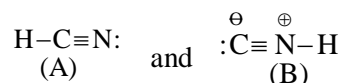


Chapter-4

FUNCTIONAL GROUP-III

Cyanides and Isocyanides

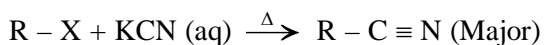
Hydrocyanic acid is known to exist in two tautomeric forms.



Hence even the alkyl and phenyl derivatives of (A) and (B) are cyanides and isocyanides respectively.
i.e. $\text{R}-\text{C}\equiv\text{N}$: and $\text{R}-\text{NC}$

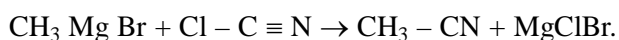
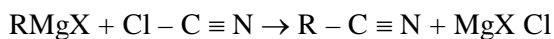
Preparation :

1) From Alkyl halides



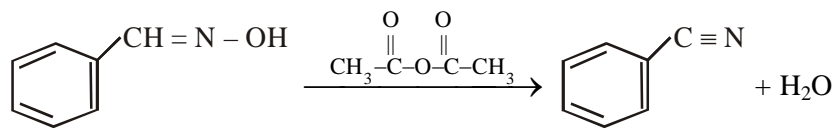
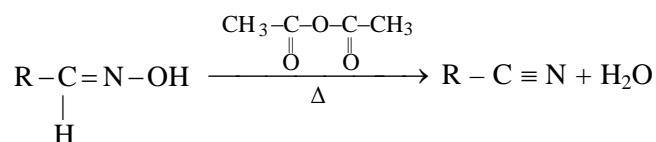
2) From Grignard Reagent

When chlorocyanogen is reacted with Grignard reagent, we get $\text{R}-\text{CN}$



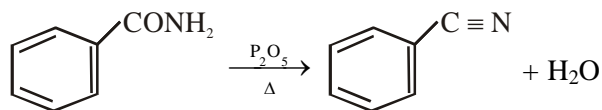
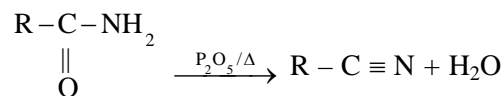
3) From Aldoximes

Aldoximes on dehydration with acetic anhydride give alkane nitrile



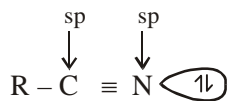
4) From Acid amides

Acid amides undergo dehydration to form alkyl cyanides



5) Physical properties

The structure of $R - C \equiv N$ consists of the carbon atom of the $-C \equiv N$ being sp - hybridized and also the nitrogen atom being sp - hybridized with a lone pair.



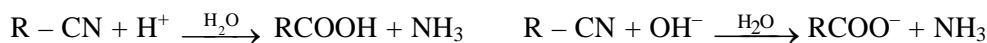
Due to higher electronegativity of Nitrogen when compared to carbon, both the σ - and π - electrons are displaced towards, nitrogen giving a very high dipole moment and making $R - C \equiv N$ highly polar and interactive forces are very strong. They have higher boiling points when compared to their corresponding isonitriles.

They have pleasant odour and are moderately soluble in water, due to H-bonding.

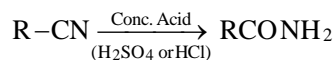
Chemical Properties

1) Hydrolysis

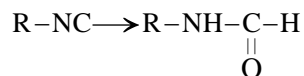
(a) All alkyl cyanides are hydrolysed to acids.



(b) Partial Hydrolysis. In the presence of concentrated acids, cyanides are partially hydrolysed to amides

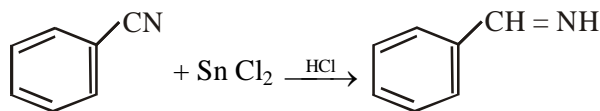
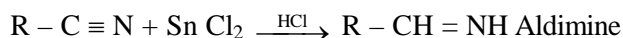


Partial hydrolysis of isonitriles give N-Alkyl amides.

