Chapter 12

Amines

Physical & Chemical Properties of Amines

Physical Properties:

(a) It is a colourless inflammable liquid. it's boiling point is 19ºC.
(b) It has fishy ammonical odour.
(c) It is highly soluble in water. Its aqueous solution is basic in nature and turns red limus blue.
The solubility in water is due to hydrogen bonding with water moelcules.

ChemicalProperties:

(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.

$$C_2H_5NH_2 + H_2O \longrightarrow C_2H_5NH_3OH$$

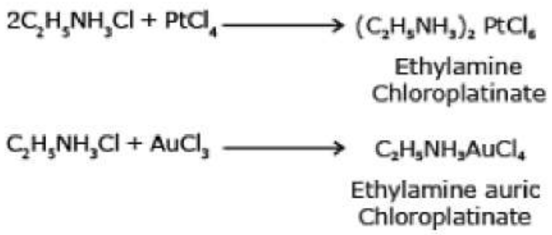
Ethyl ammonium hydroxide

Ethyl ammonium hydroxide ionises to give OH^- ions.
$C_2H_5NH_3OH \rightleftharpoons C_2H_5 + NH_3 + OH^-$
(b) It reacts with acids to form salts.
$C_2H_5NH_2 + HCl \longrightarrow C_2H_5NH_3Cl$ or $C_2H_5NH_2.HCl$
Ethyl ammonium chloride
or
Ethylamine hydrochloride
$C_2H_5NH_2 + H_2SO_4 \longrightarrow (C_2H_5NH_3)_2\ SO_4$
Ethyl ammonium sulphate
(c) Its aqueous solution behaves like ammonium hydroxide. The aqueous solution of ethylamine precipitates iron, chlromium and aluminium as hydroxides when salts are treated with it.

$$3C_2H_5NH_3OH + FeCl_3 \longrightarrow Fe(OH)_3 + 3C_2H_5NH_3Cl$$

Ethyl ammonium hydroxide | Ferric chloride | Ferric hydroxide | Ethyl ammonium chloride

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



$$2C_2H_5NH_3Cl + PtCl_4 \longrightarrow (C_2H_5NH_3)_2\,PtCl_6$$

Ethylamine Chloroplatinate

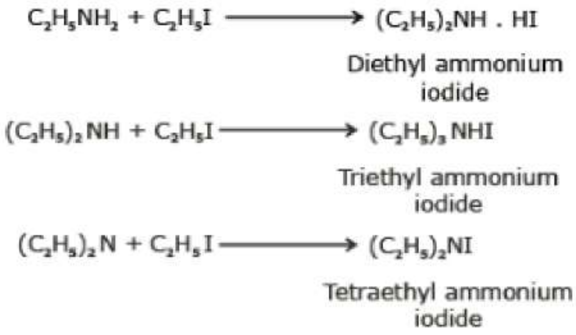
$$C_2H_5NH_3Cl + AuCl_3 \longrightarrow C_2H_5NH_3AuCl_4$$

Ethylamine auric Chloroplatinate

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.



$$C_2H_5NH_2 + C_2H_5I \longrightarrow (C_2H_5)_2NH\,.\,HI$$

Diethyl ammonium iodide

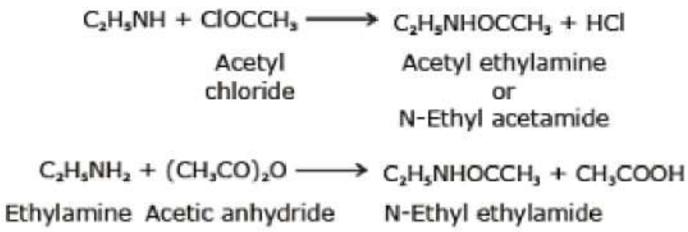
$$(C_2H_5)_2NH + C_2H_5I \longrightarrow (C_2H_5)_3\,NHI$$

Triethyl ammonium iodide

$$(C_2H_5)_2N + C_2H_5I \longrightarrow (C_2H_5)_2NI$$

Tetraethyl ammonium iodide

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



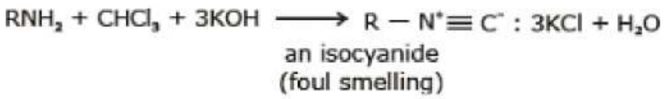
$$C_2H_5NH + ClOCCH_3 \longrightarrow C_2H_5NHOCCH_3 + HCl$$

