

AMINES

Class XII BOARD EXAM

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

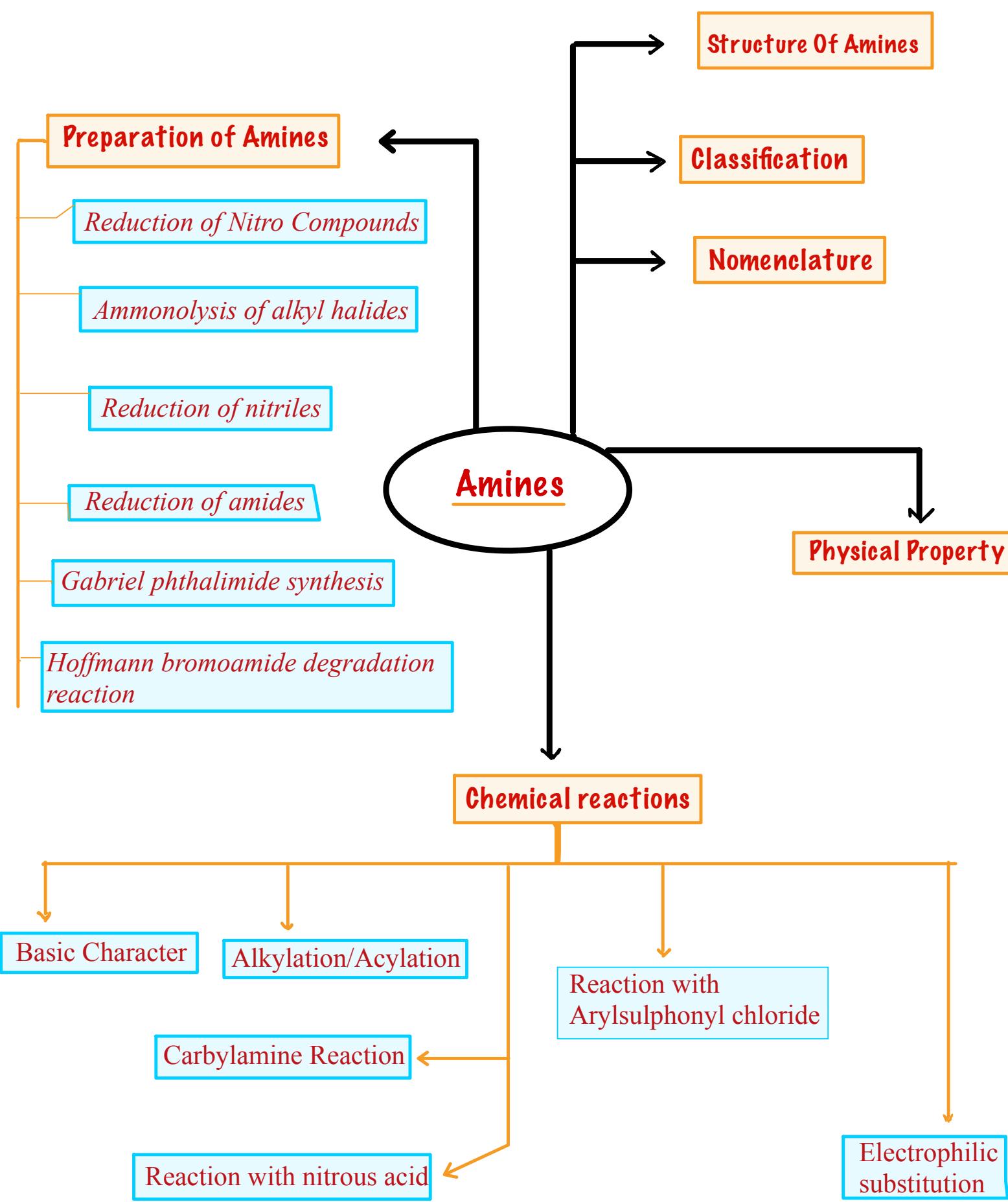
↳ As per
marking scheme

↳ All PYQ's
Integrated

Apni Kaksha

Aman Thattarwal

Flow chart

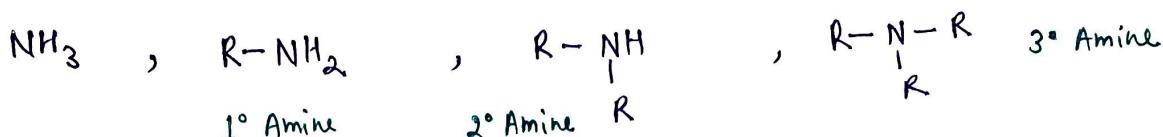


Amines (-NH₂ group)

Prefix: Amino

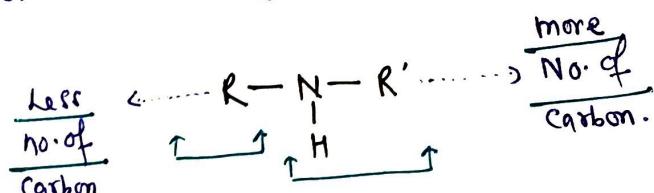
Suffix: Amine

→ Amines can be considered as derivatives of ammonia.



IUPAC Name :— Alkane - e + amine = Alkanamine ($\text{R}-\text{NH}_2$)
Alkane + diamine → for two amino group.

→ Common Name :— Alkylamine ($\text{R}-\text{NH}_2$)



Example :— $\text{CH}_3-\text{CH}_2-\text{NH}_2$ [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

→ $\begin{matrix} \text{CH}_3 & -\text{N} & -\text{CH}_2 & -\text{CH}_3 \\ | & & & | \\ \text{CH}_3 & & \text{CH}_2 & -\text{CH}_3 \end{matrix}$: 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}

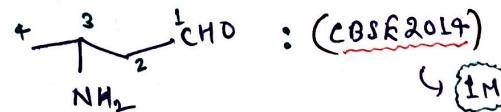
→ $\begin{matrix} \text{CH}_3 & & & \\ & \diagdown & \diagup & \\ & \text{C}=\text{C} & & \\ & | & & \\ & \text{NH}_2 & & \end{matrix}$: Prop-2-en-1-amine

[CBSF 2013] {2M}

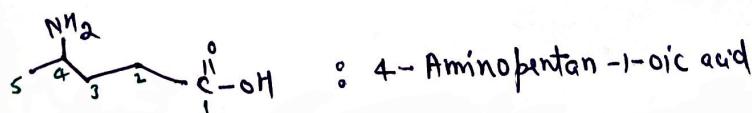
→ N-methylethanamine : $\begin{matrix} ^2\text{CH}_3 & ^1\text{CH}_2 & -\text{NH}-\text{CH}_3 \end{matrix}$

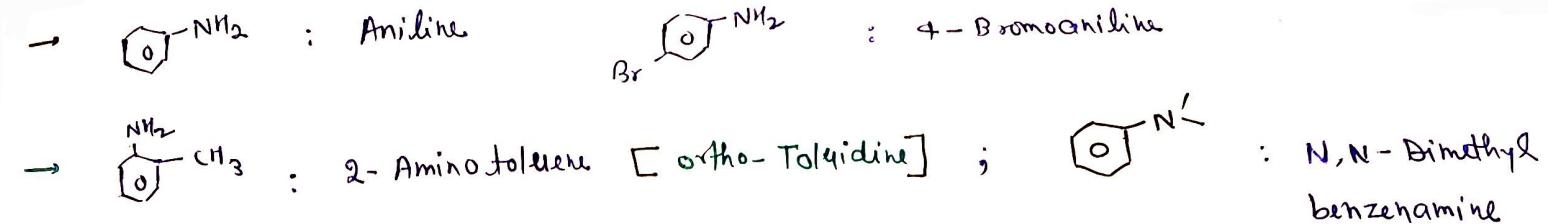
→ $\text{NH}_2-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}_2}-\overset{3}{\text{CH}}=\overset{4}{\text{CH}_2}$: But-3-en-1-amine : [Delhi 2010] {1M}

→ 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.



