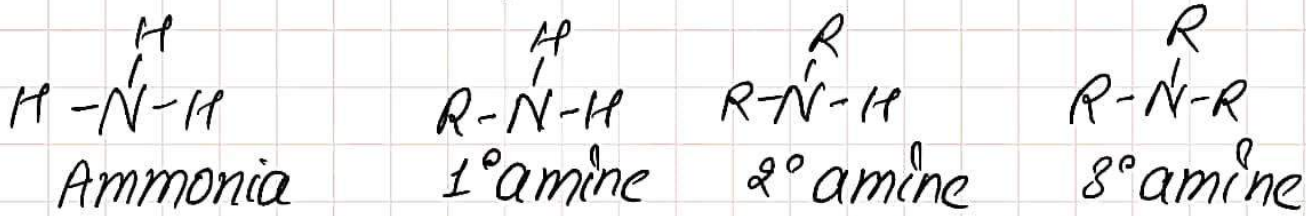
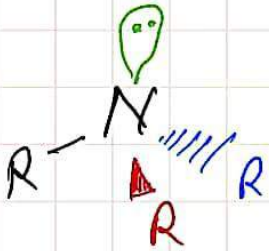
Amines

These are alkyl or aryl derivatives of Ammonia



Structure of Amines



Structure - trigonal pyramidal

3 Bond Pair + 1 Lone Pair

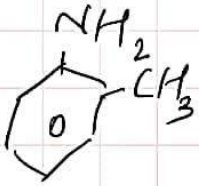
Hybrid. → sp^3

. Nomenclature ⇒

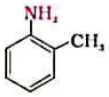
$CH_3-CH_2-CH_2-NH_2$ Propan-1-amine

$CH_3-NH-CH_2-CH_3$ N-Methyl ethanamine


Aniline

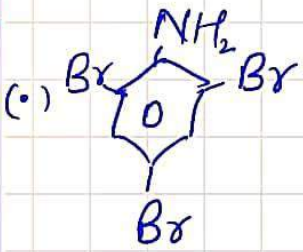

2-Amino toluene

NCERT Ques.

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3-CH(NH_2)-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-N(H)-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-N(CH_3)-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-N(C_2H_5)-CH_2-CH_2-CH_2-CH_3$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-CH_2-CH=CH_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Methylaniline
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N,N*-Dimethylaniline	N,N-Dimethylbenzenamine

P.Y.Q

(D-2016)

(•) 

2,4,6 - Tribromo aniline

(•) $CH_3-N(CH_3)-CH_2-CH_3$ (A.I-2013)

N,N- Dimethyl ethanamine

(•) $CH_2=CH-CH(CH_3)-NH_2$ (D-2012)

But-3-en-2-amine.

• Preparation of Amines :-

- Reduction of Nitro Compounds -

$$R-NO_2 \xrightarrow[\text{or } H_2/Pd]{Sn/HCl \text{ or } Fe/HCl} R-NH_2$$

Nitrobenzene

$\xrightarrow[Fe/HCl]{Sn/HCl \text{ or}}$

Aniline

- Reduction of Amides →

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{or } C_2H_5-OH/Na]{LiAlH_4/\text{ether}} R-CH_2-NH_2$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} C_2H_5-CH_2-NH_2$$

- **Hoffmann Bromamide Degradation**

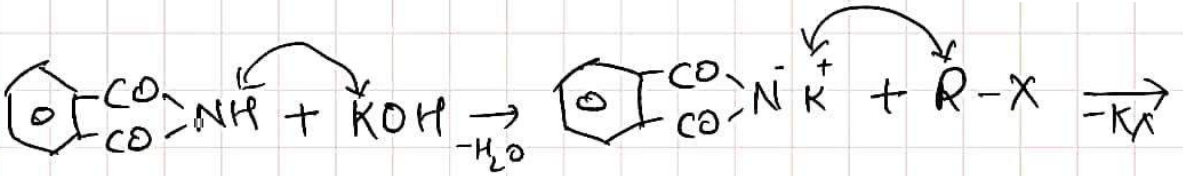
Trick - Baby को Base पसंद है।

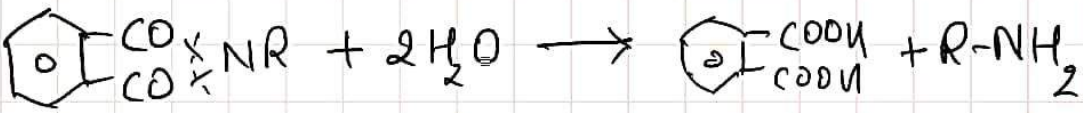
$$R-CO-NH_2 + Br_2 + 4KOH \xrightarrow[-2KBr \; -K_2CO_3 \; -2H_2O]{\Delta} R-NH_2$$

