

# AMINES

Class XII BOARD EXAM

↳ Target 100  
↳ Verified by Top  
Faculties & CBSE  
Science Board  
Topper

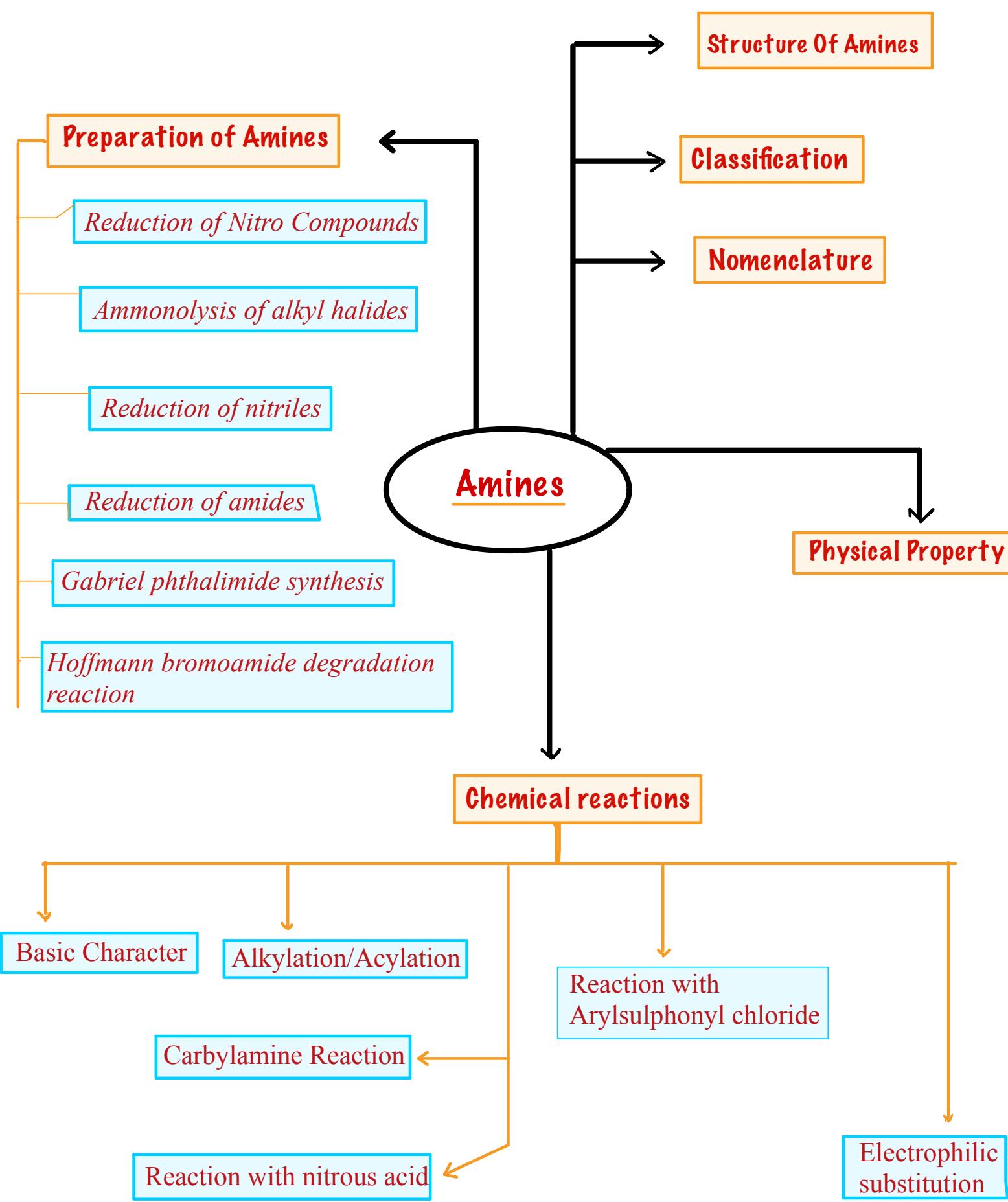
↳ As per  
marking scheme

↳ All PYQ's  
Integrated

Apni Kaksha

Aman Thattarwal

# Flow chart

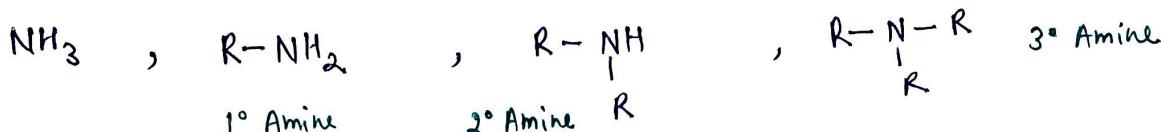


**Amines** (-NH<sub>2</sub> group)

Prefix: Amino

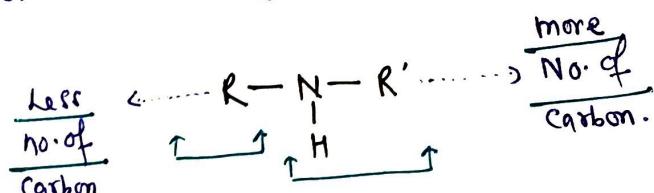
Suffix: Amine

→ Amines can be considered as derivatives of ammonia.



IUPAC Name :- Alkane - e + amine = Alkanamine (R-NH<sub>2</sub>)  
Alkane + diamine → for two amino group.

→ Common Name :- Alkylamine (R-NH<sub>2</sub>)



Example :- CH<sub>3</sub>-CH<sub>2</sub>-NH<sub>2</sub> [Ethanamine]  $\xrightarrow{\text{IUPAC}}$   
[Ethylamine]  $\xrightarrow{\text{Common name}}$

N-Alkylalkanamine

→  $\begin{matrix} ^3\text{CH}_3 & ^2\text{CH}_2 & ^1\text{CH}_2 & -\text{NH}_2 \end{matrix}$  : n-Propylamine [Propan-1-amine]

(Ethylmethylamine)

→  $\begin{matrix} ^3\text{CH}_3 & ^2\text{CH} & ^1\text{CH}_2 \\ | & & | \\ \text{NH}_2 & & \text{CH}_3 \end{matrix}$  : Isopropylamine [Propan-2-amine]

$\rightarrow \begin{matrix} \text{CH}_3 & -\text{NH}-\text{CH}_2-\text{CH}_3 \\ | & \\ \text{CH}_3 & \end{matrix}$   
N-Methylethanamine

→  $\begin{matrix} \text{CH}_3 & -\text{N}-\text{CH}_2-\text{CH}_3 \\ | & \\ \text{CH}_3 & \end{matrix}$  : N,N-dimethylethanamine. [Delhi 2017] {1M}

→  $\begin{matrix} \text{CH}_3 & & \\ & \diagdown & \diagup \\ & \text{N}^+ & \\ & \diagup & \diagdown \\ \text{CH}_3 & & \text{CH}_3 \end{matrix}$  : N-ethyl N-methylethanamine [Delhi 2017] {1M}