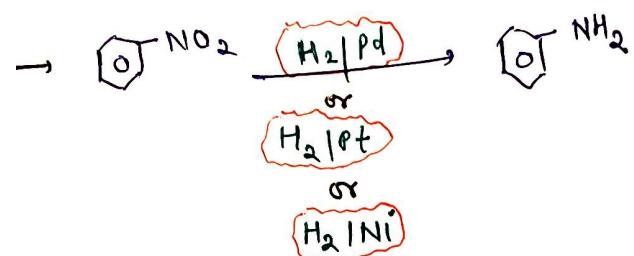
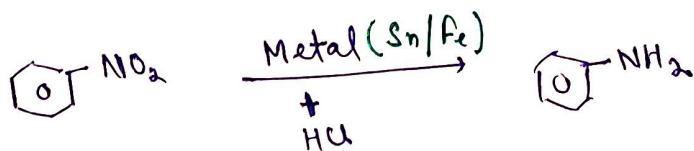
→ 3-Aminobutanal





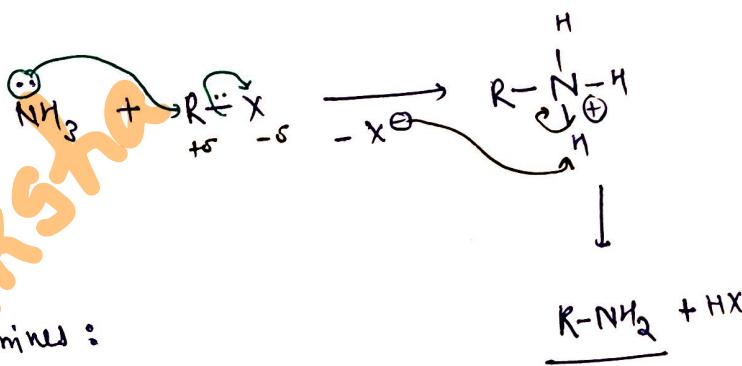
Preparation of Amines

① Reduction of nitro compounds :-

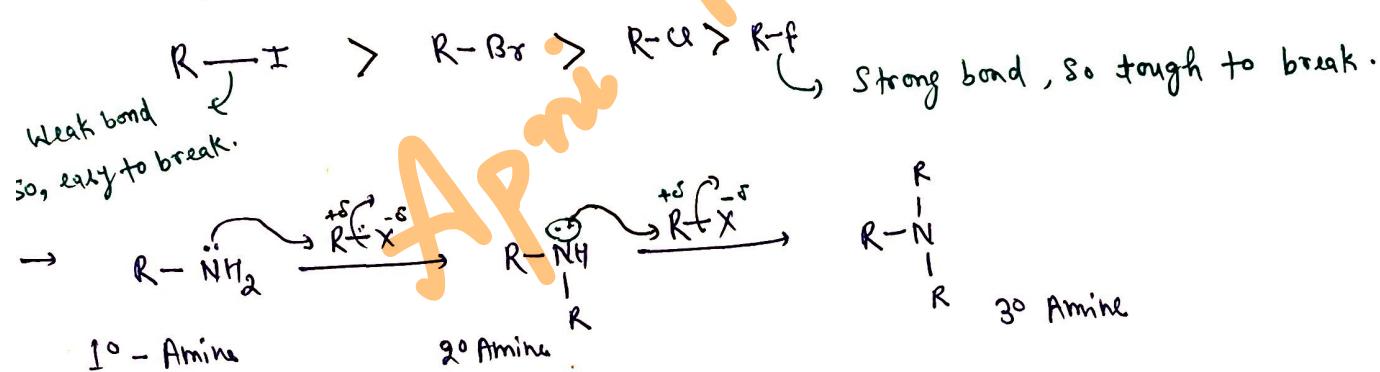


② Ammonolysis of alkyl halides :-

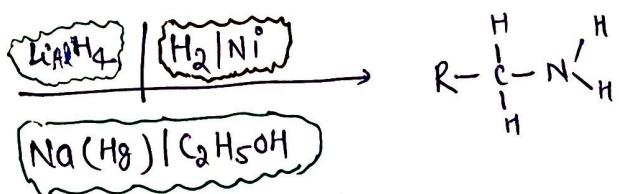
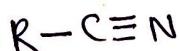
Breaking of bond by ammonia.



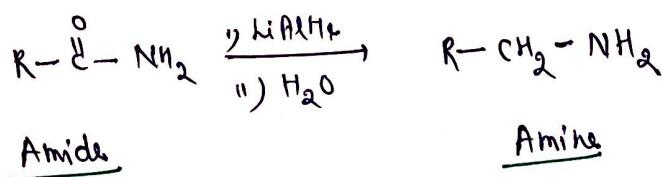
Order of reactivity of alkyl halide with amines :



③ Reduction of nitriles :-

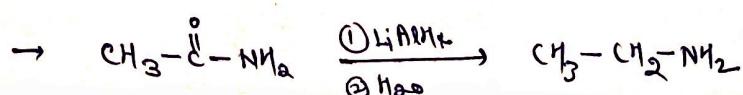
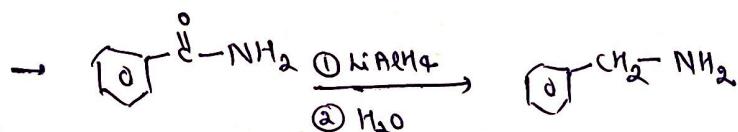


④ Reduction of amides :-



[CBSE 2012/2010]

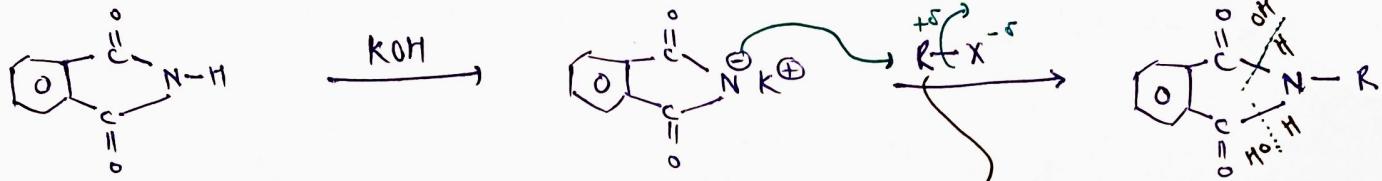
{1M}



[Delhi 2010 | CBSE 2010] {1M}

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

[Delhi]
2010



Phthalimide

→ (CBSE 2019) → [1M]

(Delhi 2012) ↓ [2012 CBSE]

only aliphatic alkyl groups

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

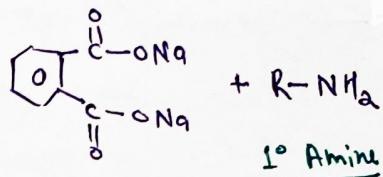
Basic
Hydrolysis [NaOH(aq.)]

6. Hoffmann bromamide degradation reaction :-

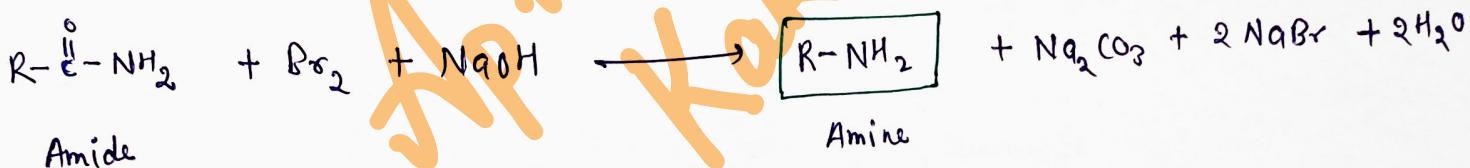
Bromine
(Br₂)