$$\underset{\text{Propanamide}}{C_2H_5-CO-NH_2} + Br_2 + 4KOH \xrightarrow[-2KBr, \; -2H_2O \; -K_2CO_3]{\Delta} \underset{\text{Ethanamide}}{C_2H_5-NH_2}$$

- **Gabriel phthalimide synthesis :-**

Trick - गाड़ी Basement में R-X को H_2O पीला।





P.T.R

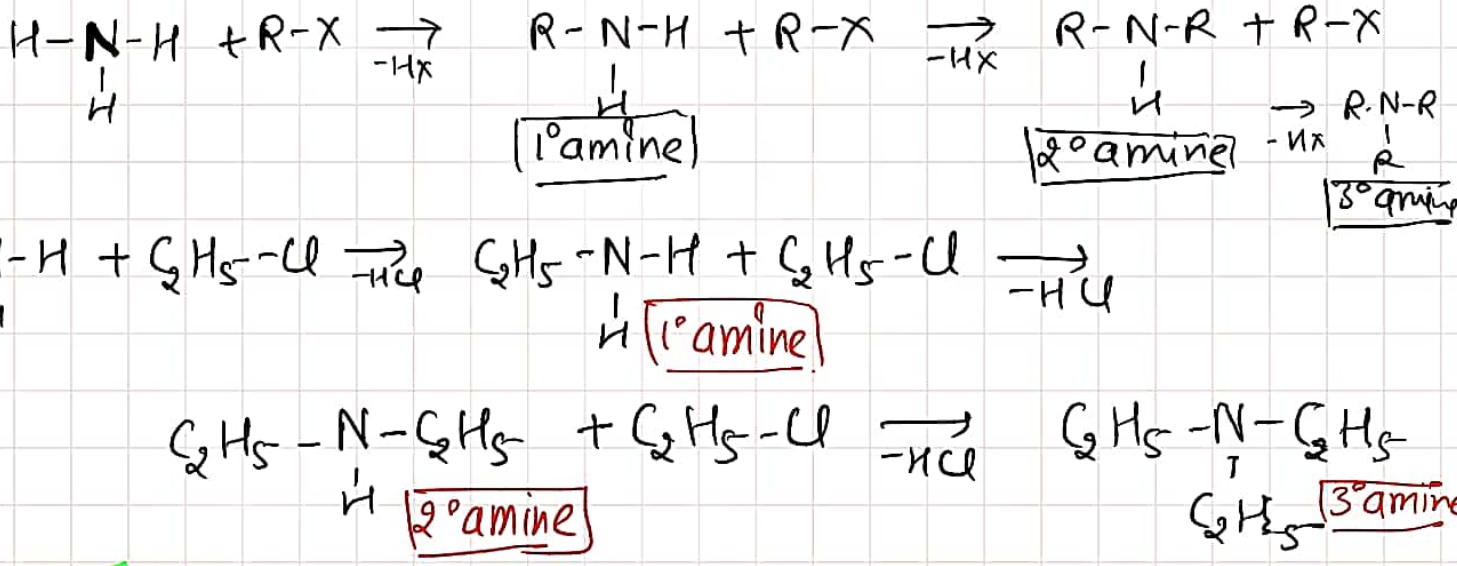
Aromatic 1° amines can't be prepared by this method because aryl halides do not undergo nucleophilic sub. with the anion formed by phthalimide.

- **Reduction of Nitriles :-**

$$R-C\equiv N + 4[H] \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

$$C_2H_5-C\equiv N + 4[H] \xrightarrow{LiAlH_4} C_2H_5-CH_2-NH_2$$

• Hoffmann Ammonolysis of Alkyl Halide



→ Physical Properties of Amines :-

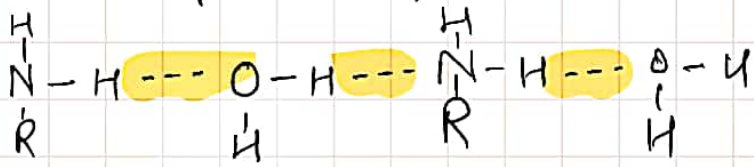
- Physical State :-

Lower amines are gases and liquids but higher amines are solids. The lower aliphatic amines are gases with fishy odour.

Arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

- Solubility :-

Lower aliphatic amines are soluble in water because they can form H-Bond with water



Primary and secondary amines are soluble in water due to H-bonding while 3° amines are insoluble in water.

- The Solubility decrease with increase in size of hydrophobic alkyl part.

P.T.R The solubility of amines is less than that of alcohol of comparable molecular mass because alcohols are more polar than amines and form stronger H-Bond.

- **Boiling Point ⇒**

The order of b.pt isomeric amines

1° amines > 2° amines > 3° amines

✓ 3° amines do not have intermolecular H-Boding because no H- is attached to N-atom.

✓ 1° amines have maximum amount of H-Bonding because two H-atoms are attached to N-atom.

Basic Character of Amines

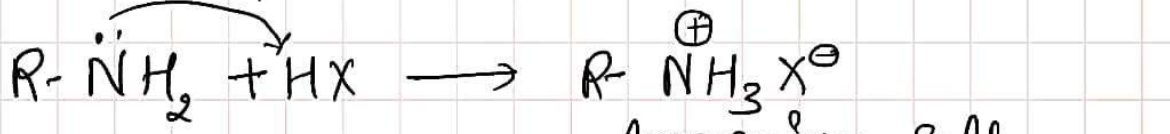
→ Amines are basic in nature due to the presence of lone pair of $e^{\ominus}$ on nitrogen atom.

→ Aliphatic amines are stronger bases than ammonia due to +I effect of Alkyl group.

→ Aromatic amines are weaker bases than ammonia due to -I effect or Aryl group.

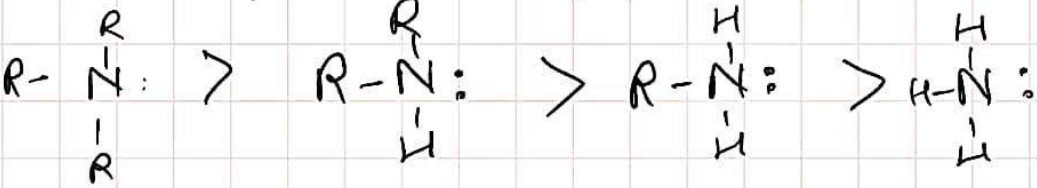
→ Besides inductive effect, effects like steric effect, solvation effect, resonance effect also affect the basic strength of amines.

Amines are basic in nature and reats with acids to form salts.



→ Order of basic character of amines in gaseous phase (Acc. to +I effect)

3° amines > 2° amines > 1° amines > NH_3



However in aqueous phase :-

There is subtle interplay of Inductive effect, steric effect and Solvation effect

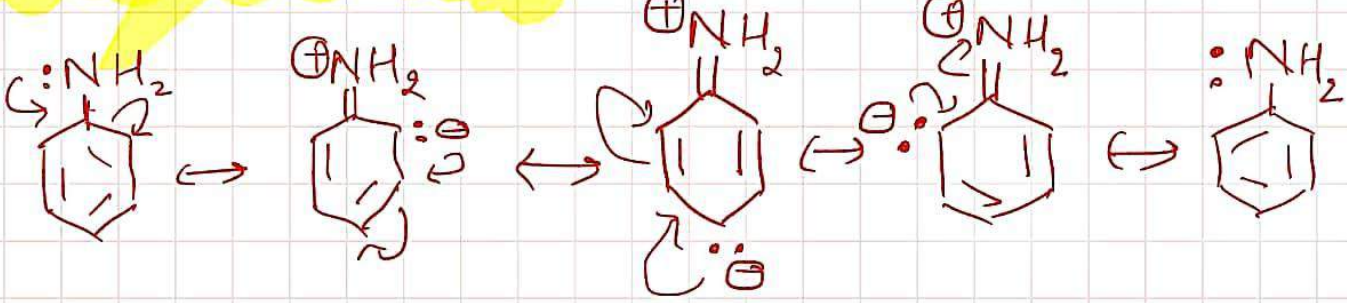
$(CH_3CH_2)-NH > (CH_3CH_2)_3N > CH_3CH_2NH_2 > NH_3$