Acetyl chloride — Acetyl ethylamine or N-Ethyl acetamide

$$C_2H_5NH_2 + (CH_3CO)_2O \longrightarrow C_2H_5NHOCCH_3 + CH_3COOH$$

Ethylamine Acetic anhydride N-Ethyl ethylamide

(iv) Carbylamine Reaction:

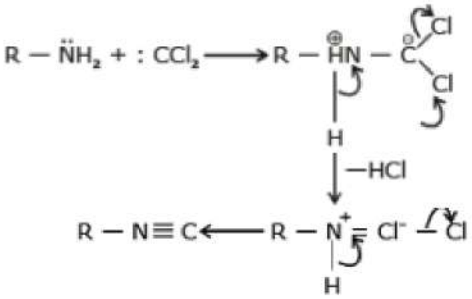


$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R - N^{+} \equiv C^{-} : 3KCl + H_2O$$

an isocyanide (foul smelling)

Nucleophilic RNH_2 attacks electrophilic intermediater $[CCl_2]$ dichlorocarbene. This reaction is used for the detection of primary amines.

Mechanism-

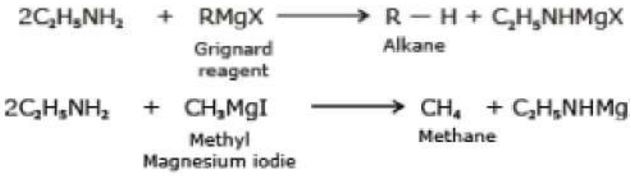


(v) Reaction with sodium: Hydrogen is evolved when ethylamine is heated with sodium.

$2C_2H_5NH_2 + 2Na \longrightarrow 2C_2H_5NHNa + H_2$

Sodium derivative of ethylamine

(vi) Reaction with Grignard's reagent: Ethylamine reacts with Grignard's reagent to form alkanes.

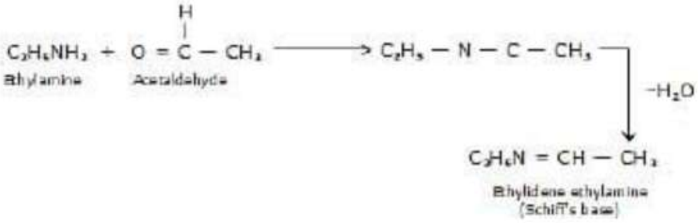


(vii) Hofmann's mustard oil reaction: Carbon disulphide reacts with ethylamine in presence of $HgCl_2$ to form ethyl isothiocyanate which has a mustard oil like smell.

$C_2H_5NH_2 + CS_2 + HgCl_2 \longrightarrow C_2H_5N = C = S + 2HCl$

Ethyl isothiocyanate

(viii) Reaction with aldehydes: Ethylamine reacts additively with aldehydes to form α-hydroxyl amines which are changed to Schiff bases with the elimination of water molecule.



DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

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 hearing 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 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:

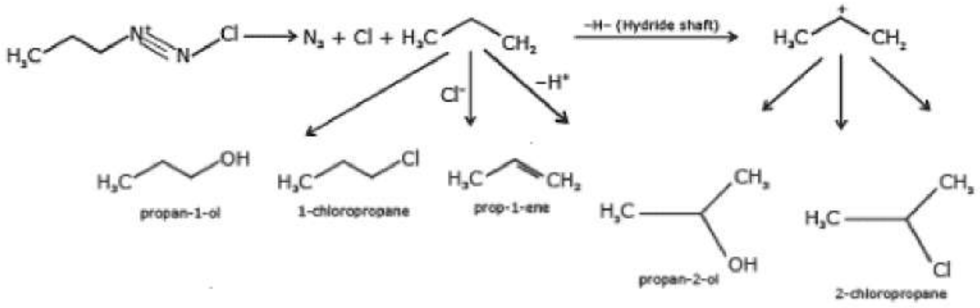
1. Primary Amines: Primary amines react with nitrous acid to produce diazonium ion as follows.

