $\xrightarrow{S=C=S}$ (carbon disulphide, CS_2) $S=C-S^-$ ($R-NH_2^{\oplus}$) $\longrightarrow$ $S=C-S-H$ ($R-N-H$)

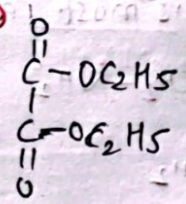
· $S=C-S-H$ ($R-N-H$) $\xrightarrow{HgCl_2}$ $R-N=C=S$.
$-2HCl$
$-HgS$
alkyl isothiocynate (smell of mustard oil).

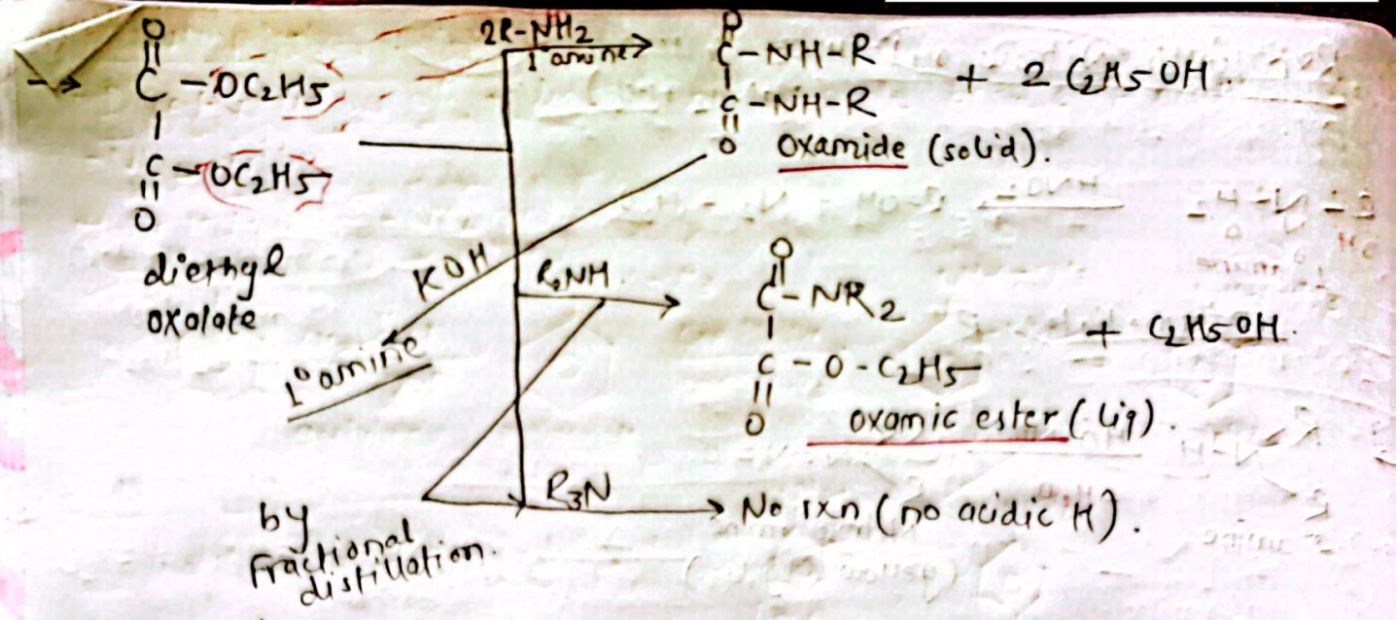
→ $R-NH_2$ $\xrightarrow[(II)\ HgCl_2]{(I)\ CS_2}$ $R-N=C=S$.
(smell of mustard oil)

Separation of mixture of 1°, 2° & 3° amines

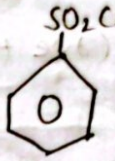
(1) Hoffman's Method

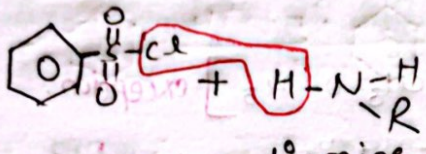
→ 1°, 2°, 3° amines are treated with diethyl oxalate (Hofman's reagent)





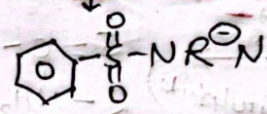
② Hinsberg method :-

↳ Benzene sulphonyl chloride → 

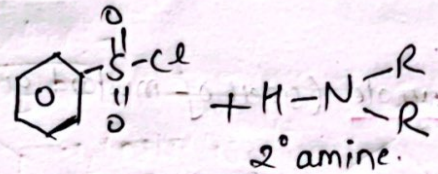
(i) 

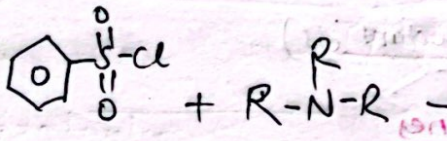
white ppt

↓ NaOH (base)



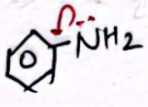
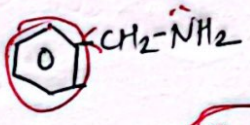
soluble salt (clear soln).