R-C(=O)-NH₂

Reduction of no. of carbon



1° Amine



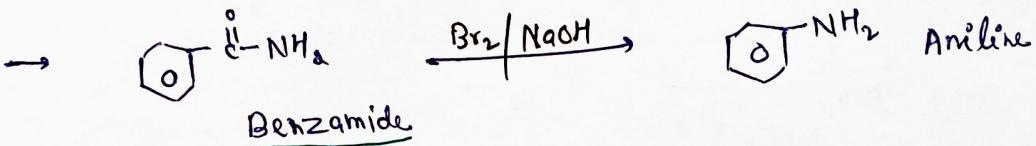
Amide

Amine



Butanamide

Propanamine

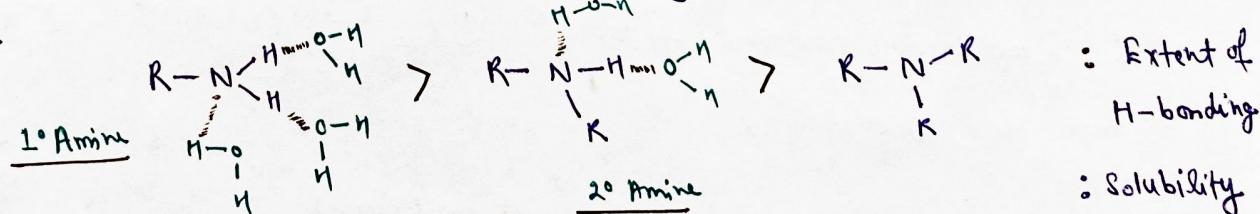


Benzamide

Aniline

Physical properties :-

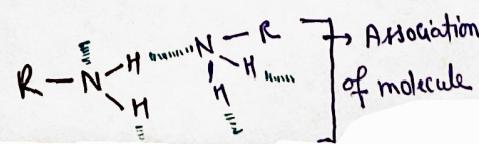
→ Lower amines are soluble in water because they can form hydrogen bonding with water molecules.



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

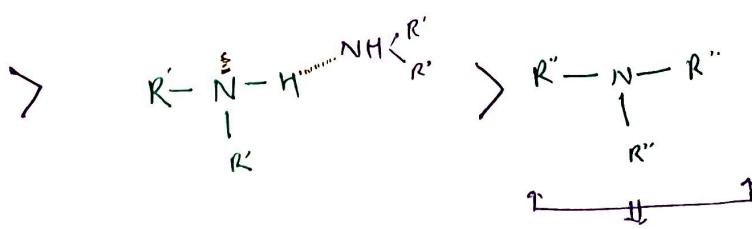
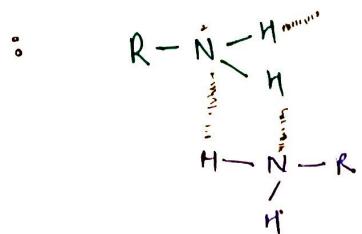
Boiling Point :- Order of B.P. : 1° Amine > 2° Amine > 3° Amine

→ This is because of order of extent of H-bonding.



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

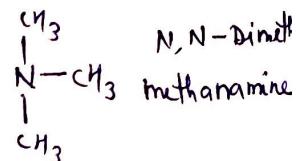
Extent of H-bonding in it :



No Hydrogen bond between itself.

→ Because 3° 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 H^+ towards itself.

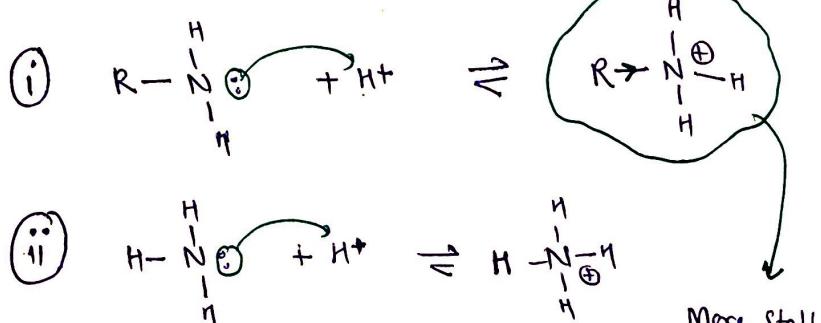
→ Basicity is represented by K_b .

→ $pK_b = -\log K_b$ 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 NH_4^+ , equilibrium constant for reaction

(i) is more than reaction (ii).



More Stable than NH_4^+

due to dispersal of positive charge by $+I$ effect of alkyl group.

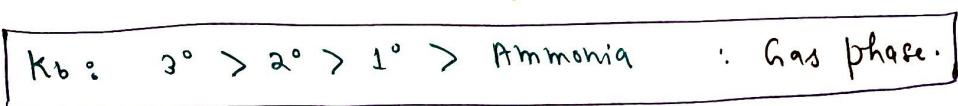
→ Means that, Aliphatic amines are stronger bases than ammonia. $\text{CH}_3-\ddot{\text{N}}\text{H}_2 > \ddot{\text{N}}\text{H}_3 : K_b$

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

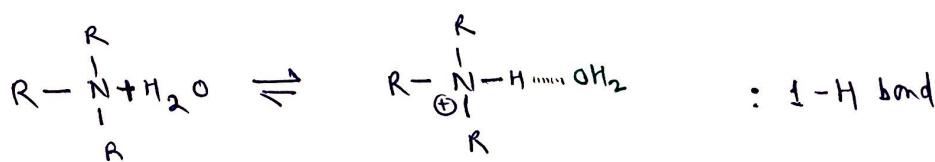
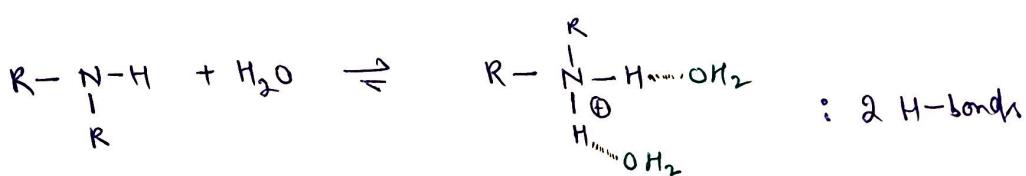
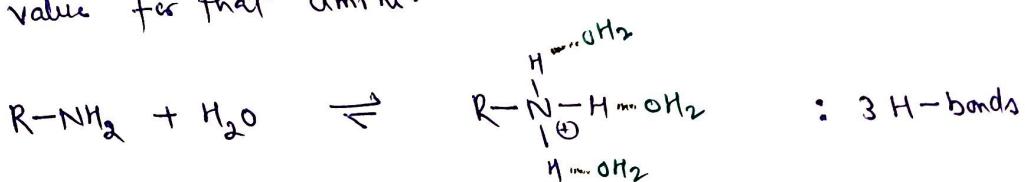




: [Delhi 2019] → 1M

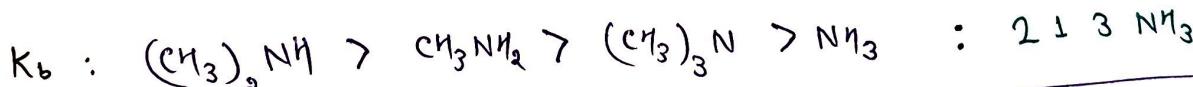


- Basicity of amines in g_g phase :- Above order is not true in aqueous medium. The substituted ammonium cations get stabilised not only by electron releasing effect of alkyl group (+I) but also by solvation with water molecules.
- The ion having more hydrogen bonds with water molecule, are more stable.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



- More solvation \Rightarrow More stable ion

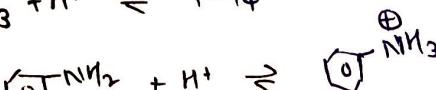
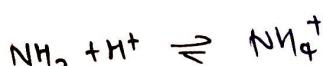
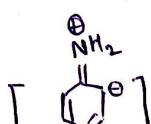
According to solvation effect $K_b : 1^\circ > 2^\circ > 3^\circ$



Basic
Strength in
aq. soln

[Delhi 2013]
[2012] 1M

- Aryl amines vs. Ammonia :-

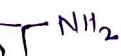
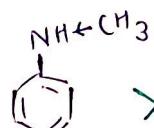
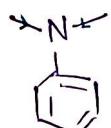


→ Lone pair of nitrogen on ammonia is available for protonation. But in aniline lone pair is not easily available due to resonance with benzene ring.

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

Localised lone pair

Delocalised 1p, so not available for protonation.



+I effect
of -CH₃ group.

[CBSE 2014]

(1M)

→ K_b : > >

Localised lone pair, free for protonation.