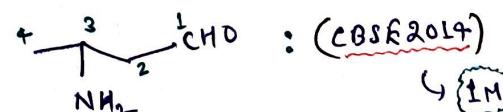
→  $\begin{matrix} \text{CH}_3 & & \\ & \diagdown & \diagup \\ & \text{C}=\text{C} & \\ & \diagup & \diagdown \\ & \text{NH}_2 & \end{matrix}$  : Prop-2-en-1-amine

[CBSF 2013] {2M}

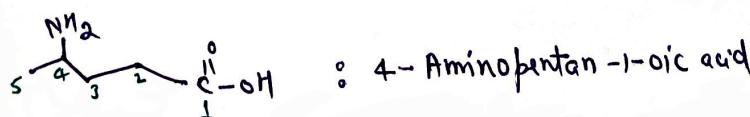
→ N-methylethanamine :  $\begin{matrix} ^2\text{CH}_3 & ^1\text{CH}_2 & -\text{NH}-\text{CH}_3 \end{matrix}$

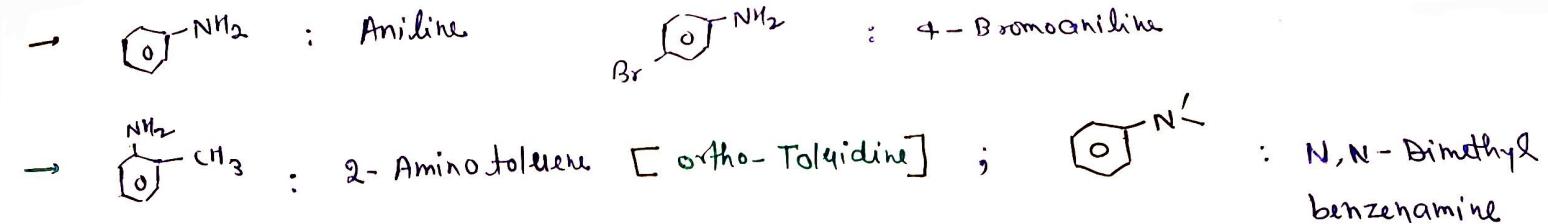
→ NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub> : But-3-en-1-amine : [Delhi 2010] {1M}

→ Senior functional group makes 2° suffix and junior functional groups are treated as substituent. For naming of junior functional group we use prefix of that group.



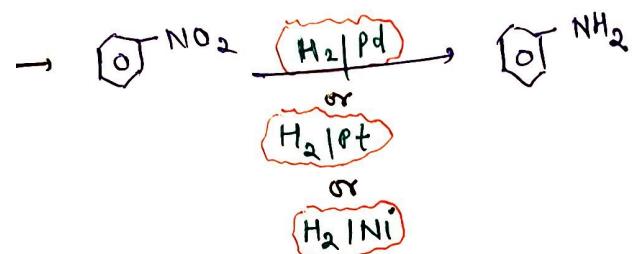
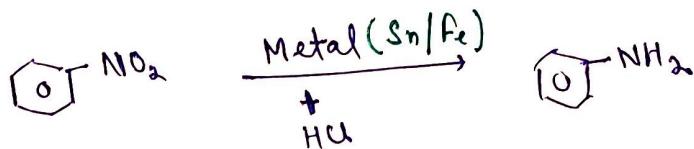
→ 3-Aminobutanal





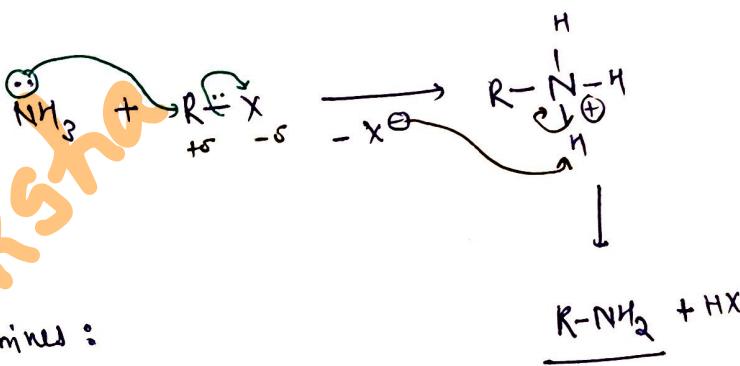
### Preparation of Amines

#### ① Reduction of nitro compounds :-

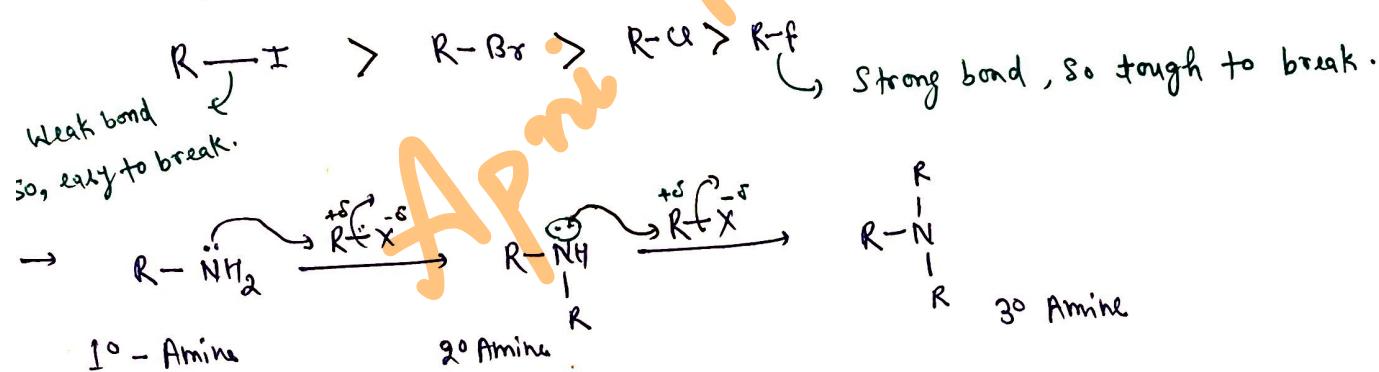


#### ② Ammonolysis of alkyl halides :-

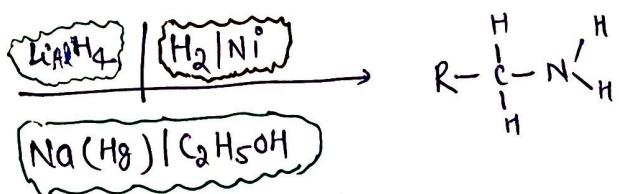
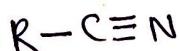
Breaking of bond by ammonia.



