

Chapter 12

Amines

Physical & Chemical Properties of Amines

Physical Properties:

- (a) It is a colourless inflammable liquid. its boiling point is 19°C.
 - (b) It has fishy ammoniacal odour.
 - (c) It is highly soluble in water. Its aqueous solution is basic in nature and turns red litmus blue.
- The solubility in water is due to hydrogen bonding with water molecules.

Chemical Properties:

(i) **Basic nature:** It is more basic than ammonia. Following reactions prove its basic nature.

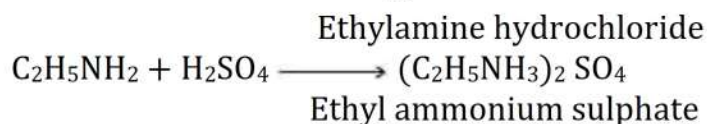
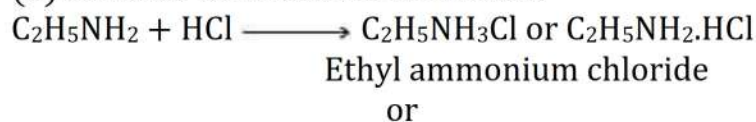
- (a) It forms ethyl ammonium hydroxide when dissolved in water.



Ethyl ammonium hydroxide ionises to give OH^- ions.



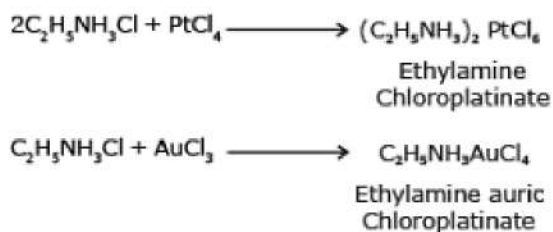
- (b) It reacts with acids to form salts.



- (c) Its aqueous solution behaves like ammonium hydroxide. The aqueous solution of ethylamine precipitates iron, chromium and aluminium as hydroxides when salts are treated with it.



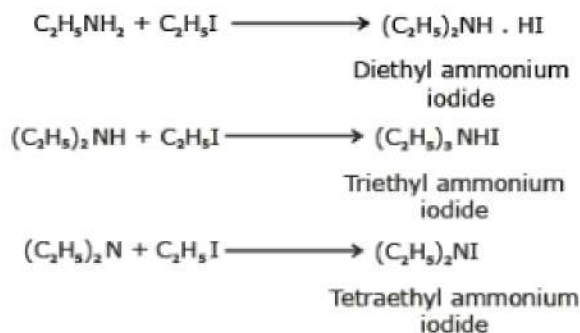
(d) It's hydrochloride, like ammonium chloride, forms double salts with PtCl_4 and AuCl_3 .



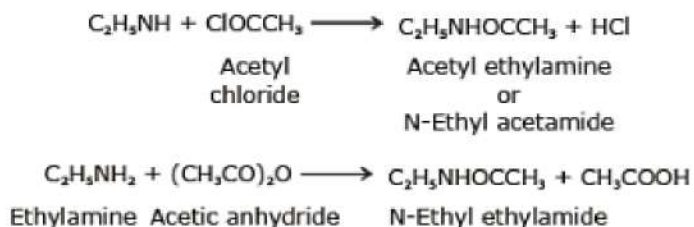
These double salts decompose on heating to pure metal and this method is used to determine the molecular mass of amines.

(ii) Reaction with alkyl halides (Alkylation):

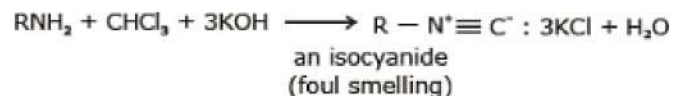
Ethylamine reacts with alkyl halides and form secondary, tertiary amines and quaternary ammonium salt.