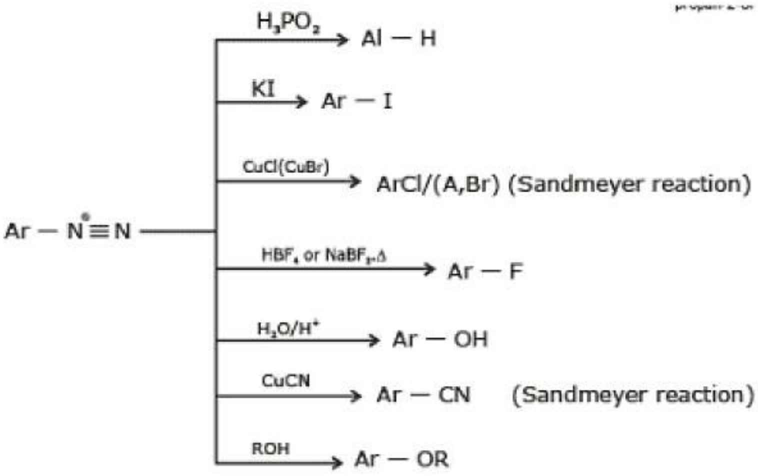
$ArNH_2 + HNO_2 \longrightarrow Ar - N^+ \equiv N:$

$R - NH_2 + HNO_2 \longrightarrow R - N^+ \equiv N$

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

$R - N^+ \equiv N \xrightarrow{-N_2} R^+$ (Carbocation)

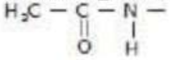




Ring Reactions of Aromatic Amines:

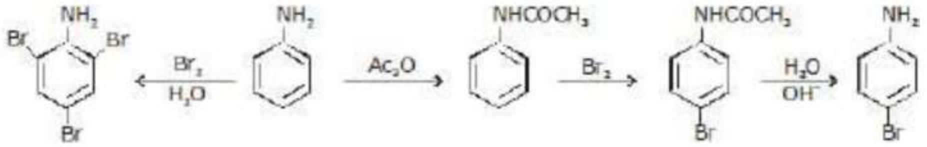
NH_2 — NHR and —NR_2 strongly activate the benzene ring toward electrophilic substitution.

1. Haogenation: For monohalogenation, —NH_2 is first acetylated, because

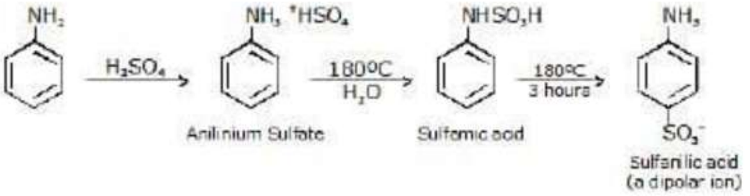


$H_3C - \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} -$

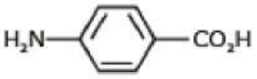
is only moderately activating and is o and p-director in nature.



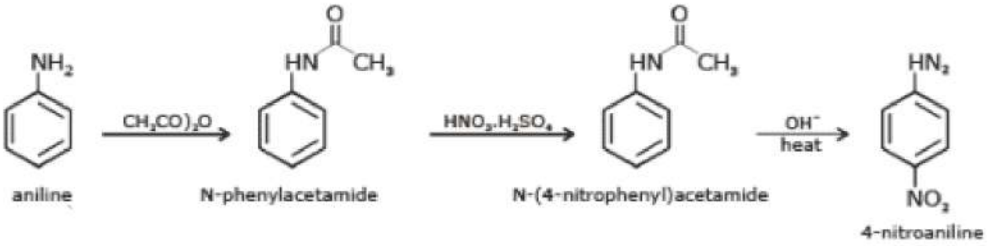
2. Sulfonation:

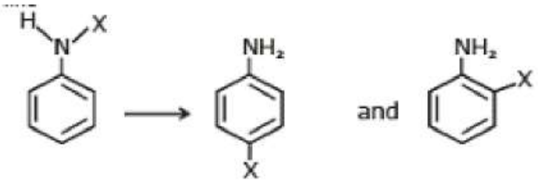


The dipolar ion structure of sulfanilic acid account for its (a) high melting point, (b) insolubility in H_2O and organic solvents, (c) solubility in aqueous NaOH, (d) insolubility in aqeous HCl.