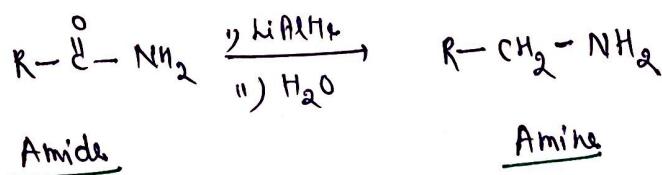
Order of reactivity of alkyl halide with amines :



#### ③ Reduction of nitriles :-

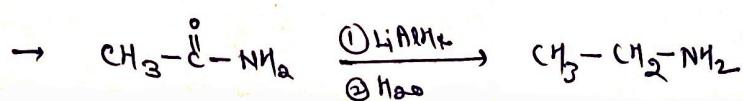
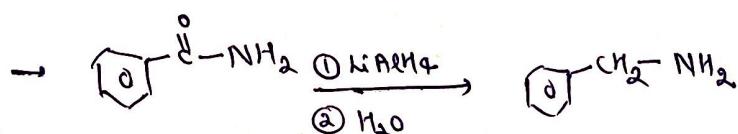


#### ④ Reduction of amides :-



[CBSE 2012/2010]

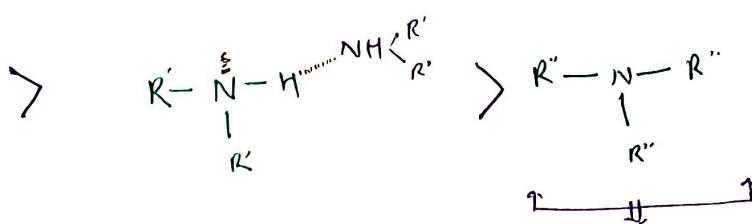
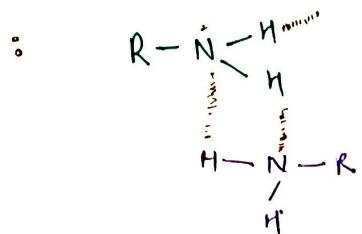
{1M}



[Delhi 2010 | CBSE 2010] {1M}

→ This intermolecular association is more in primary amines than in  $2^\circ$  amines as there are two hydrogen atoms available for hydrogen bond formation in it.

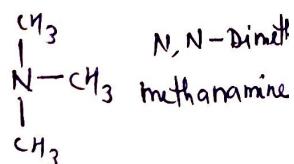
Extent of H-bonding in it :



No Hydrogen bond between itself.

→ Because  $3^\circ$  amines have no hydrogen bond between itself. So, primary amines have higher B.P. [CBSE 2011] 1M

For example → B.P. : Propanamine  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2 >$   
1M ← [CBSE 2019]



### Basicity of amines

→  $R-\ddot{\text{N}}\text{H}_2 + \text{H}\ddot{\text{E}}_x^- \rightleftharpoons R-\overset{\oplus}{\text{N}}\text{H}_3^+$  (Salt) ; Basic Nature of amine is due to its lone pair which attracts  $\text{H}^+$  towards itself.

→ Basicity is represented by  $K_b$ .

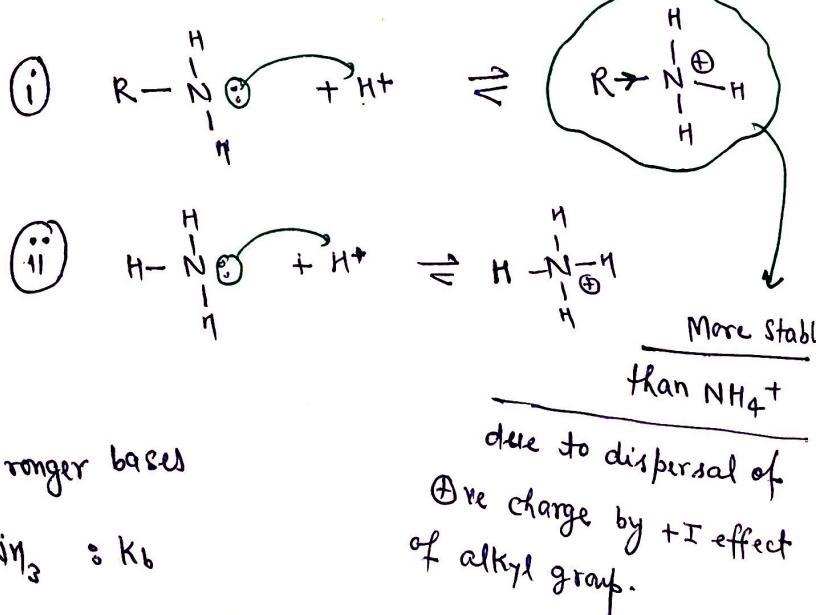
→  $pK_b = -\log K_b$  then  $K_b \propto \frac{1}{pK_b}$

→ Alkanamines Vs. Ammonia :-

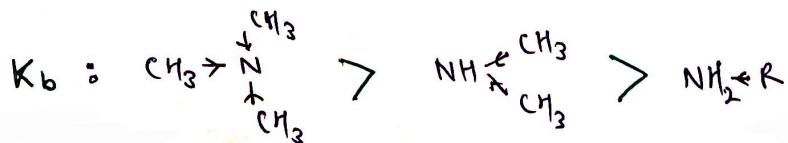
Due to stability of  $R-\overset{\oplus}{\text{N}}\text{H}_3^+$  with respect to  $\text{NH}_4^+$ , equilibrium constant for reaction

(i) is more than reaction (ii).

→ Means that, Aliphatic amines are stronger bases than ammonia.  $\text{CH}_3-\ddot{\text{N}}\text{H}_2 > \ddot{\text{N}}\text{H}_3^+ : K_b$

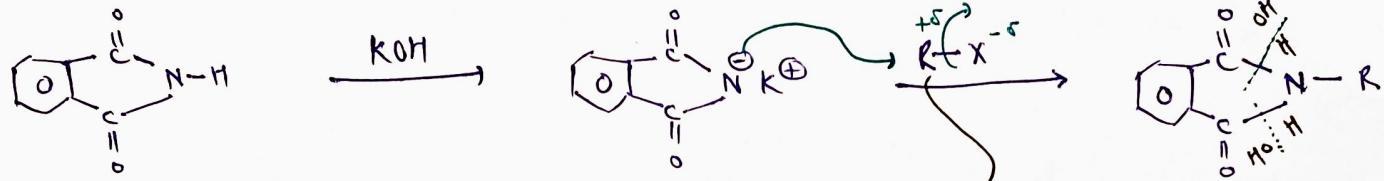


→ Order of basicity in gas phase : Explain it by  $+I$  effect, as there is no solvent.



5. Gabriel Phthalimide Synthesis :- (for preparation of 1° Amines)

Delhi  
2010



Phthalimide

$\rightarrow$  (CBSE 2019)  $\rightarrow$  [1M]

(Delhi 2012)  $\downarrow$  [2012 CBSE]

only aliphatic alkyl groups

because in aromatic (as phenyl)  
group has double bond character  
in bond with halogens.