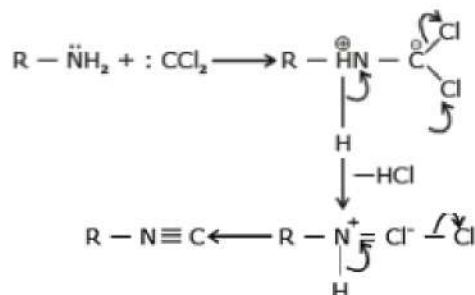
(iii) **Reaction with acetyl chloride or acetic anhydride:** Acetylation takes place when ethylamine combines with acetyl chloride or acetic anhydride.



(iv) Carbylamine Reaction:



Mechanism-


$$2\text{C}_2\text{H}_5\text{NH}_2 + 2\text{Na} \longrightarrow 2\text{C}_2\text{H}_5\text{NHNa} + \text{H}_2$$

Sodium derivative
of ethylamine

$$\begin{array}{lcl}
 2\text{C}_2\text{H}_5\text{NH}_2 & + & \text{RMgX} \longrightarrow \text{R-H} + \text{C}_2\text{H}_5\text{NHMgX} \\
 & & \text{Grignard reagent} \qquad \text{Alkane} \\
 \\
 2\text{C}_2\text{H}_5\text{NH}_2 & + & \text{CH}_3\text{MgI} \longrightarrow \text{CH}_4 + \text{C}_2\text{H}_5\text{NHMgI} \\
 & & \text{Methyl} \qquad \qquad \text{Methane} \\
 & & \text{Magnesium iodide}
 \end{array}$$
$$\text{C}_2\text{H}_5\text{NH}_2 + \text{CS}_2 + \text{HgCl}_2 \longrightarrow \text{C}_2\text{H}_5\text{N}=\text{C}=\text{S} + 2\text{HCl}$$

Ethyl isothiocyanate

$$\begin{array}{c} \text{C}_2\text{H}_5\text{NH}_2 + \text{O} = \overset{\text{H}}{\underset{|}{\text{C}}} - \text{CH}_3 \longrightarrow \text{C}_2\text{H}_5 - \text{N} - \text{C} - \text{CH}_3 \\ \text{Ethylamine} \quad \text{Acetaldehyde} \end{array}$$

$$\downarrow -\text{H}_2\text{O}$$
$$\text{C}_2\text{H}_5\text{N} = \text{CH} - \text{CH}_3$$

Phyldene ethylamine
(Schiff's base)

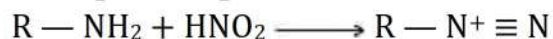
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Test	Primary amine	Secondary amine	Tertiary amine
1. Action Test CHCl_3 and alcoholic KOH.	Bad smelling carbyl-amine (Isocyanide is formed)	No action.	No action.
2. Action of CS_2 and HgCl_2 . (Mustard Oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action.
3. Action of Nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test.)	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.
4. Action of acetyl chloride.	Acetyl derivative is formed	Acetyl derivative is formed	No action.
5. Action of Hinsberg's reagent	Monoalkyl sulphon-amide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
6. Action of methyl iodide.	3 molecules (moles) of CH_3I to form quaternary salt with one mole of primary amine.	2 moles of CH_3I to form quaternary salt with one mole of secondary amine.	One mole of CH_3I to form quaternary salt with one mole of tertiary amine.