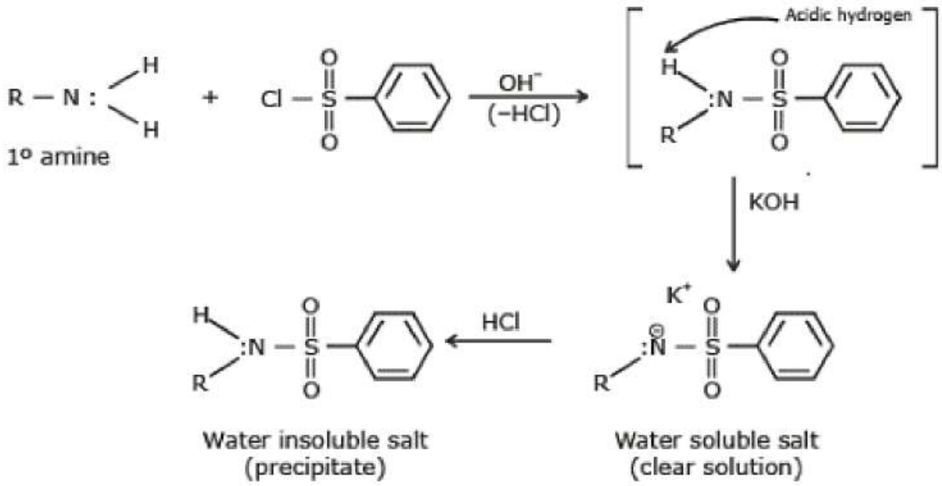
will not exists as a dipolar ino since, -COOH is too weakly acidic to transfer an H to the weakly basic $-NH_2$ attached to the electron withdrawing benzene ring. When attached to an aliphatic C, the NH_2 is sufficiently basic to accept H^- from COOH.



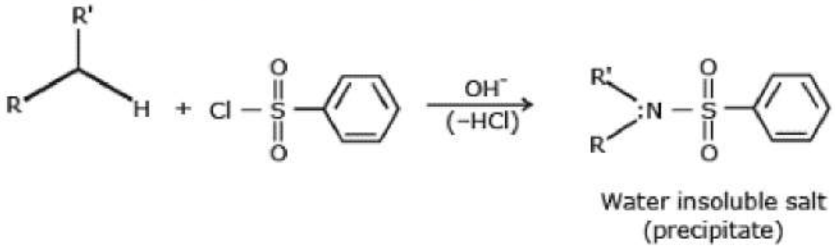


(i) The Hinsberg Test

Ths 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 amies react with benzenesulfonyl chloride in aqueous potassium hydryoxide to form insoluble, N - N-disubstituted sulfonamides that precipitate after the first stage. N_3N^-
Disubstituted sulfonamides do not dissolve in aqueous potassium hydroxide.

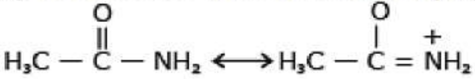


If the amine is a tertiary amine and if it is water insoluble, no apparent change will take place in the mixture as we shake it with benzenesulfonyl choride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

Basic Character & Preparation of Amines

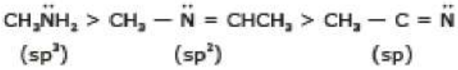
1. BASIC NATURE OF AMINES

1. Aniline is less basic than ammonia. The phenyl group exerts- I (inductive effect, i.e., it with draw 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.



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \longleftrightarrow H_3C-\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{N}H_2$$

3. The compound with least `s' character (sp³ hydrolized) is most basic and with more `s' character (sp-hydrilized) is least basic. Examples in decreasing order of basicity are :

(i) 

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

(ii) $CH_3CH_2CH_2NH_2 > H_2C = CHCH_2NH_2 > HC \equiv CCH_2NH_2$

(iii) $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$

Electron withdrawing (C_6H_5—) groups cause decrease in electron density on nitrogen atom and there by decreasing basicity.

(v) $CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$

2. METHODS OF PREPARATION

1. Hafmann'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.

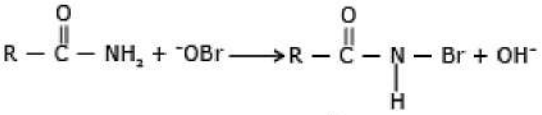
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Mechanism of above reaction has been proposed as given below

$Br_2 + KOH \longrightarrow K^+O^-Br + HBr$

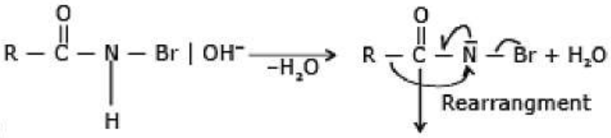
Mechanism

$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$

(a) 

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + {}^-OBr \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br + OH^-$$

N-bromoacetone

(b) 

$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br \mid OH^- \xrightarrow[-H_2O]{} R-\overset{\overset{O}{\|}}{C}-\ddot{N}-Br + H_2O$$

Rearrangment

$R - NH_2 + CO_2 \xleftarrow{H_2O} R - N = C = O$ (Isocyanate)

2. Curtius, Schmidt and Lossen Rearrangment: These reaction are basically rearrangement reactions in which carbon migrates from carbon to nitrogen with the formation of an isocyanate. In these migration i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be

— Br in Hoffmann rearrangement.