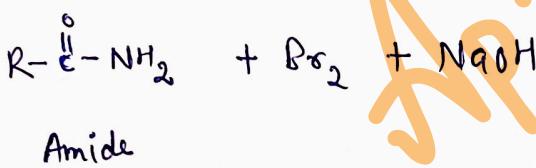
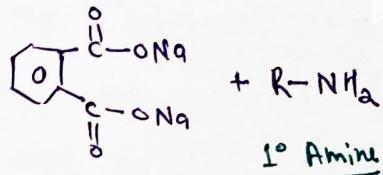
Basic  
Hydrolysis  $[NaOH(aq.)]$

6. Hoffmann bromamide degradation reaction :-

Bromine  
( $Br_2$ )

$R-\overset{\overset{\bullet}{O}}{C}-NH_2$

Reduction of no. of carbon



Amide

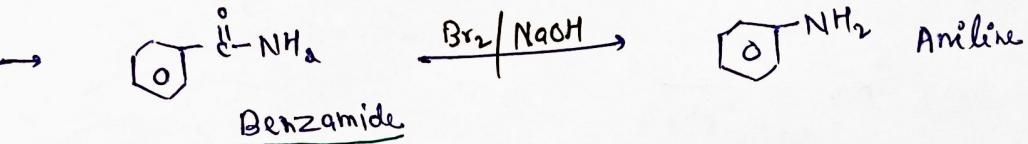
$R-NH_2$

Amine



Butanamide

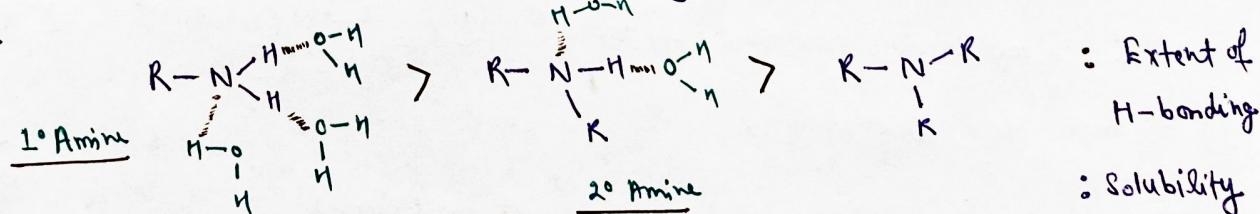
Propanamine



Benzamide

Physical properties :-

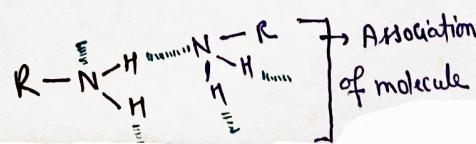
$\rightarrow$  Lower amines are soluble in water because they can form hydrogen bonding with water molecules.



$\rightarrow$  Aromatic amines (such as aniline) are insoluble in water due to large hydrocarbon part (non-interacting with water). [CBSE 2011] [1M]

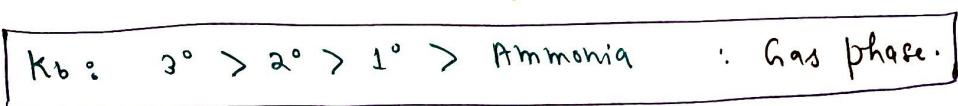
Boiling Point - : Order of B.P. :  $1^\circ$  Amine  $>$   $2^\circ$  Amine  $>$   $3^\circ$  Amine

$\rightarrow$  This is because of order of extent of H-bonding.

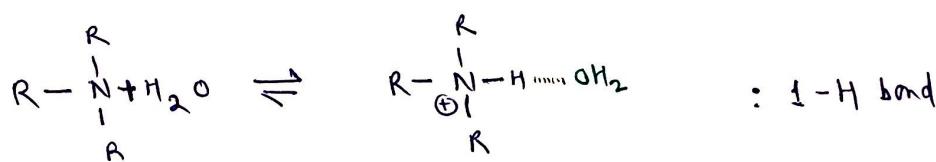
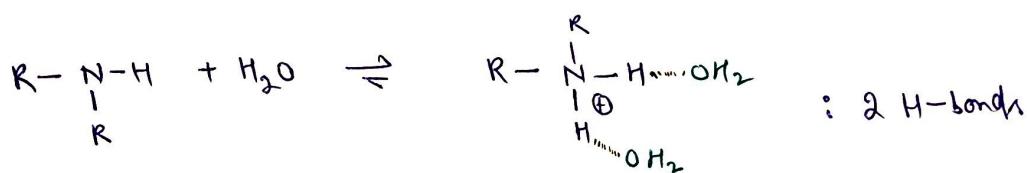
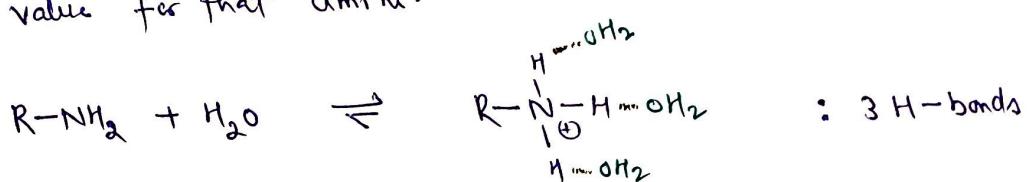




: [Delhi 2019] → 1M



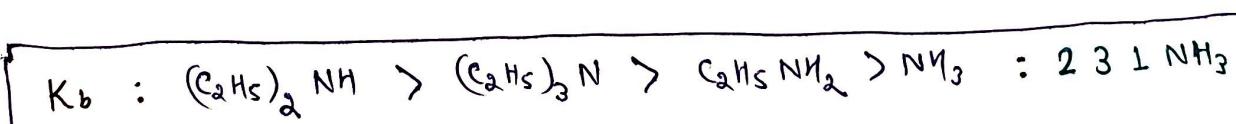
- Basicity of amines in g<sub>g</sub> phase :- Above order is not true in aqueous medium. The substituted ammonium cations get stabilised not only by electron releasing effect of alkyl group (+I) but also by solvation with water molecules.
- The ion having more hydrogen bonds with water molecule, are more stable. So more will be  $K_b$  value for that amine.



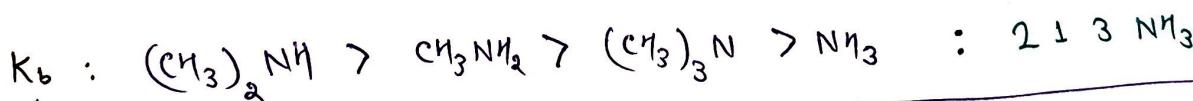
- More solvation  $\Rightarrow$  More stable ion

According to solvation effect  $K_b : 1^\circ > 2^\circ > 3^\circ$

#

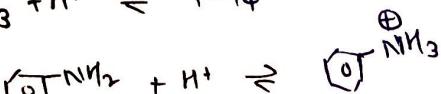
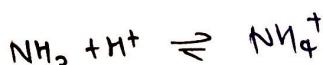
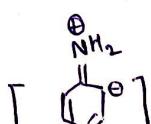


Basic  
Strength in  
aq. soln



[Delhi 2013]  
[2012] 1M

- Aryl amines vs. Ammonia :-



→ Lone pair of nitrogen on ammonia is available for protonation. But in aniline lone pair is not easily available due to resonance with benzene ring.