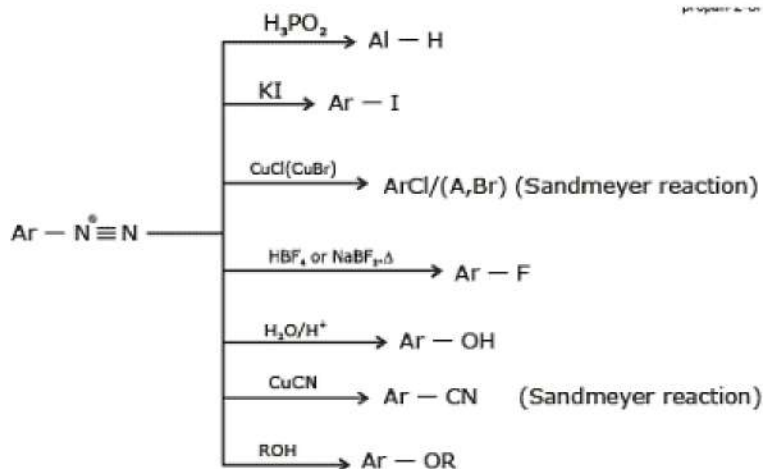
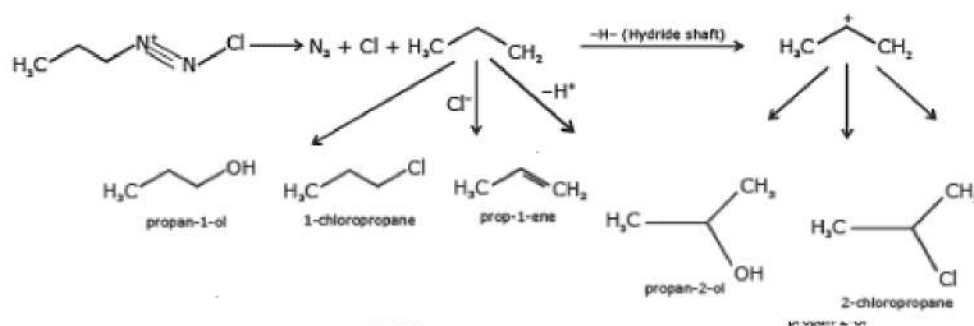
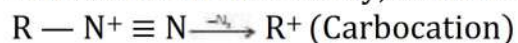
General Chemical Properties of Aromatic Amines:

Reaction with nitrous acid:

1. Primary Amines: Primary amines react with nitrous acid to produce diazonium ion as follows.



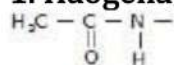
But the diazonium ions of aliphatic amines are very unstable and produce carbocation immediately, which can produce different products.



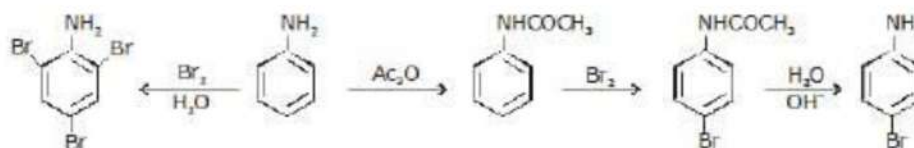
Ring Reactions of Aromatic Amines:

NH_2 — NHR and $-\text{NR}_2$ strongly activate the benzene ring toward electrophilic substitution.

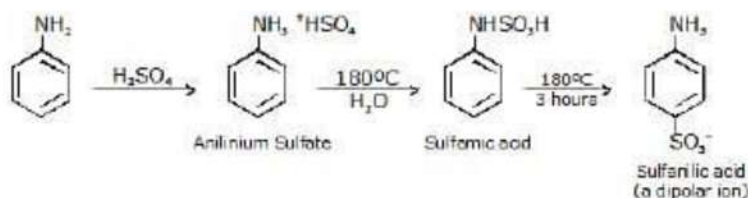
1. Haogenation: For monohalogenation, $-\text{NH}_2$ is first acetylated, because



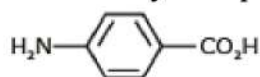
is only moderately activating and is o and p-director in nature.