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

: [CBSE 2014]

(1M)

→ K_b : < < $\text{CH}_3 \rightarrow \text{NH}_2$ <

↓
lone pair is in resonance
so not available for protonation.

↑
+I effect of alkyl group.

→ K_b : > >

EDG

-CH₃ | -C₂H₅ | -OCN₃

→ Electron donating group increases electron density at nitrogen of anilines. So, it can easily donate lone pair to H⁺.

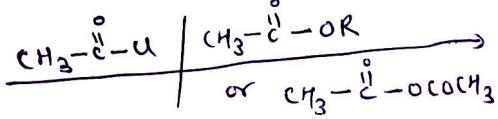
→ > >

: [CBSE 2015 C]

(1M)

[Delhi 2010] (1M)
Acylation of amines :— (Addition of -C⁺-R group.)

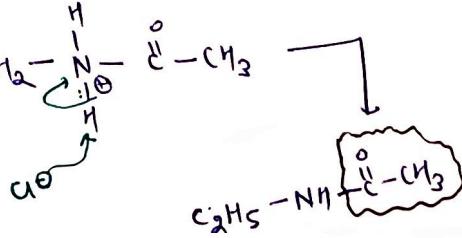
→ 1° | 2° Amines

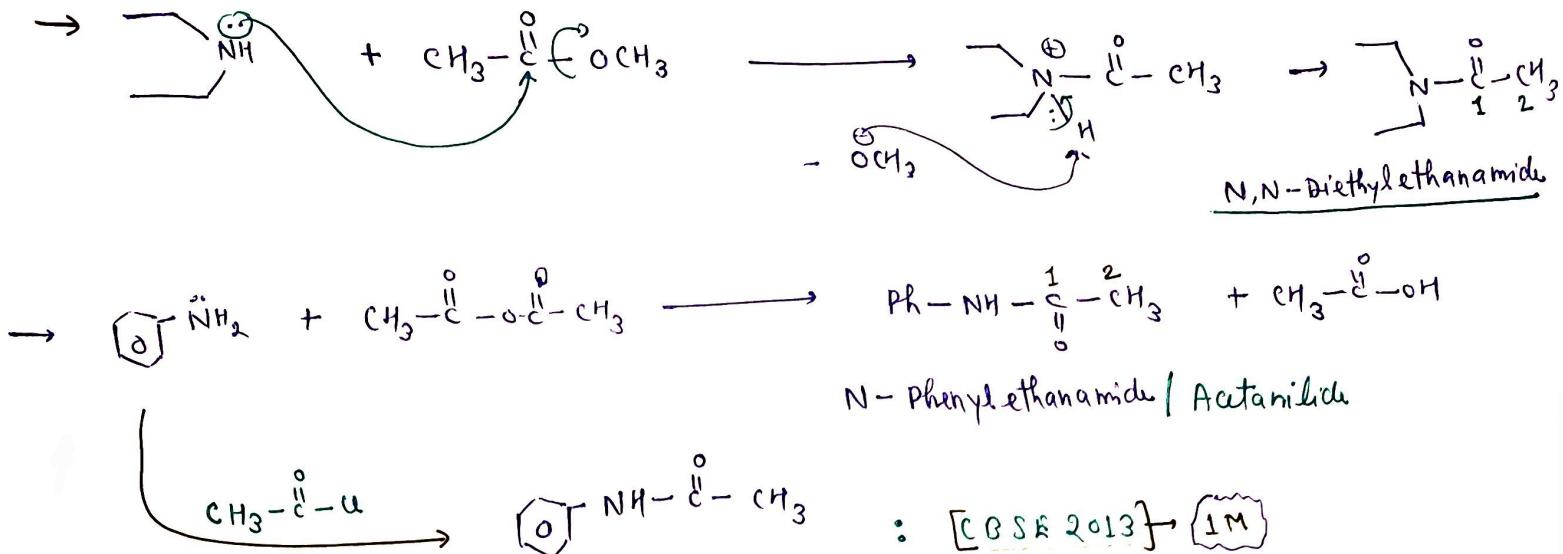


Acylation of product of 1° | 2° Amines

→ $\text{CH}_3-\text{CH}_2-\ddot{\text{N}}\text{H}_2 + \text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{---}}}-\text{U} \xrightarrow[-\text{UO}]{} \text{CH}_3-\text{CH}_2-\overset{\text{H}}{\underset{\text{N}^{\oplus}}{\text{---}}}(\text{---})\text{---}\overset{\text{O}}{\underset{\text{C}}{\text{---}}}-\text{CH}_3$

→ Replacement of Hydrogen by $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{---}}}-$: Acylation.



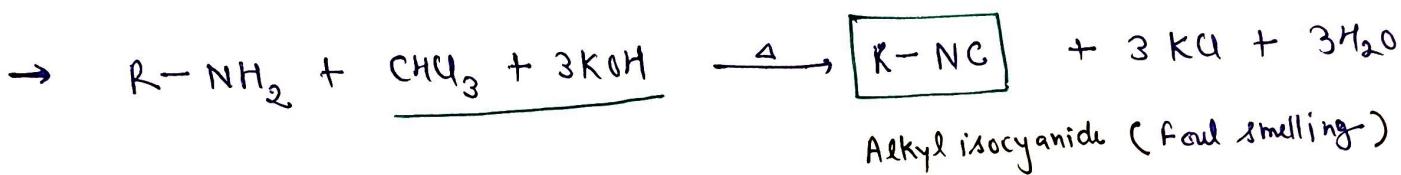


Carbylamine Reaction :- [Test for 1° Amines : Presence of 2 Hydrogen is necessary]

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

[CBSE 2012
Delhi 2012]

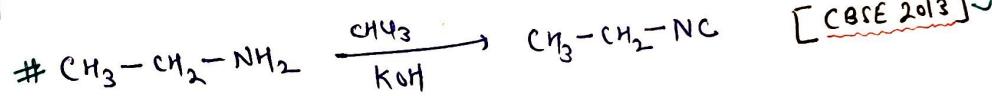
[1M]



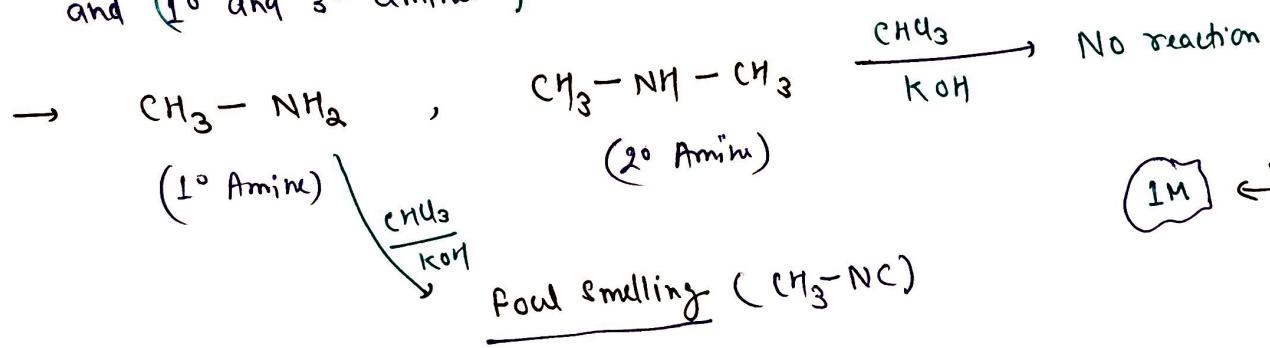
[1M]

This test is also called

Isocyanide test.



By using this reaction (test) we can distinguish (1° and 2° amines) and (2° and 3° amines).



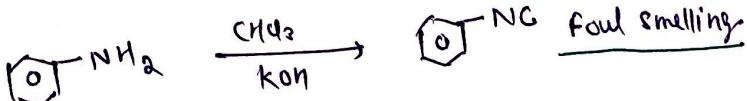
[1M] \leftarrow [CBSE 2019]

Similarly Ethylamine ($\sim\text{NH}_2$) and Diethylamine ($\sim\text{NH}\sim$) can be distinguished by carbylamine test. 1° Amine ($\sim\text{NH}_2$) gives foul smelling with CH_4O and KOH .