→ Basicity Order ( $k_b$ ) :  $\text{CH}_3\text{NH}_2 > \text{C}_6\text{H}_5\text{NH}_2$  [CBSE 2011] [1M]

$\rightarrow K_b :$

Localised lone pair, free for protonation.

Delocalised lone pair, so lone pair is not available for protonation.

: [CBSE 2014] 1 M

$K_b:$ 
  
 Lone pair is in resonance  
 So not available for protonation.

$\xrightarrow{\quad}$   $\text{NH}_2$   $>$   $\text{NH}_2$   $>$   $\text{NH}_2$   
 $\text{EDG}$   $\text{EWG}$   $\text{EWG}$   
 $\text{-CH}_3 \mid -\text{C}_2\text{H}_5 \mid -\text{OC}_2\text{H}_5$

→ Electron donating group increases electron density at nitrogen of anilin. So, it can easily donate lone pair to  $\text{H}^+$ .

$\xrightarrow{\quad}$  > Aniline >

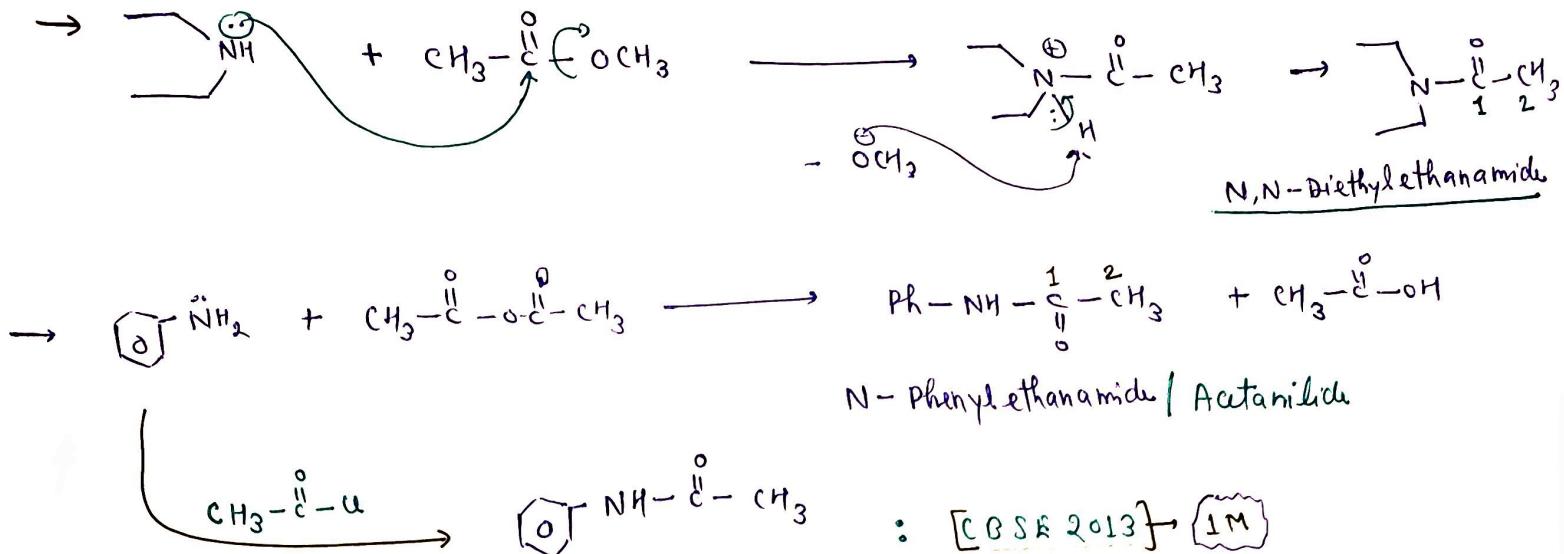
Acylation of amines :- (Addition of  $\text{C}^{\text{II}}\text{-R}$  group.)

$\rightarrow$   $1^{\circ}$  |  $2^{\circ}$  Amines       $\begin{array}{c|c} \text{CH}_3-\overset{\text{O}}{\underset{\text{C}-\text{H}_3}{\text{C}}} & \text{CH}_3-\overset{\text{O}}{\underset{\text{C}-\text{OR}}{\text{C}}} \\ \hline & \text{or } \text{CH}_3-\overset{\text{O}}{\underset{\text{C}-\text{OCOCH}_3}{\text{C}}} \end{array}$

## Acylation of product of $1^{\circ}$ / $2^{\circ}$ Amino

$$\xrightarrow{\quad} \text{CH}_3-\text{CH}_2-\ddot{\text{N}}\text{H}_2 + \text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{C}\text{---}\text{U} \xrightarrow[-\text{U}^\ominus]{} \text{CH}_3-\text{CH}_2-\overset{\text{H}}{\underset{\text{N}^\oplus}{\text{---}}} \text{---}\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{---}\text{CH}_3$$

→ Replacement of Hydrogen by  $\text{CH}_3\text{-C}^{\ddagger}$  : Acylation.

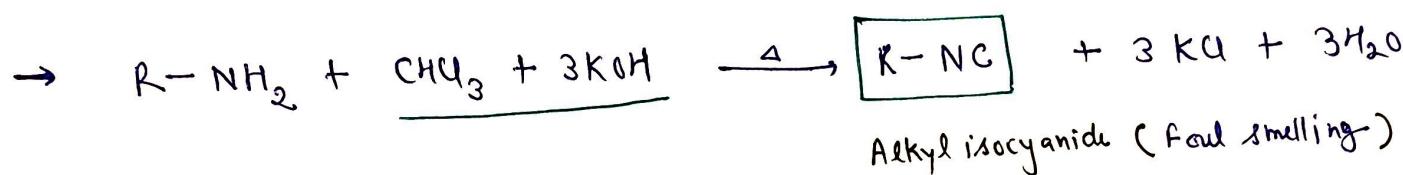


Carbylamine Reaction :- [ Test for  $1^\circ$  Amines : Presence of 2 Hydrogen at  $\text{C}=\text{N}$  ]

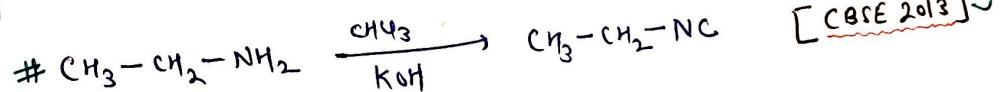
→ 2° / 3° Amines do not give this reaction.

necessary ]