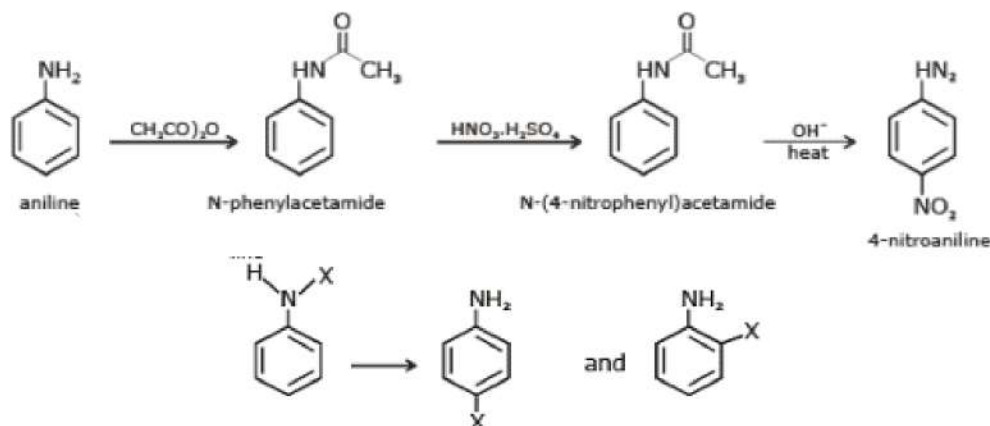
2. Sulfonation:



The dipolar ion structure of sulfanilic acid account for its (a) high melting point, (b) insolubility in H_2O and organic solvents, (c) solubility in aqueous NaOH , (d) insolubility in aqueous HCl .

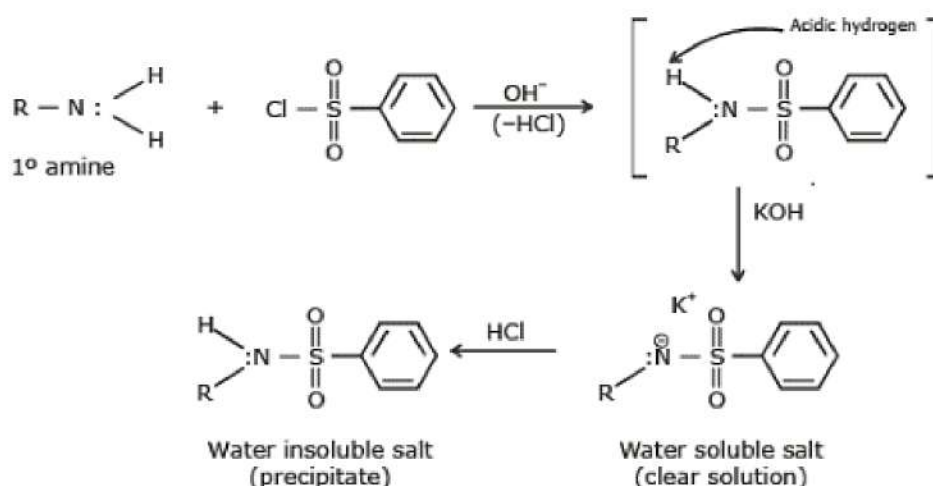


will not exists as a dipolar ion since, $-\text{COOH}$ is too weakly acidic to transfer an H^+ to the weakly basic $-\text{NH}_2$ attached to the electron withdrawing benzene ring. When attached to an aliphatic C, the NH_2 is sufficiently basic to accept H^+ from COOH .

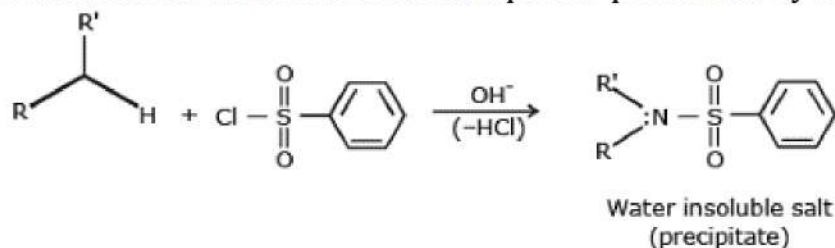


(i) The Hinsberg Test

This test can be used to demonstrate whether an amine is primary, secondary or tertiary. Primary amines react with benzenesulfonyl chloride to form N-substituted benzenesulfonamides. These, in turn, undergo acid-base reactions with the excess potassium hydroxide to form water-soluble potassium salt. Acidification of this solution will, cause the water-soluble in the next stage, cause the water-insoluble N-substituted sulfonamide to precipitate.