[Delhi 2013 C] \rightarrow [1M]

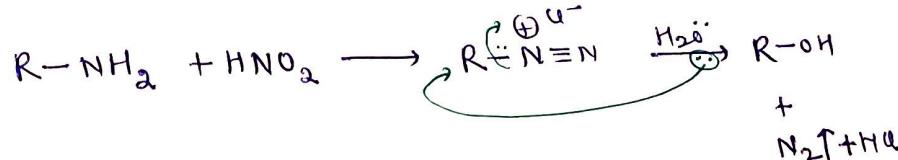
Amine & N-methylamine :-

[CBSE - 2010] [1M]



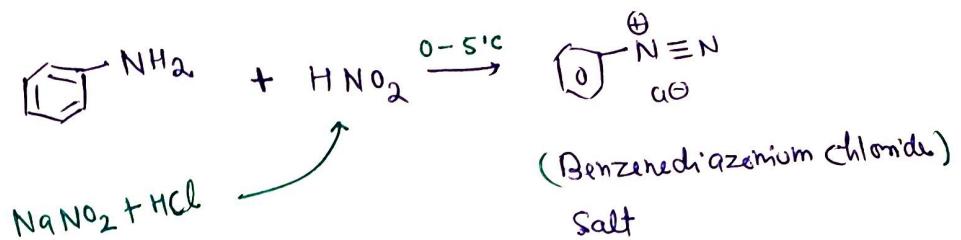
Reaction with HNO_2 [Nitrous Acid] -:

① Primary aliphatic amines :-



→ Evolution of nitrogen.

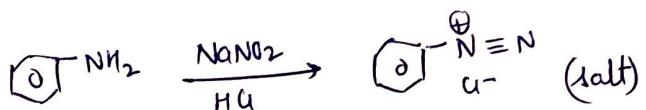
② Aromatic Amines :-



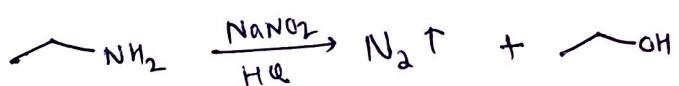
→ Aromatic and aliphatic amines can be distinguished by above reaction.

For example:-

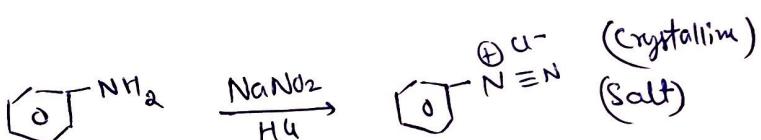
Aniline and Ethylamine



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

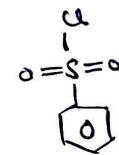


Aniline and Benzylamine



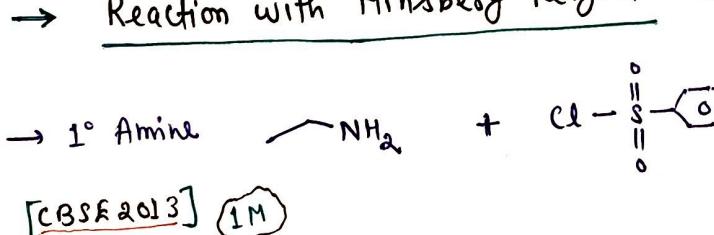
(CBSE 2014C) → 1M

(1° Amine) Benzylamine.

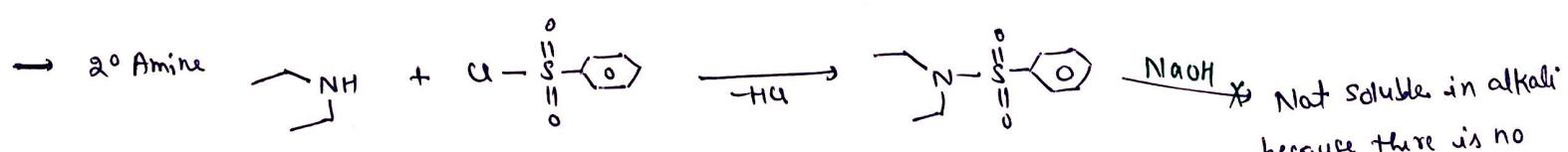
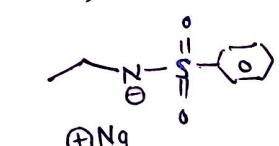
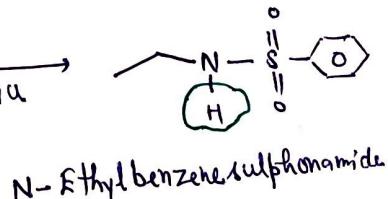


Benzensulfonyl
chloride.

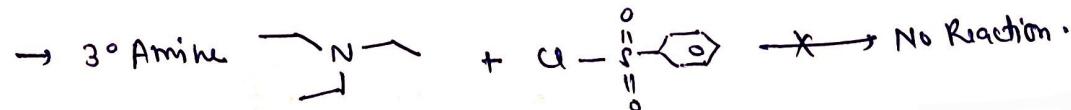
Hinsberg Reagent :-



[CBSE 2013] 1M



Not soluble in alkali
because there is no
acidic hydrogen.

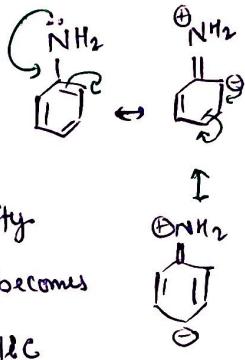


→ This reagent can be used to distinguish 1° / 2° / 3° Amines.

Electrophilic Substitution Reaction :-

→ -NH₂ group is ortho-para directing, and powerful activating group.

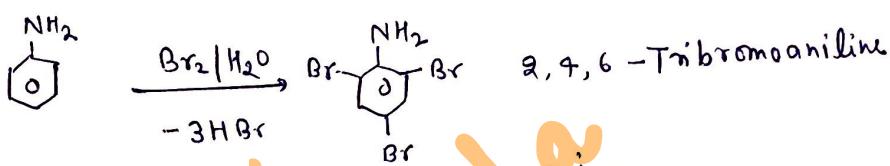
In resonating structure, \ominus ve charge is present at ortho and para position.



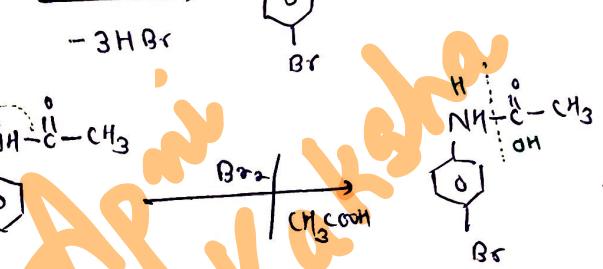
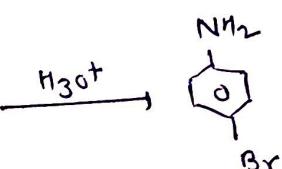
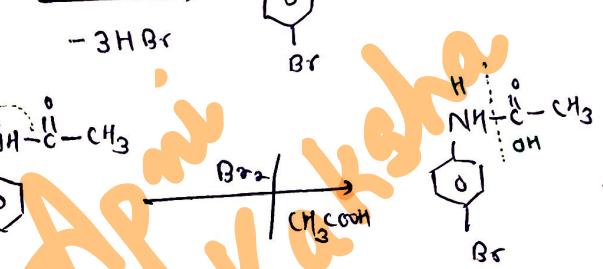
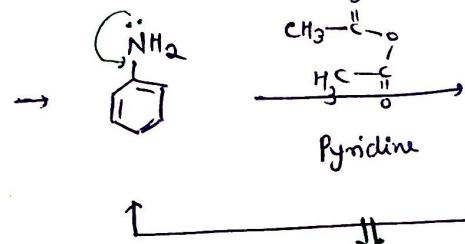
It donates electron density to benzene ring & ring becomes more active for electrophilic reaction.