(ii) 

(iii) 

Q. Which is most reactive towards H_2SO_4 ?

(a) $CH_3CH_2-\ddot{N}H_2$ (b) $C_6H_5-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2$

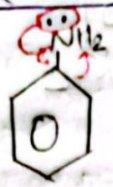
(c)  (d) 

a > d basic

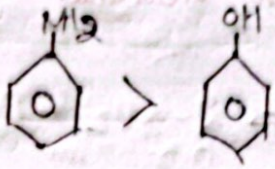
Q. (A) $\xrightarrow[\text{chloride}]{\text{Benzene sulphonyl}}$ B $\xrightarrow{NaOH}$ insoluble. In this rxn, A will be :-

(a) 1° amine $CH_3-CH(CH_3)-NH_2$ (b) ~~2° amine~~ $CH_3-NH-CH_2-CH_3$ (c) 3° amine $CH_3-N(CH_3)-CH_3$ (d) None.

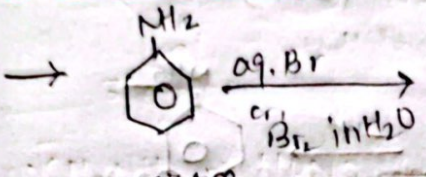
Reactions of Aniline

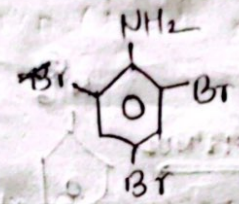


$-NH_2$: strong activator
→ Resonance effect
– o, p director
– Benzene ring activator



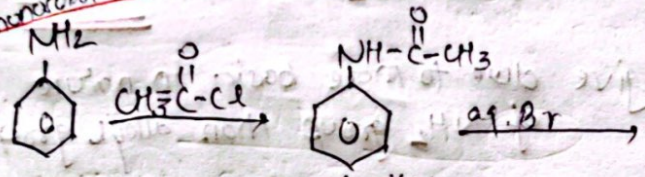
(1) Bromination



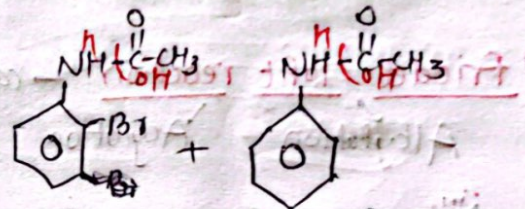


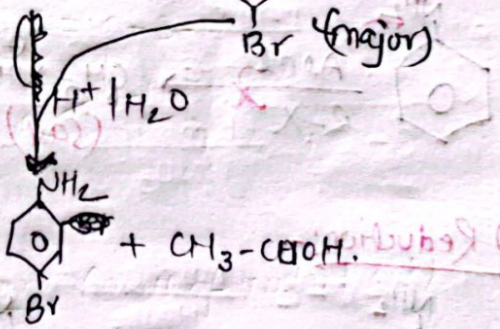
2,4,6-Tribromoaniline (white ppt).

For monosubstitution

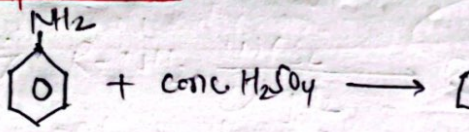


acetanilide.



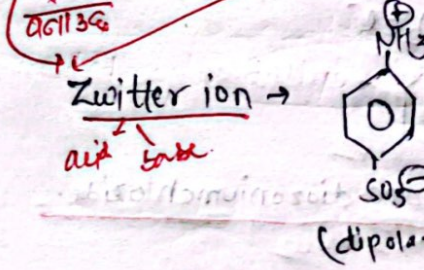


(2) Sulphonation



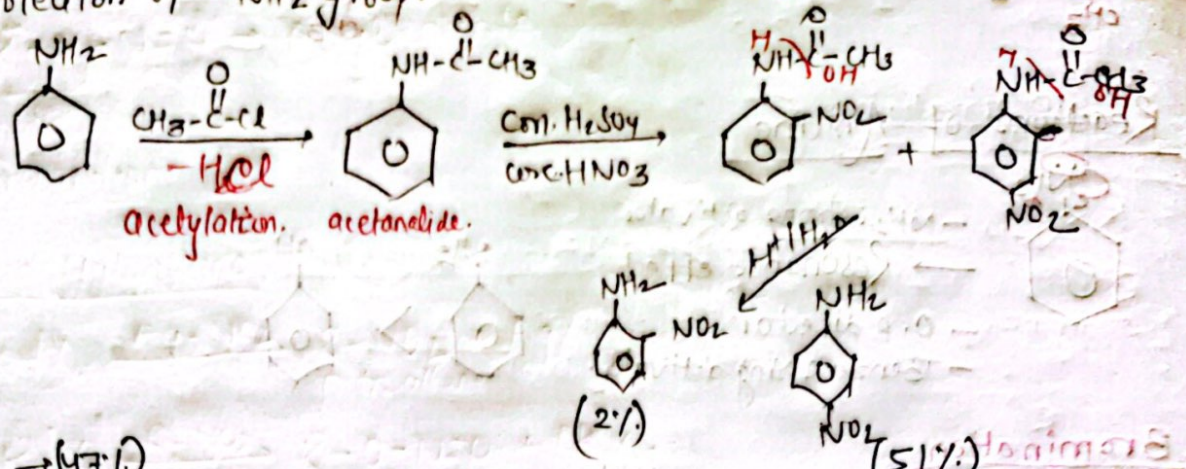
O-sulphanilic acid (minor).