Secondary amines react with benzenesulfonyl chloride in aqueous potassium hydroxide to form insoluble, N - N-disubstituted sulfonamides that precipitate after the first stage. N₃N-
Disubstituted sulfonamides do not dissolve in aqueous potassium hydroxide.

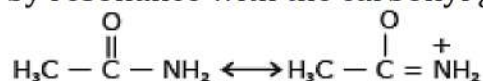


If the amine is a tertiary amine and if it is water insoluble, no apparent change will take place in the mixture as we shake it with benzenesulfonyl chloride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

Basic Character & Preparation of Amines

1. BASIC NATURE OF AMINES

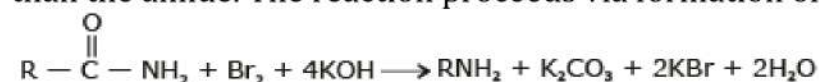
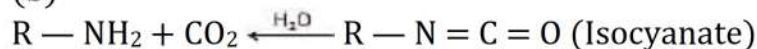
1. Aniline is less basic than ammonia. The phenyl group exerts -I (inductive effect, i.e., it withdraws electrons. This results in the lower availability of electrons on nitrogen for protonation.
2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.



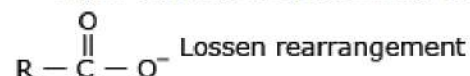
$$(i) \quad \underset{(sp^3)}{CH_3\ddot{N}H_2} > \underset{(sp^2)}{CH_2 - \ddot{N} = CHCH_3} > \underset{(sp)}{CH_3 - C \equiv \ddot{N}}$$


(v) $\text{CH}_3\text{CH}_2\text{NH}_2 > \text{C}_6\text{H}_5\text{CONH}_2 > \text{CH}_3\text{CONH}_2$

1. Hofmann's bromamide reaction: Amines (only primary) can also be prepared by Hoffmann degradation. In this method the amine will have one carbon atom less than the amide. The reaction proceeds via formation of nitrene.

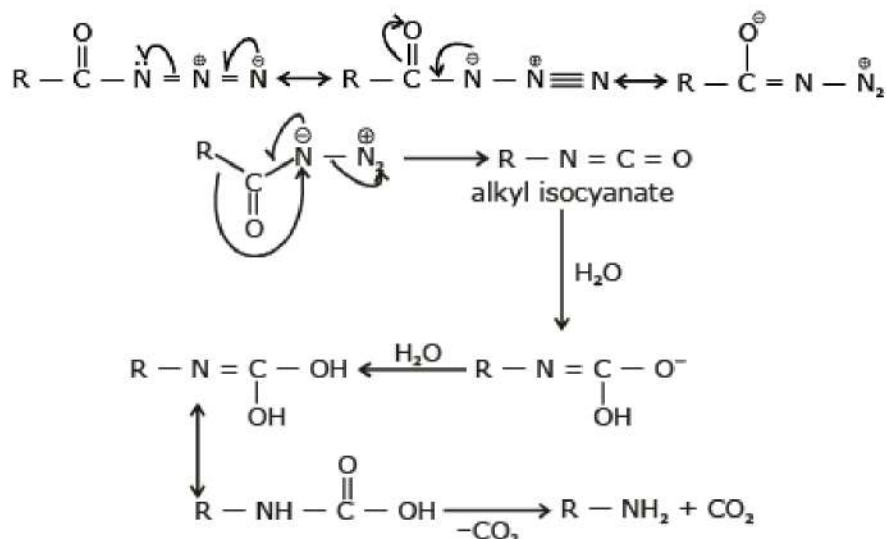
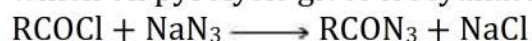

$$\text{Br}_2 + \text{KOH} \longrightarrow \text{K}^+\text{O}^-\text{Br} + \text{HBr}$$
$$2\text{NaOH} + \text{Br}_2 \longrightarrow \text{NaOBr} + \text{NaBr} + \text{H}_2\text{O}$$


— N_2 in Curtius and Schmidt rearrangement.