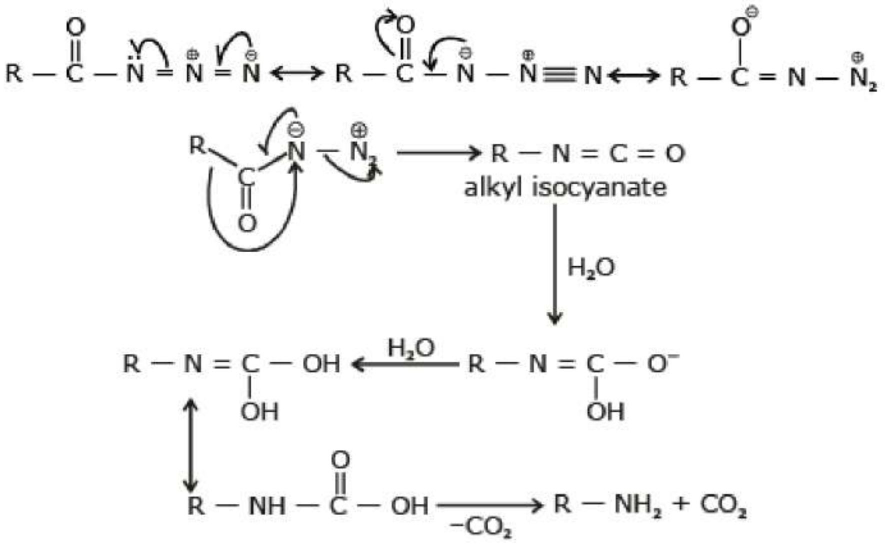
— N_2 in Curtius and Schmidt rearrangement.

$$R-\overset{\overset{O}{\|}}{C}-O^-$$ Lossen rearrangement

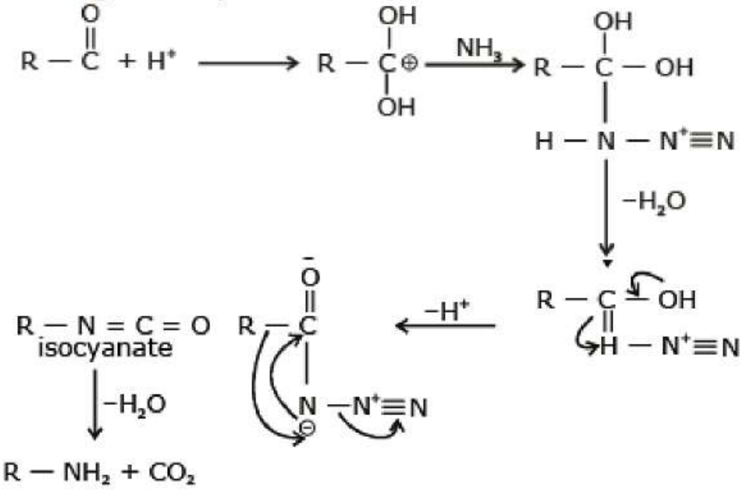
The isocyanate formed on hydrolysis gives amine.

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

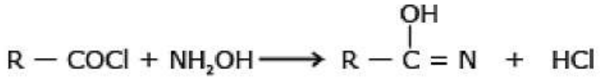
$RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$



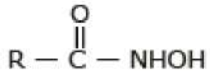
(b) Schmidt Reaction: Carboxylic acid reacts with hydrozoic acid in presence of concentrated H_2SO_4 to give isocyanates.



(c) Lossen Reaction: Hydroxylamine on treatement 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 hydroximic acid.