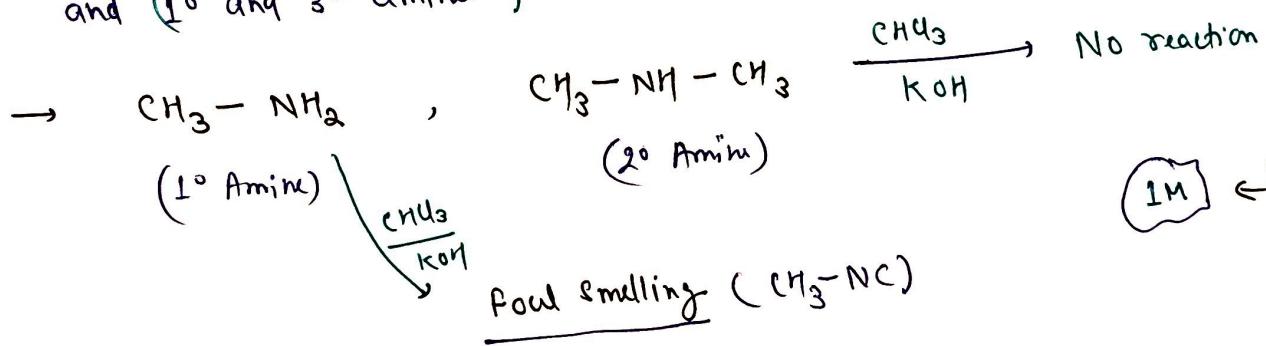
CBSE 2012  
Delhi 2012



→ This test is also called  
Isocyanide test.



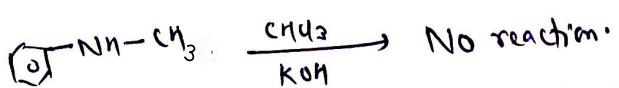
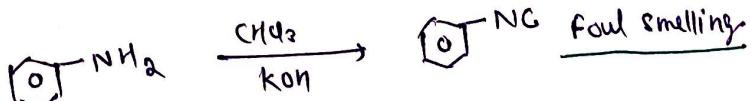
Isocyanide test.  
→ By using this reaction (test) we can distinguish ( $1^\circ$  and  $2^\circ$  amines) and ( $1^\circ$  and  $3^\circ$  amines).



→ similarly Ethylamine ( $\sim\text{NH}_2$ ) and Diethylamine ( $\sim\text{NH}\sim$ ) can be distinguished by carbylamine test.  $1^\circ$  Amine ( $\sim\text{NH}_2$ ) gives foul smelling with  $\text{CH}_3\text{I}$  and  $\text{KOH}$ .

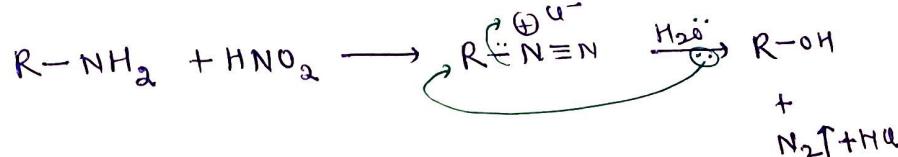
→ Aniline & N-methyl aniline :-

TCSSE-2010 ] 1M



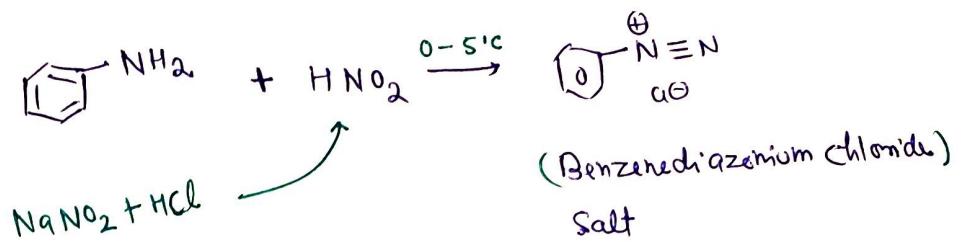
## Reaction with $\text{HNO}_2$ [ Nitrous Acid ] -:

① Primary aliphatic amines :-



→ Evolution of nitrogen.

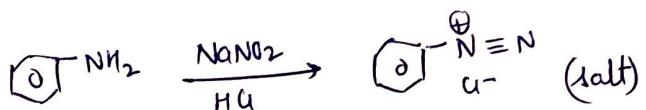
② Aromatic Amines :-



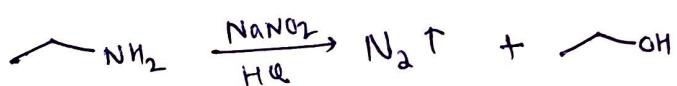
→ Aromatic and aliphatic amines can be distinguished by above reaction.

For example:-

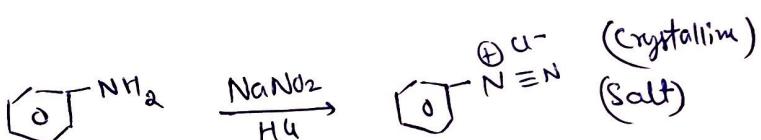
Aniline and Ethylamine



[CBSE 2014 C | 2019]  
[Delhi 2013 C]



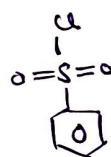
Aniline and Benzylamine



(CBSE 2014 C) → 1M

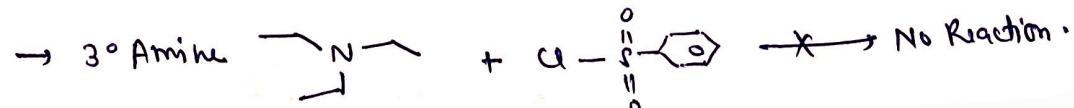
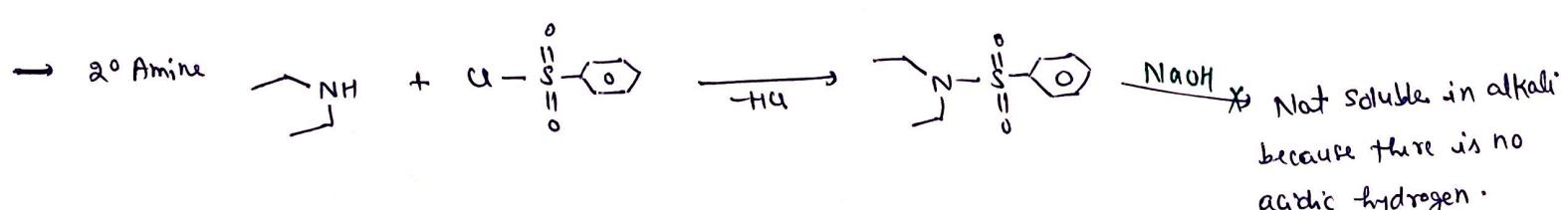
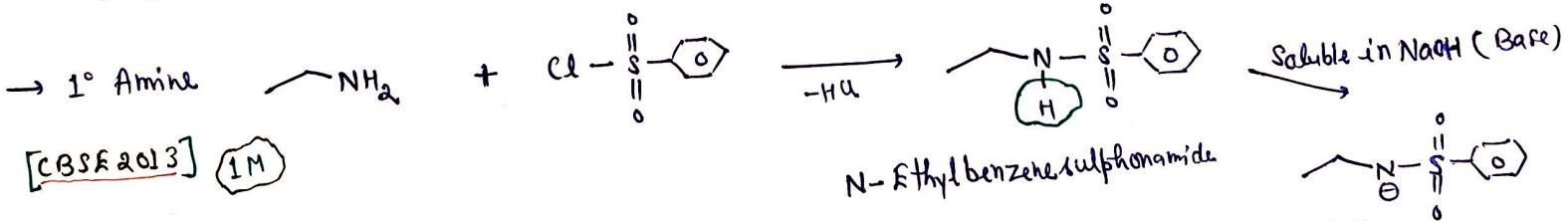
(1° Amine)      Benzylamine.