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

i) Bromination :-

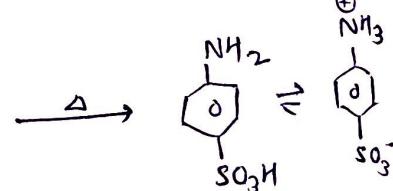
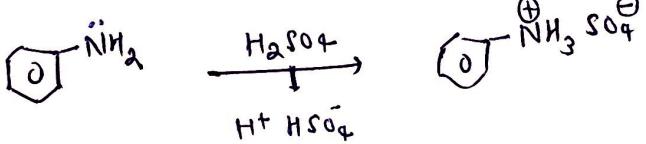


[2013] 1M



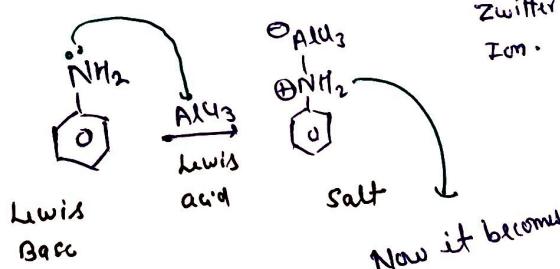
→ Activating effect of $-\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{CH}_3$ group is less than that of $-\text{NH}_2$ group, because in $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{N}}{\text{||}}}-\text{CH}_3 \leftrightarrow \text{C}_6\text{H}_5-\text{NH}-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{CH}_3$ lone pair of nitrogen is shared also with $-\overset{\text{O}}{\text{C}}-$ group. So it can not activate benzene ring as ^{much as} $-\text{NH}_2$ group.

ii) Sulphonation :-



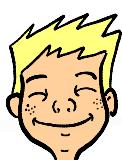
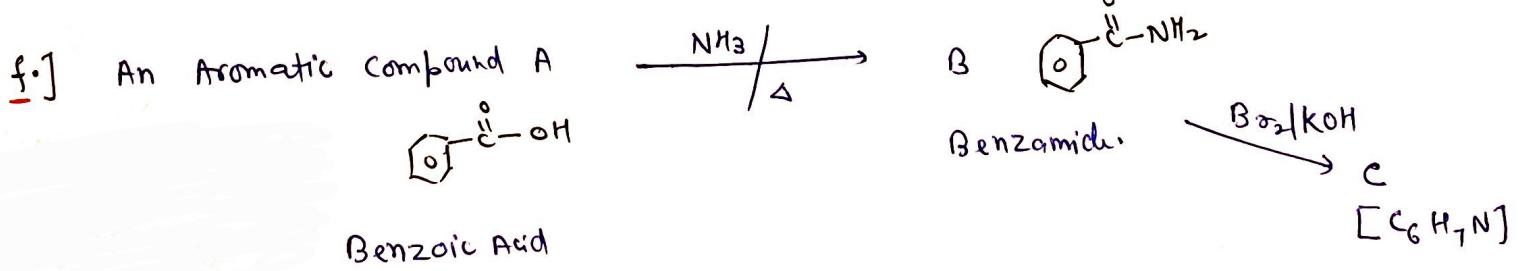
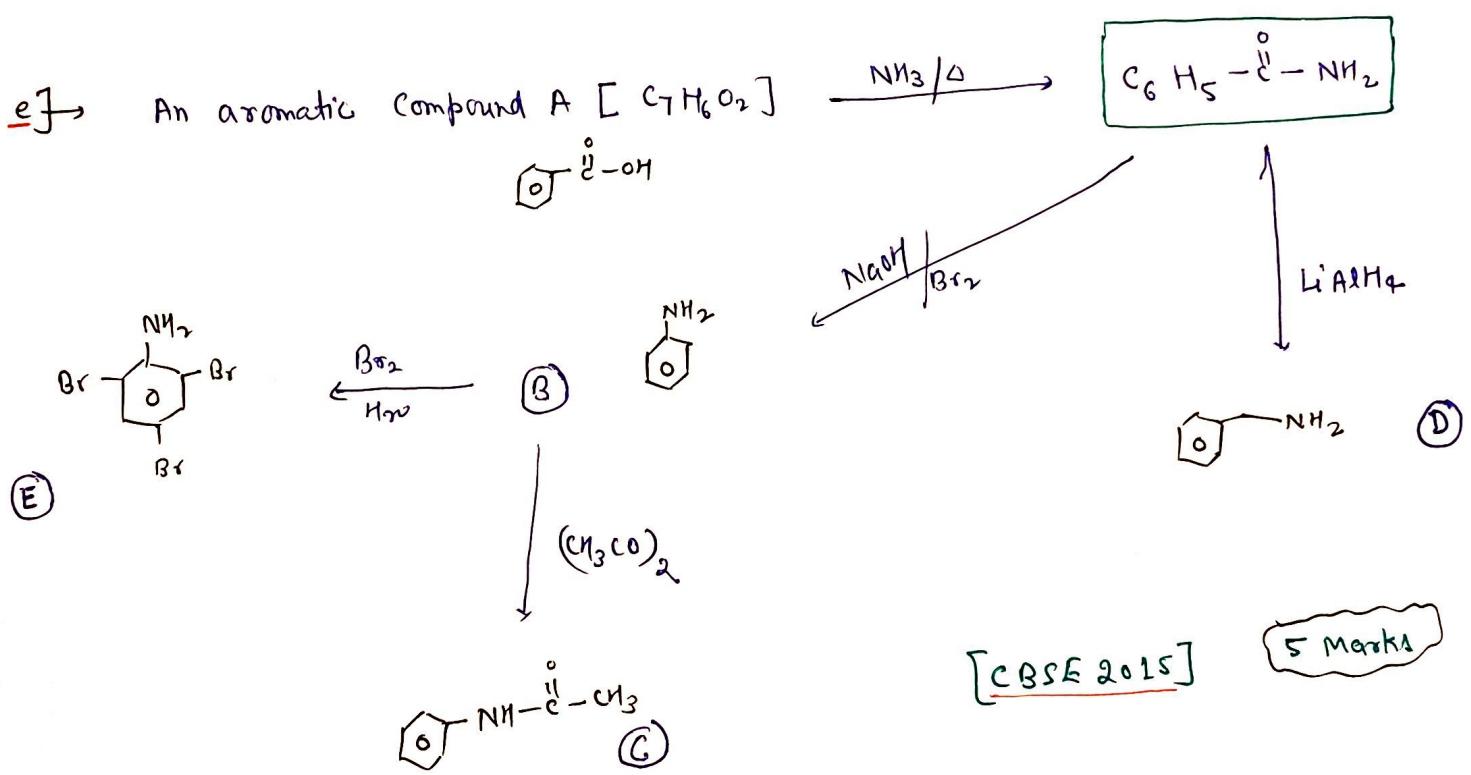
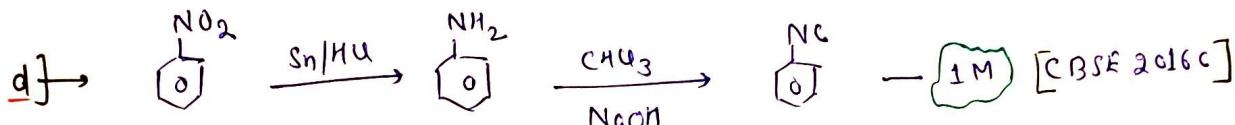
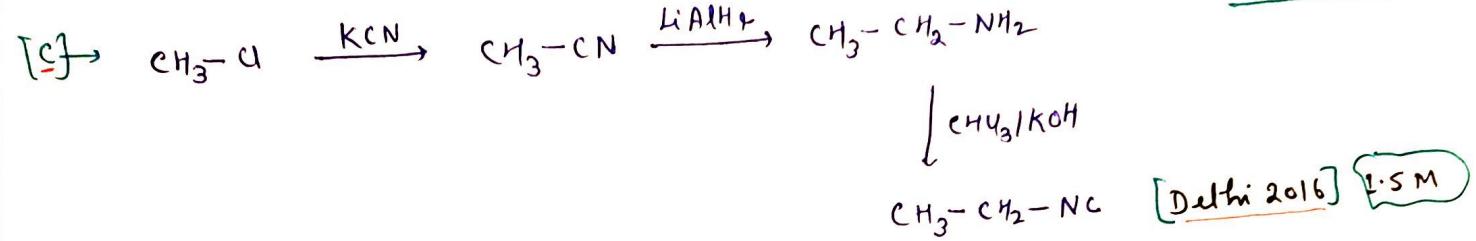
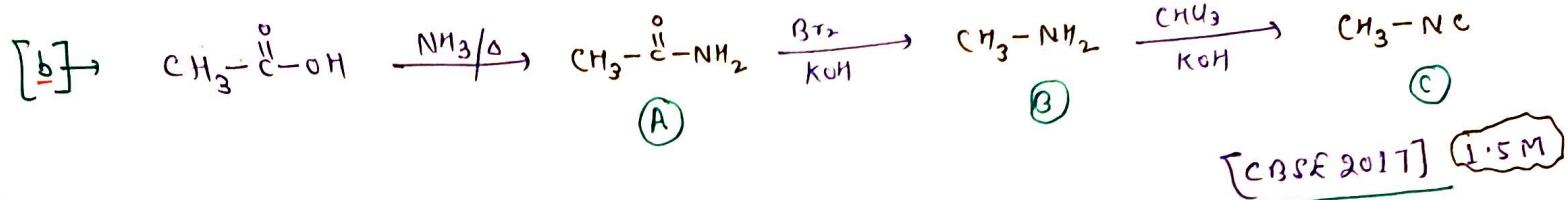
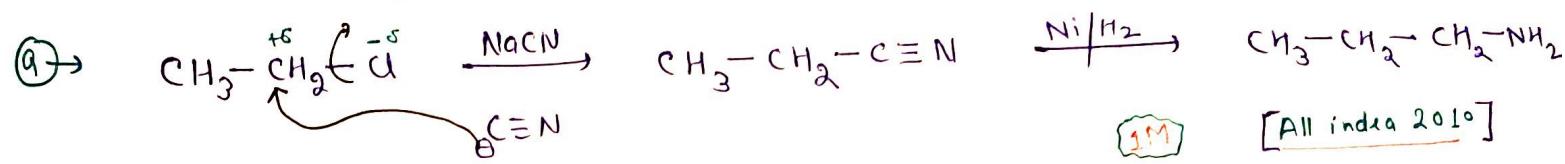
→ Aniline does not undergo Friedel-Crafts Reaction due to salt formation with Al₂O₃. Hence acts as a strong deactivating group for further reaction.