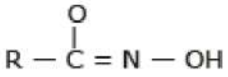


$$R-COCl + NH_2OH \longrightarrow R-\overset{OH}{\overset{|}{C}}=N + HCl$$



$R-\overset{\overset{O}{\parallel}}{C}-NHOH$

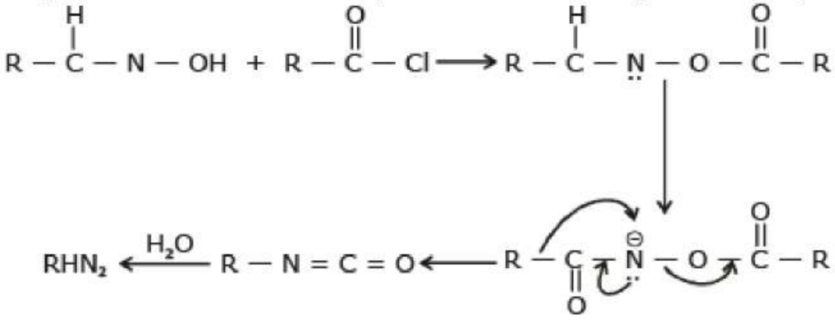
Keto form the
hydroxamic from



$R-\overset{\overset{O}{|}}{C}=N-OH$

The hydroximic
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:

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} + 6[H] \xrightarrow{Sn + HCl} \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O$$

4. By reduction of methyl cyanide:

$$\underset{\substack{\text{Methyl}\\ \text{cyanide}}}{CH_3CN} + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

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.

$$\underset{\text{Methyl cyanide}}{CH_3CONH_2} + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

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.

$$\underset{\text{Acetaloxime}}{CH_3CH = NOH} + 4[H] \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

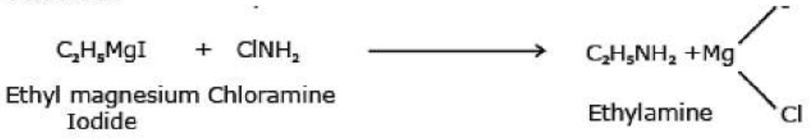
7. By the hydrolysis of ethyl isocyanate: Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.

$$\underset{\text{Ethyl isocyanate}}{C_2H_5NCO} + 2KOH \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + K_2CO_3$$

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

$$\underset{\text{Ethyl isocyanate}}{C_2H_5NC} + 2H_2O \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Formic acid}}{HCOOH}$$

9. By Schmidt reaction:



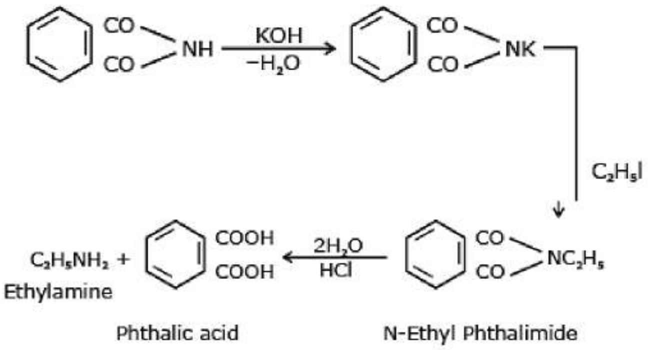
$$\underset{\text{Ethyl magnesium Iodide}}{C_2H_5MgI} + \underset{\text{Chloramine}}{ClNH_2} \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + Mg\langle^{I}_{Cl}$$

In this reaction the acyl azide (RCON)2 and alkyl isocyanate (R —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 ethylmine occurs.

$$\underset{\text{Propionic acid}}{C_2H_5COOH} + \underset{\text{Hydrazoic acid}}{N_3H} \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + N_2 + CO_2$$

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.

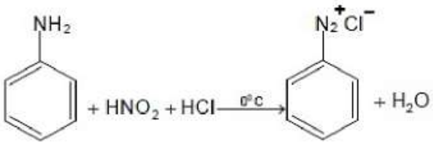
$$C_2H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_2H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Propionamide Ethylamine

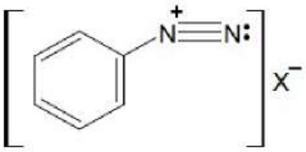
Diazonium Salt & Diazotisation

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:

$$HO-NO + H^+ \underset{}{\overset{fast}{\rightleftharpoons}} H_2O^+-NO \overset{fast}{\rightleftharpoons} H_2O + NO^+$$

Nitrosonium ion

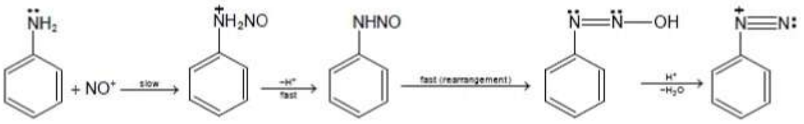


Illustration:

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.