2° 3° 1°

$(CH_3)_2NH > CH_3-NH_2 > (CH_3)_3N > NH_3$

2° 1° 3°

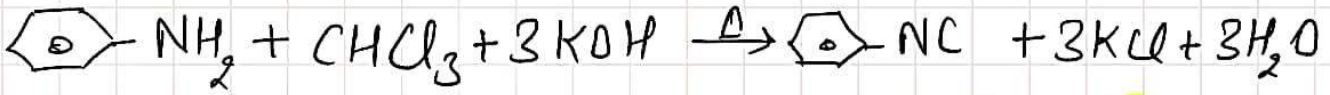
Resonance in Aniline



- **Carbylamine Reaction**

$$R\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{-}N{\equiv}C + 3KCl + 3H_2O$$

$$C_2H_5\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_2H_5\text{-}NC + 3KCl + 3H_2O$$



- **Reaction with Grignard Reagent ⇒**

$$R\text{-}NH_2 + CH_3\text{-}MgI \longrightarrow CH_4 + R\text{-}NH\text{-}MgI$$

$$\begin{matrix} R \\ R \end{matrix}\!\!>NH + CH_3\text{-}MgI \longrightarrow CH_4 + R_2\text{-}N\text{-}MgI$$

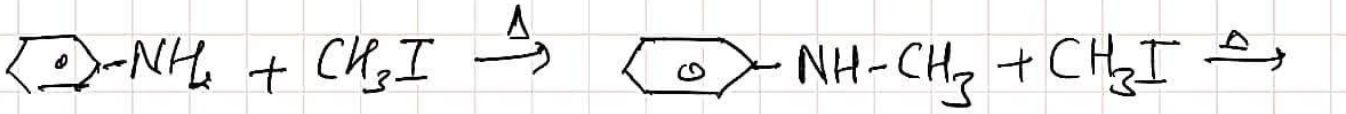
P.T.R Tertiary amines do not react with Grignard reagents as they do not contain active H-atoms.

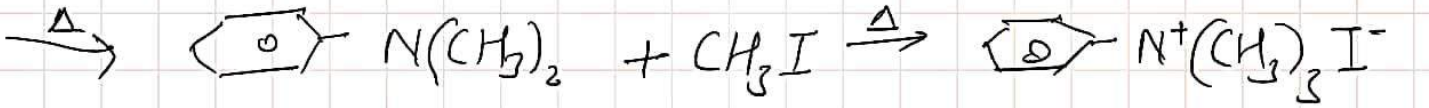
ALKYLATION

⇒ $C_2H_5\text{-}NH_2 + C_2H_5\text{-}Br \xrightarrow[-HBr]{} (C_2H_5)_2\text{-}NH$

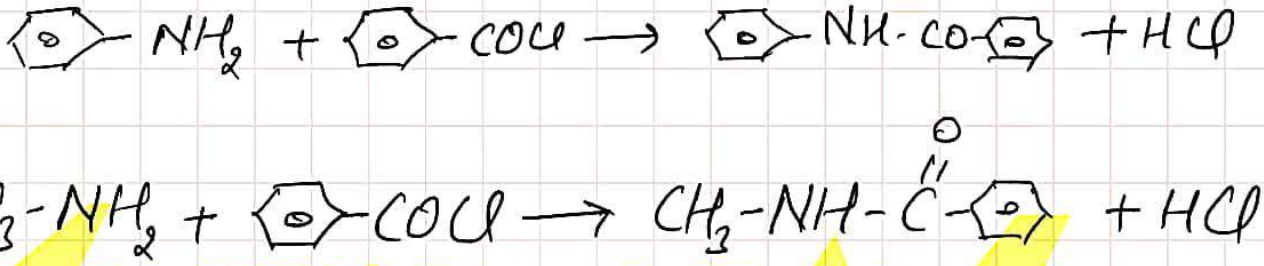
$+ \; C_2H_5\text{-}Br \xrightarrow[-HBr]{} (C_2H_5)_3N + C_2H_5\text{-}Br$