p-sulphanilic acid (major)

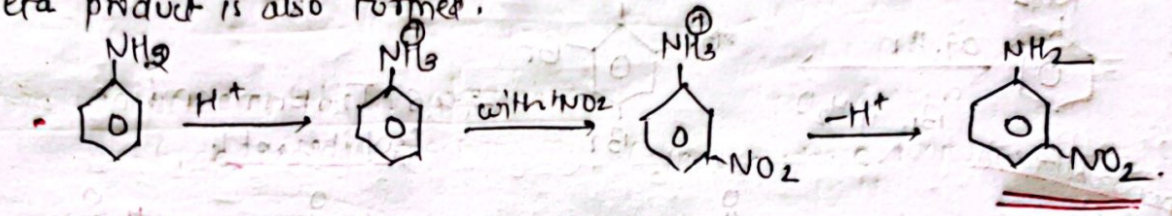


Zwitter ion → (dipolar ion)

- Direct nitration of aniline is not possible because of oxidation of $-NH_2$ group.
- Protection of $-NH_2$ group.

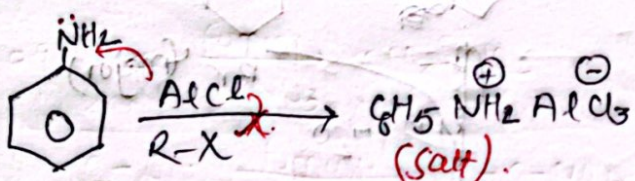


- Meta (47%) product is also formed.

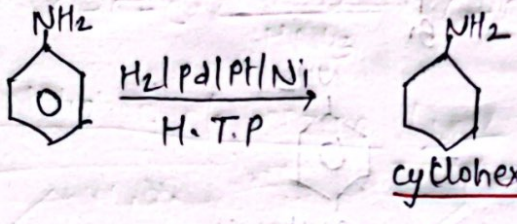


(4) Friedel craft reaction — can't give due to more basic in nature of NH_2 group than alkyl group.

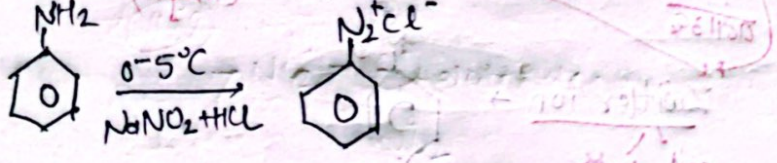
Alkylation Acylation.



(5) Reduction:-



(6) Diazotisation



Q.A.D

Q. Primary, 2° & 3° amines can be distinguished by:-

(a) Schiff's test (b) Fehling test

(c) Tollen's test (d) Hinsberg test (SO_2Cl in benzene).

Q. Arrange the following in the increasing order of their basic strength

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3NH$, NH_3.

→ $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ $\boxed{2\ 1\ 3\ NH_3}$

Q. From the following compound which does not react with $C_6H_5SO_2Cl$? (Hingsberg)

(a) CH_3NH_2 (1°) (b) $(C_2H_5)_3N$ (3°) (c) $C_2H_5NH_2$ (2°) (d) $(CH_3)_2NH$ (1°)

Q. Which one of the following is called as carbylamine?

(a) RCN (b) $RCONH_2$ (c) RCH=NH (d) RNC

Q. Complete the sequence:-

$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{hydrolysis}]{\text{partial}} B \xrightarrow{Br_2/NaOH} C$. The major product 'C' is:-

(A = CH_3CH_2CN; B = $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$)

(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2-\overset{O}{\overset{\|}{C}}-NHBr$

(c) $CH_3CH_2COONH_2$ (d) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}N-Br_2$

Q. Amino group is ortho, para-directing for electrophilic substitution on nitration of aniline good amount of m-aniline is added. This is due to:-

→ NH_2 becomes NH_3^+ - which is meta-directing

Q. Which of the following exist as zwitter ion?

(a) p-aminophenol (b) salicylic acid.

(c) sulphanilic acid (d) Ethanol amine.

Q. How many 1° isomers are possible with the formula $C_4H_{11}N$?

(a) 1 (b) 2 (c) 3 (d) 4

Q. Which of the following gives a yellow oily liquid with nitrous acid?

(a) Methylamine (b) Aniline (c) Dimethylamine (2°) (d) Tri-methyl amine

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