Hinsberg Reagent :-



Benzensulfonyl chloride.

→ Reaction with Hinsberg Reagent :-

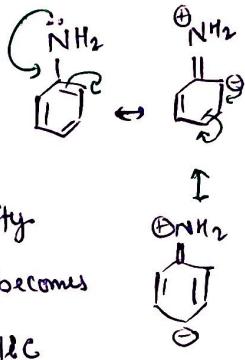


→ This reagent can be used to distinguish 1°/2°/3° Amines.

## Electrophilic Substitution Reaction :-

→ -NH<sub>2</sub> group is ortho-para directing, and powerful activating group.

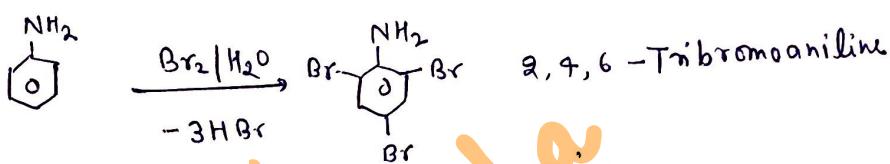
In resonating structure,  $\ominus$ ve charge is present at ortho and para position.



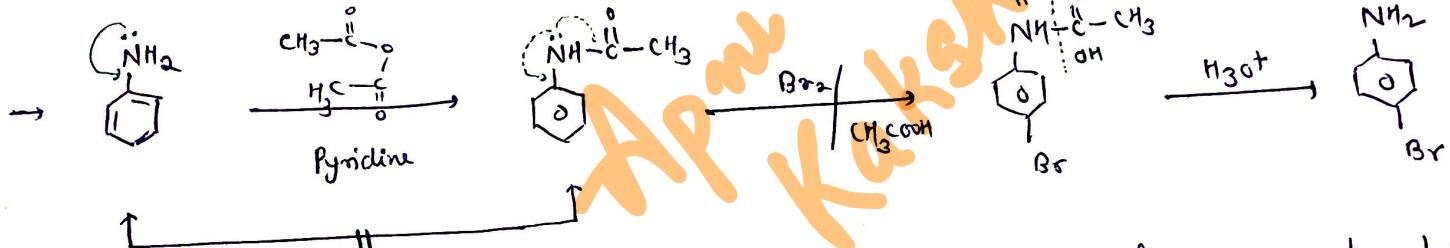
It donates electron density to benzene ring & ring becomes more active for electrophilic reaction.

→ That's why electrophilic substitution takes place more readily in aromatic amines than benzene. [Delhi 2010C] 1M

### i) Bromination :-

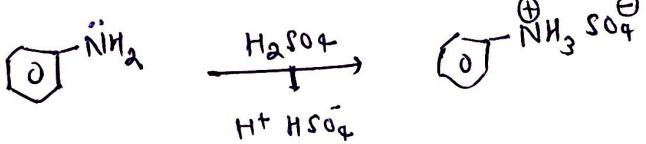


[2013] 1M



→ Activating effect of  $-NH-C(=O)-CH_3$  group is less than that of  $-NH_2$  group, because in  $\text{C}_6\text{H}_5-NH-C(=O)-CH_3 \leftrightarrow \text{C}_6\text{H}_5-\overset{\delta}{N}H-C(=O)-CH_3$  lone pair of nitrogen is shared also with  $-CH_3$  group. So it can not activate benzene ring as  $-NH_2$  group.