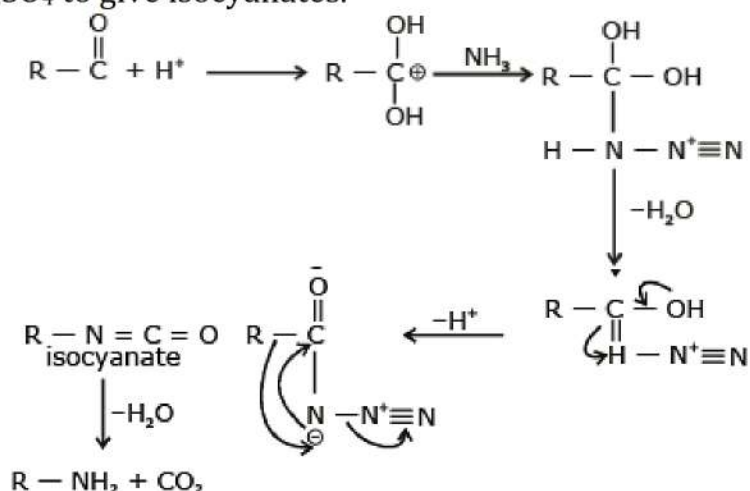


The isocyanate formed on hydrolysis gives amine.

(a) Curtius Reaction: Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates on hydrolysis gives corresponding amines.

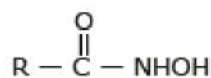


(b) Schmidt Reaction: Carboxylic acid reacts with hydrazoic acid in presence of concentrated H₂SO₄ to give isocyanates.

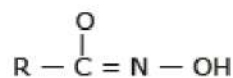


(c) Lossen Reaction: Hydroxylamine on treatment with acid chloride gives acyl derivatives of hydroxyl amine the acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroxamic acid.



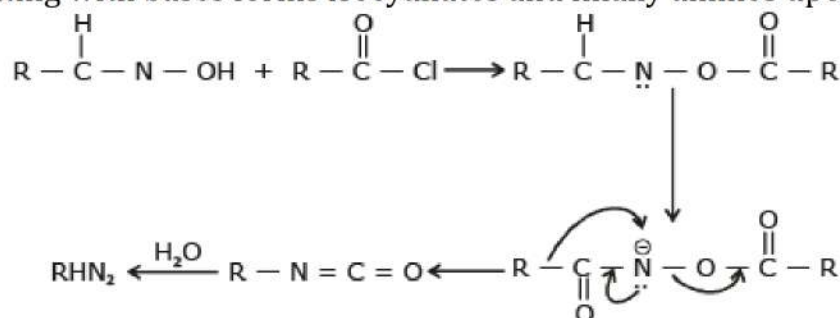


Keto form the
hydroxamic form



The hydroxamic
form (enol form)

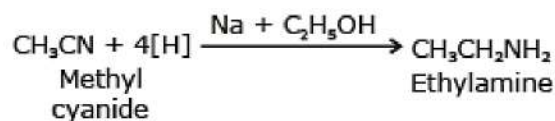
The hydroxamic form (keto form) forms o-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.



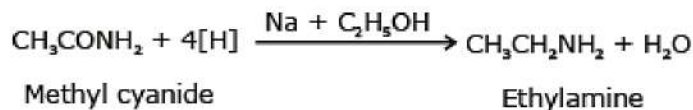
3. By reduction of nitroethane:



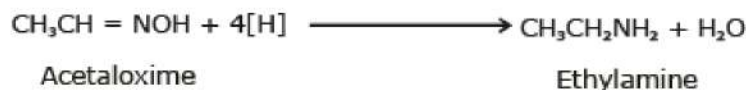
4. By reduction of methyl cyanide:



5. By reduction of acetamide: Ethylamine is obtained by reduction of acetamide with sodium and absolute alcohol or LiAlH_4 in ether or hydrogen in presence of nickel catalyst.