[Delhi 2014C] 1M

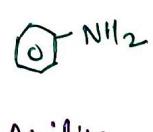


Now it becomes deactivating group.

Complete the following reaction?

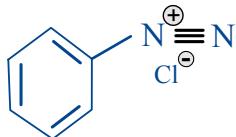
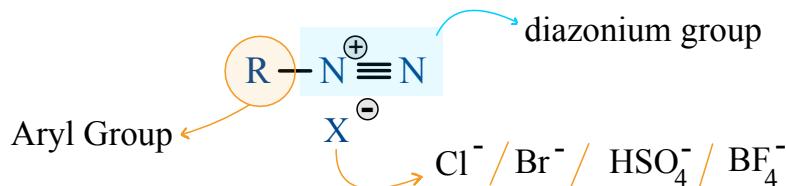


JAD AB
PHODO!

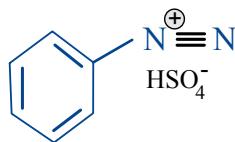


Diazonium Salts

General formula :



(Benzenediazonium Chloride)



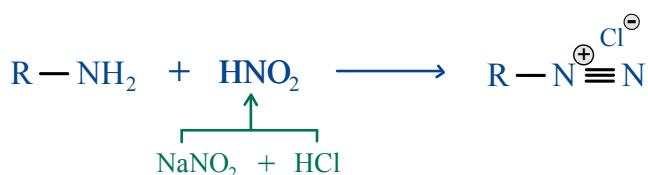
(Benzenediazonium hydrogensulphate)

Methods of Preparation :

Diazotisation :

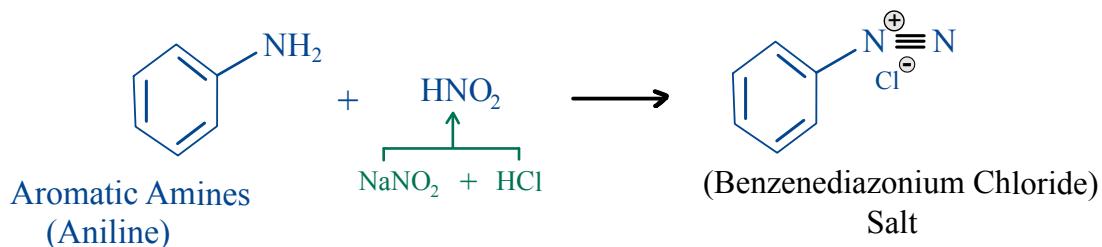
The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

1) Primary aliphatic amines :-



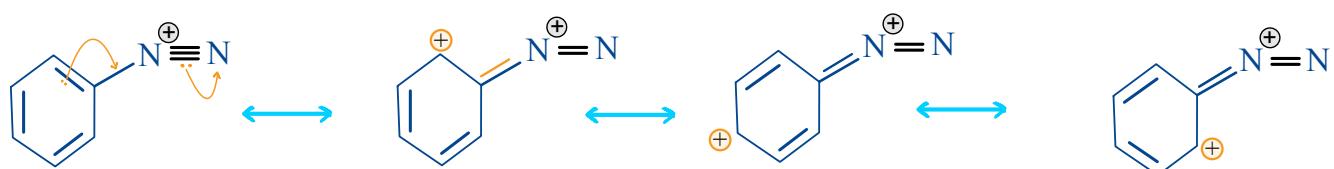
Primary aliphatic amines form highly unstable alkyldiazonium salts.

2) Aromatic Amines :-

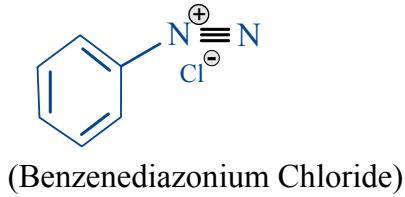


Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (0-5 °C).

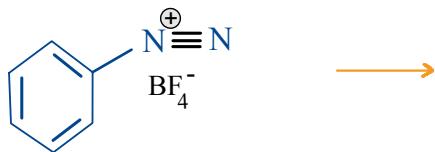
Reason for stability of arenediazonium : Resonance phenomenon



Physical Properties :



→ Colourless crystalline solid
 → It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