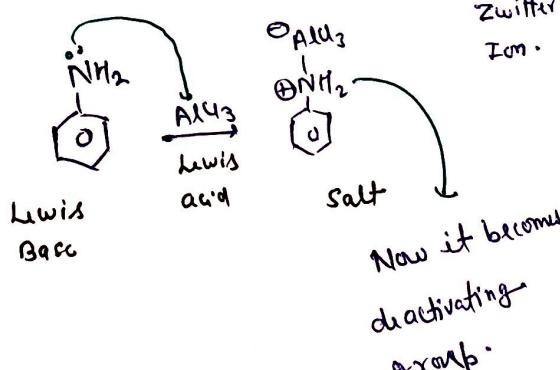
### ii) Sulphonation :-



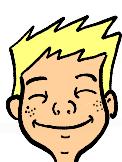
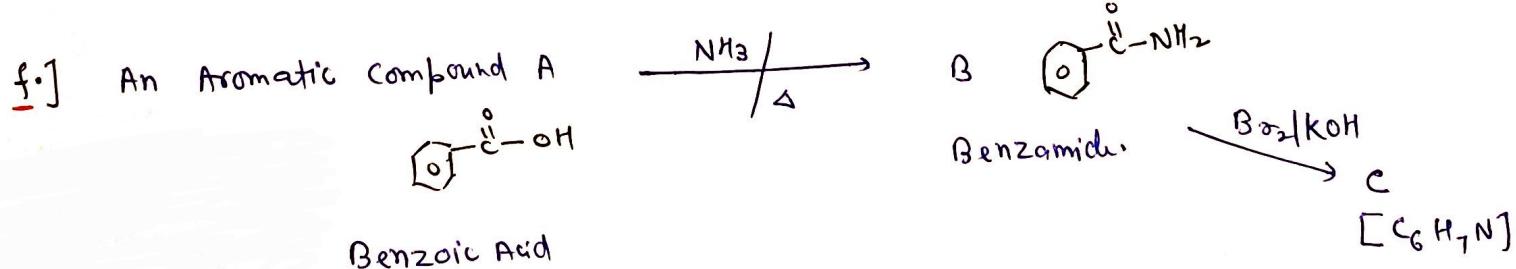
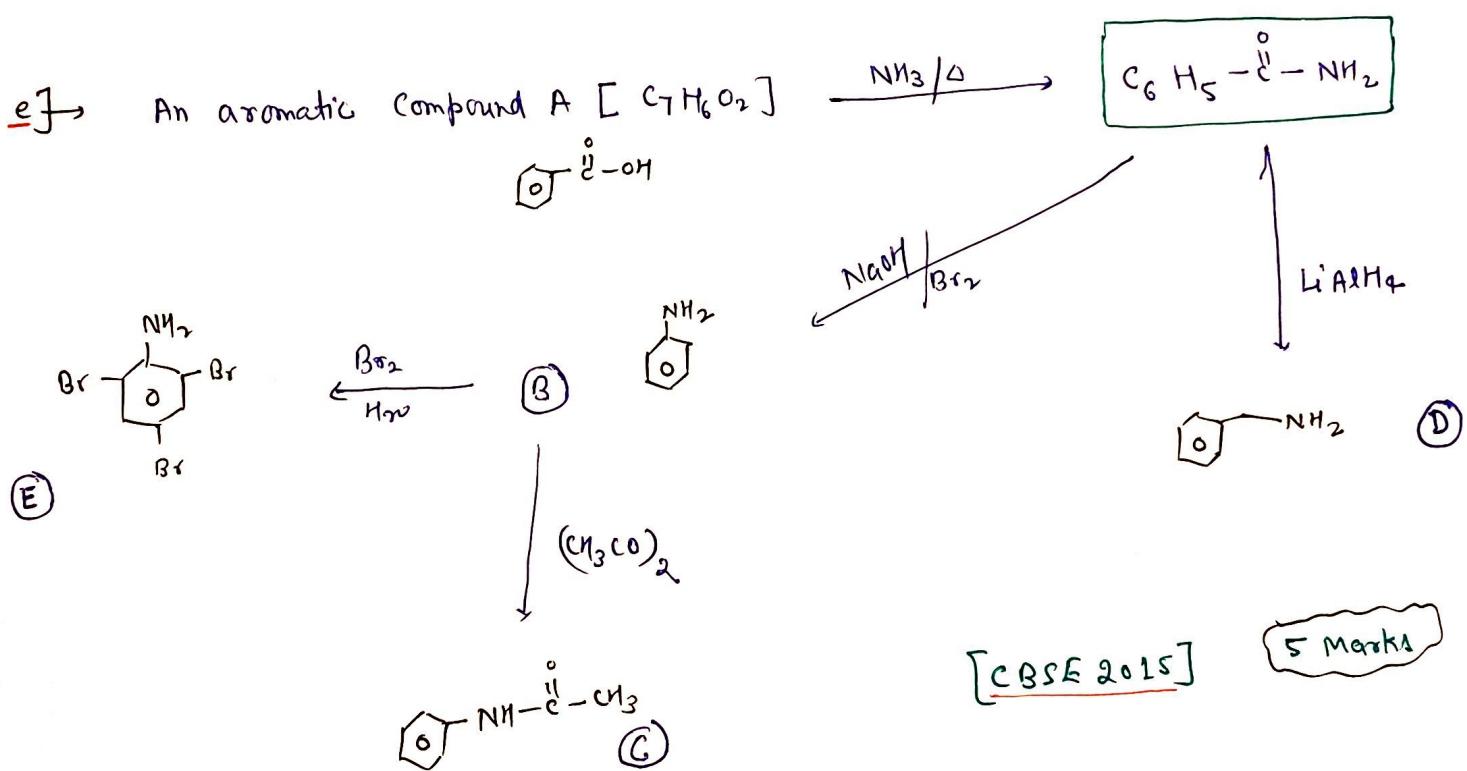
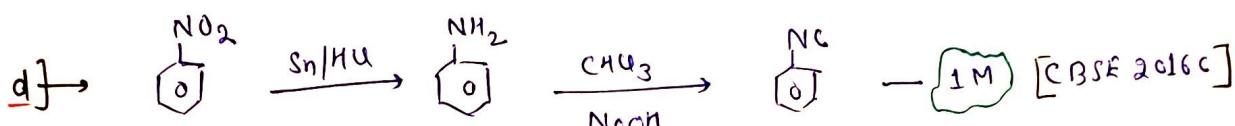
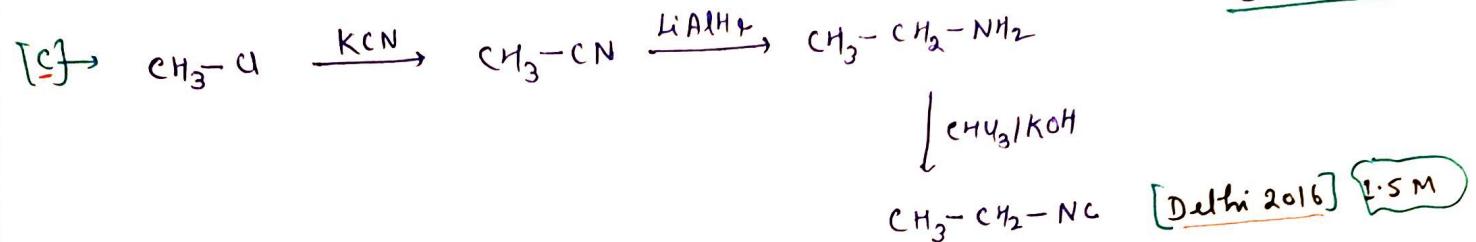
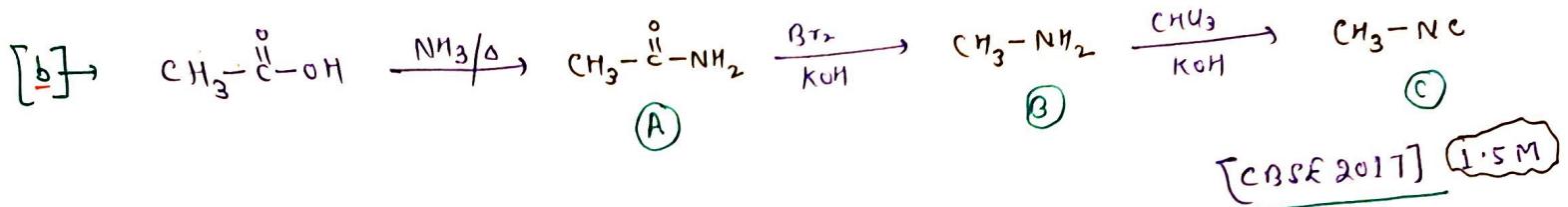
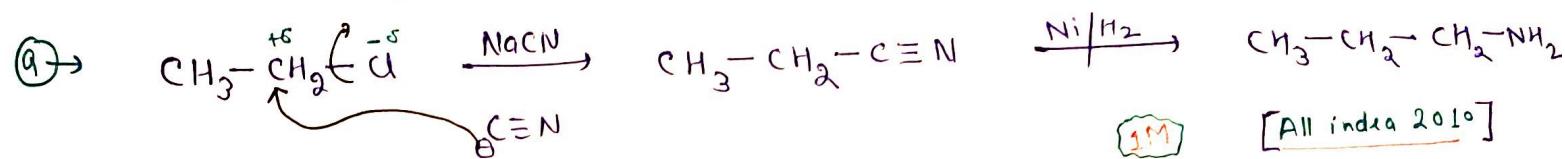
zwitter ion.

→ Aniline does not undergo Friedel-Crafts Reaction due to salt formation with Al<sub>2</sub>O<sub>3</sub>. Hence acts as a strong deactivating group for further reaction.

[Delhi 2014C] 1M



Complete the following reaction?



JAO AB  
PHODO!



## Amine