$\xrightarrow[-HBr]{} (C_2H_5)_4N^+Br^-$ Tetraethyl ammonium bromide

⇒ 

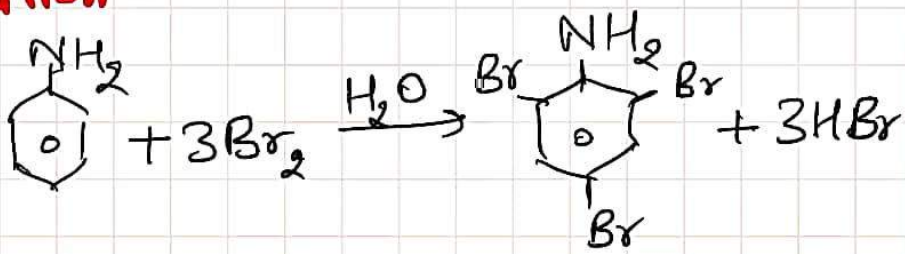


· Acylation

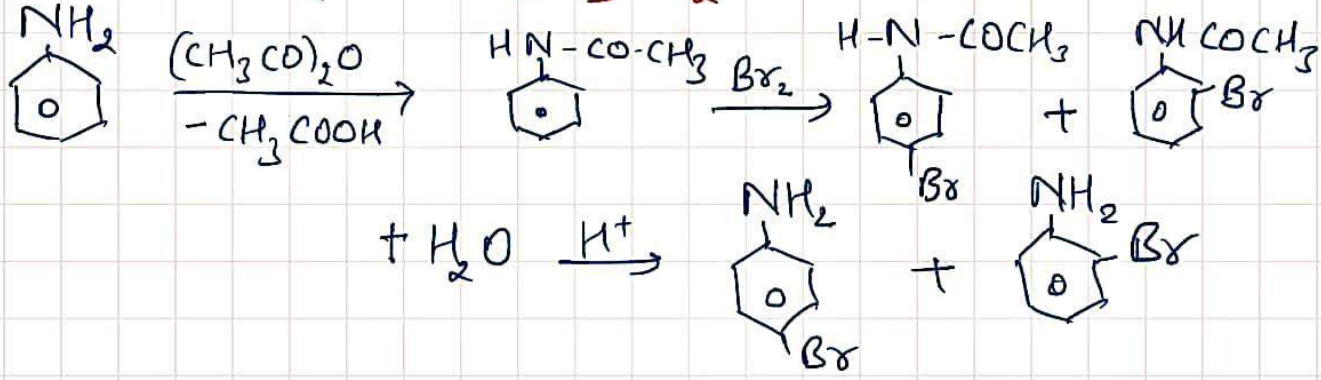


- Electrophilic Substitution Reaction :-

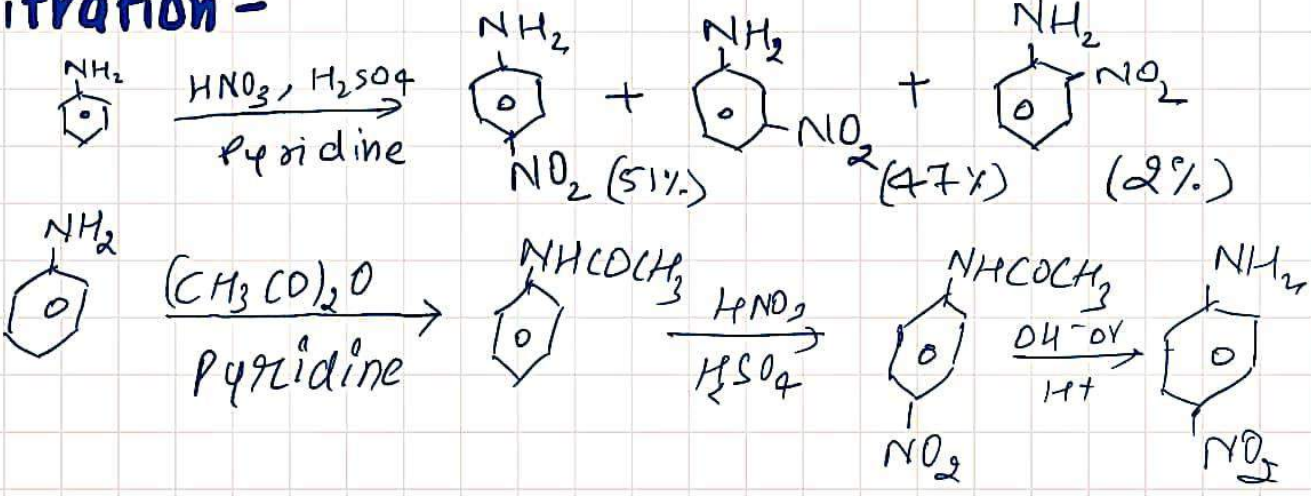
(i) Bromination -



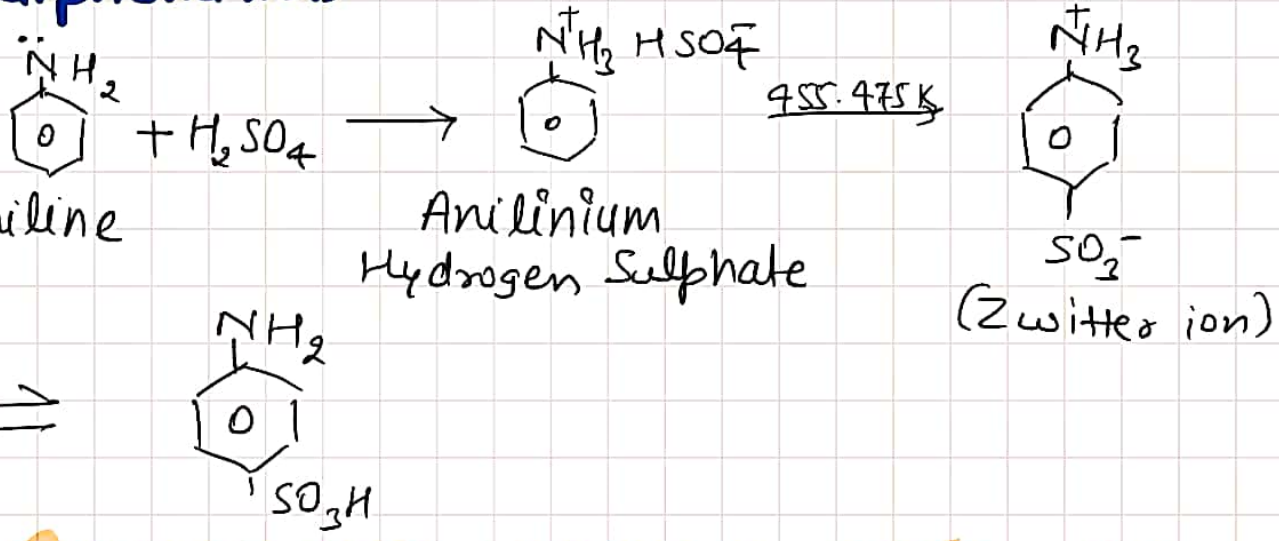
P.T.R For monobromination, treat aniline with acetic anhydride $(CH_3CO)_2O$



(ii) Nitration -



Sulphonation



Hinsberg Test (benzene sulphonyl Chloride $C_6H_5SO_2Cl$ (Hinsberg Reagent))

1° Amines

$$C_6H_5SO_2Cl + H_2N\text{-}R \rightarrow C_6H_5SO_2\text{-}NH\text{-}R$$ (Soluble in alkali)

1° amine

2° Amines

$$C_6H_5SO_2Cl + HN\text{-}R_2 \rightarrow C_6H_5SO_2\text{-}NR_2$$ (insoble in alkali)

2° amine