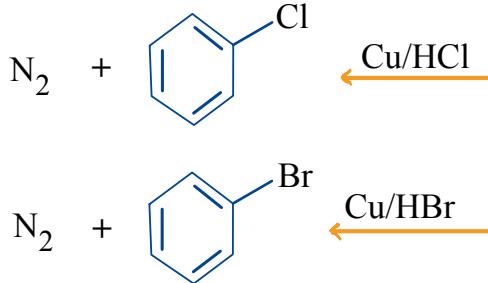


→ Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

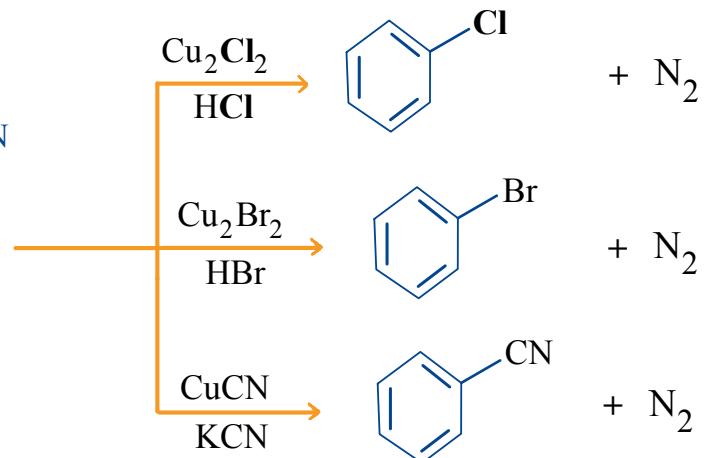
Chemical Reactions

Reactions involving displacement of nitrogen

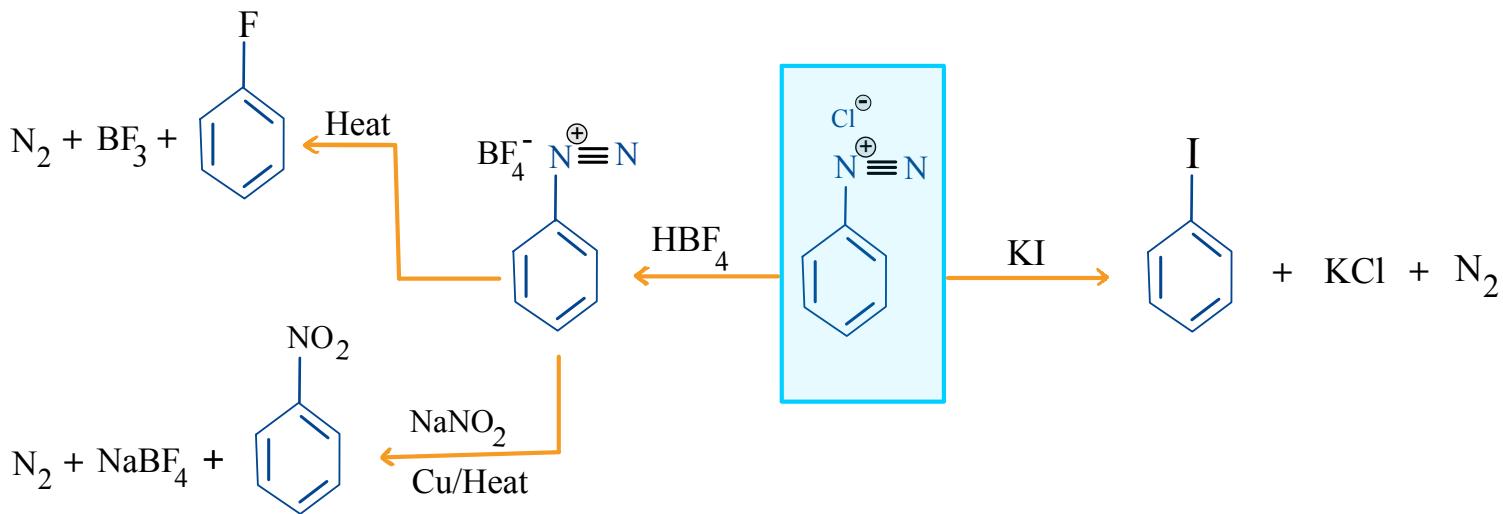
Gattermann Reaction

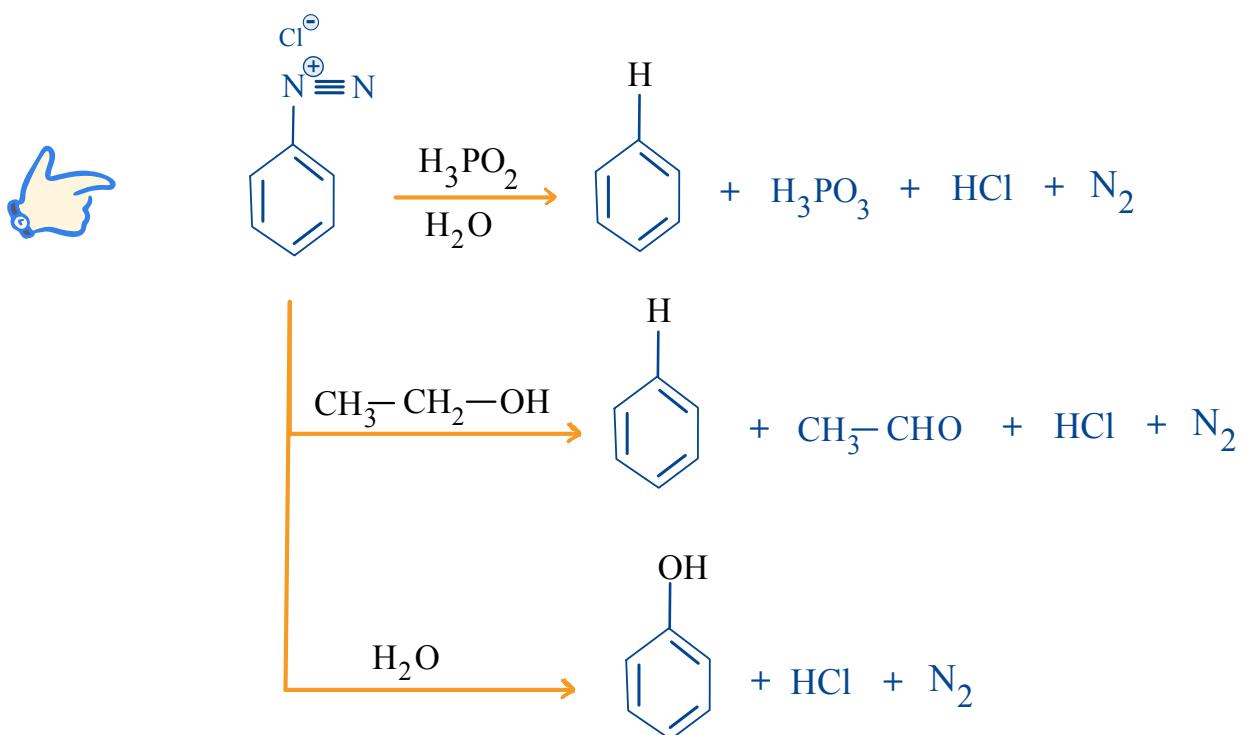


Sandmeyer reaction

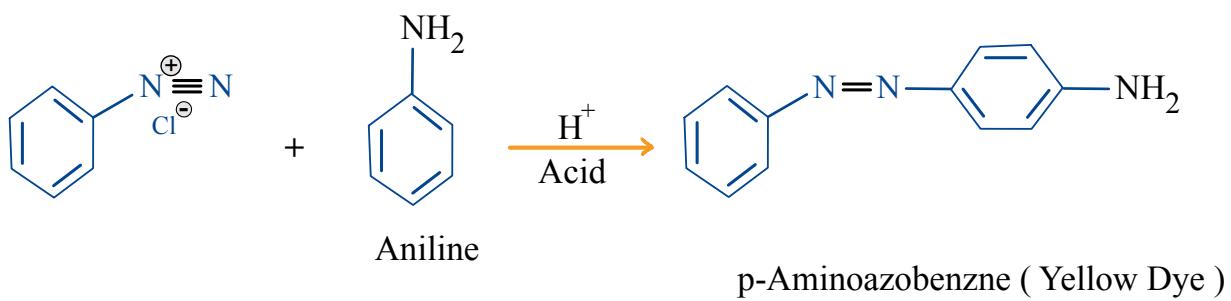
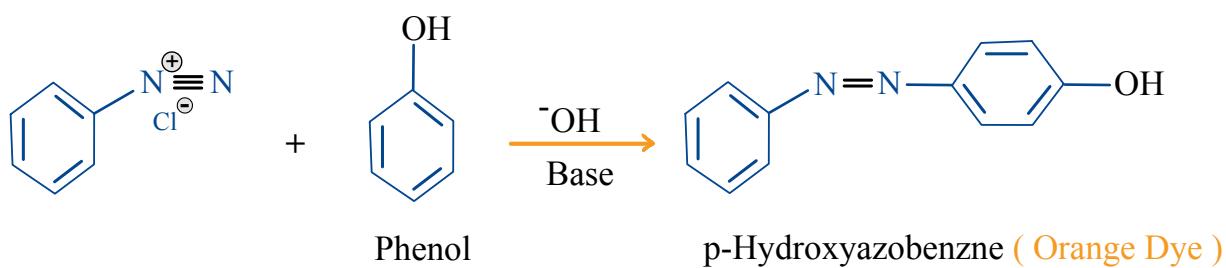


Other important reactions :





Coupling Reaction :



The azo products obtained have an extended conjugate system having both the aromatic rings joined through the $-\text{N}=\text{N}-$ bond. These compounds are often coloured and are used as dyes.