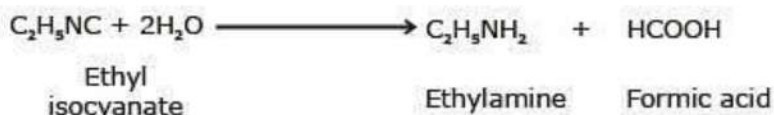
6. By reduction of aldoxime: Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or LiAlH_4 in ether yields ethylamine.



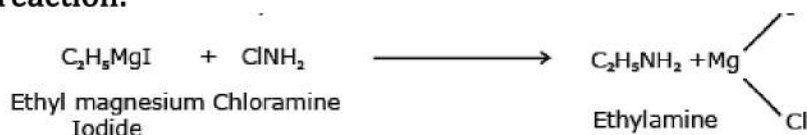
7. By the hydrolysis of ethyl isocyanate: Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.



8. By the acid hydrolysis of ethyl isocyanide: Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.



9. By Schmidt reaction:

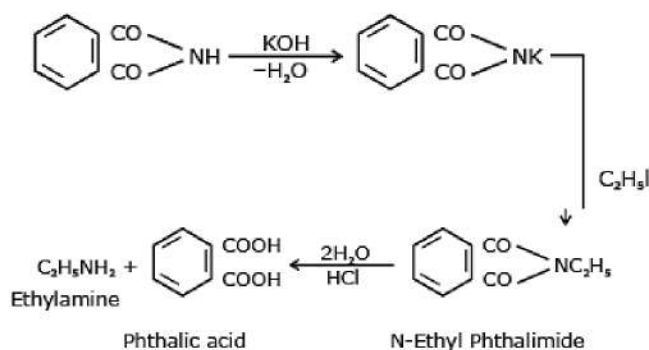


In this reaction the acyl azide $(\text{RCON})_2$ and alkyl isocyanate $(\text{R}-\text{NCO})$ are formed as an intermediate.

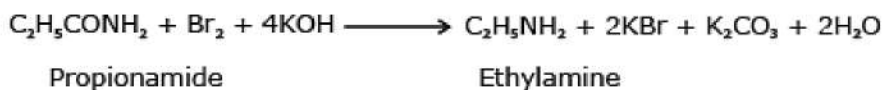
10. By the action of chloramine on Grignard reagent: When chloramine reacts with ethyl magnesium iodide, the formation of ethylamine occurs.



11. By Gabriel's phthalimide reaction:



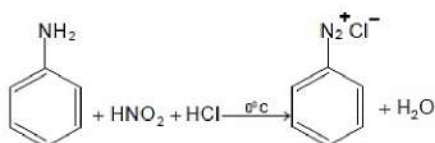
12. Laboratory preparation of ethylamine: Ethylamine is prepared in the laboratory by Hoffmann's bromide reaction. Propionamides are heated with bromine and potassium hydroxide solution.



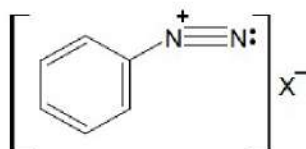
Diazonium Salt & Diazotisation

Diazonium Salt:

When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.



This reaction is known as diazotisation. Diazonium salts have the structure



Mechanism of diazotisation:

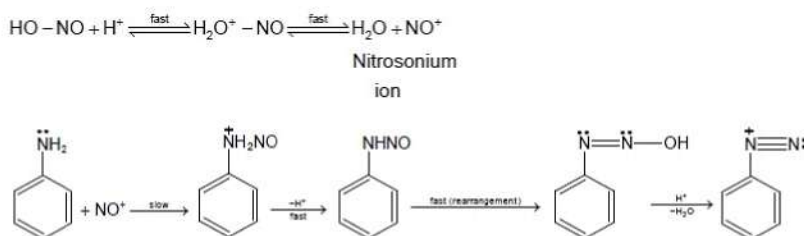


Illustration:

Why icecold condition have to be maintained in the diazotisation reaction of aniline?

Ans: Because benzene diazonium chloride is unstable and decomposes to give phenol above 278k.