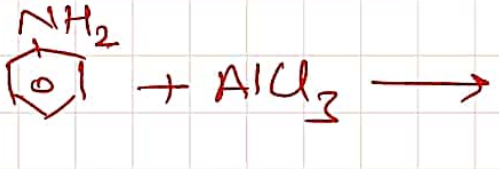
3° Amines

$$C_6H_5SO_2Cl + N\text{-}R_3 \rightarrow$$ No Reaction

3° Amine

P.T.R Friedal craft Rxn are not possible for 

because it form salt with anhy. $AlCl_3$ that is used as catalyst in the reaction.

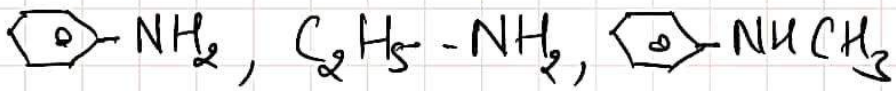


(due to +ve charge it act as strong deactivating group)

Basic Character $\propto K_b$

Basic Character $\propto \frac{1}{pK_b}$

- Arrange the following in the increasing order of p^{K_b} values: (C.B.S.E -2018)



Solution :- $C_2H_5-NH_2 <$  $<$ 

(•) Give reasons : $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution (C.B.S.E -2018)

Ans: $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution due to less steric hindrance.