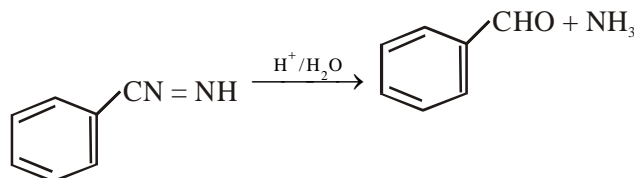
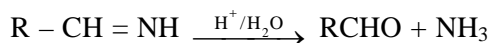


2) Reduction

a) Partial Reduction

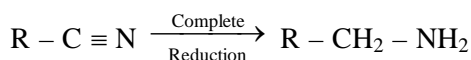


Aldimines on hydrolysis gives aldehydes



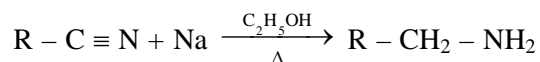
This complete reaction of nitriles to aldehydes is called **Stephen's reduction**.

b) Complete reduction



This can be achieved by using H_2/Ni , H_2/Pt , H_2/Pd , LiAlH_4 , or $\text{Na}/\text{C}_2\text{H}_5\text{OH}$

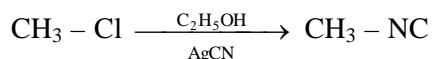
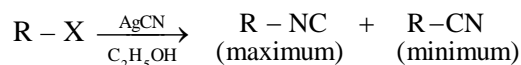
When $\text{Na} + \text{C}_2\text{H}_5\text{OH}$ is used the reduction is called **Mendius Reduction**.



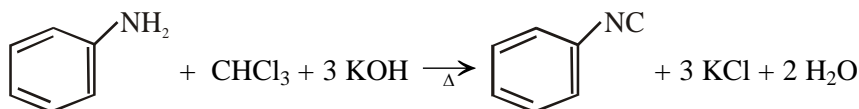
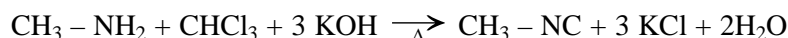
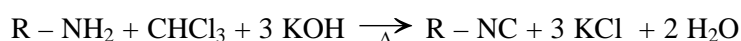
Isocyanide

Preparations :

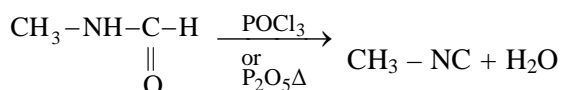
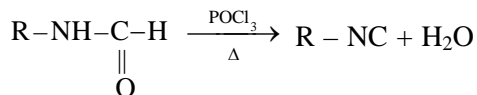
1) Alkyl halides



2) From Primary amines (Carbylamine Reaction)

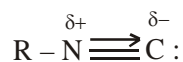


3) From N-alkyl Formamide



Properties :

All alkyl isocyanides are nonpolar.



The dipole moment of the σ -bond between nitrogen and carbon is exactly cancelled by the dipole moment of the π -bond between nitrogen and carbon. There by they are nonpolar.

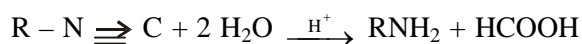
They are colourless and have unpleasant smell. They are insoluble in water but soluble in organic solutions.

They have low B.P. as compared to their corresponding cyanides.

Chemical Properties :

1) Hydrolysis

They are hydrolysed by dilute acids (and not by alkali) to 1°-amines and formic acids.



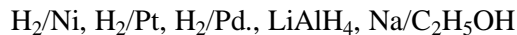
In the presence of concentrated acids they are partially hydrolysed.

Reductions

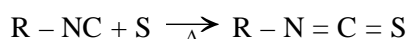
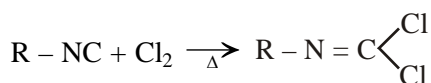
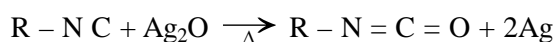
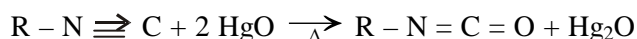
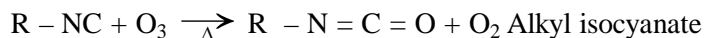
All isonitriles are reduced to s-amines i.e. N-methyl amines



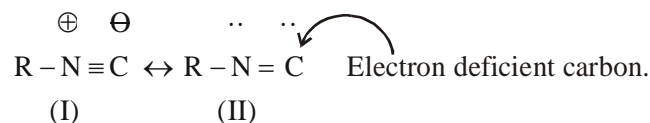
The reducing agents used are



Addition Reaction



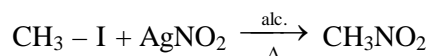
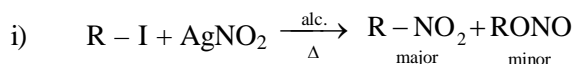
All these reactions are due to the resonance in RNC which makes carbon electron deficient for addition reaction.



Nitro Compounds

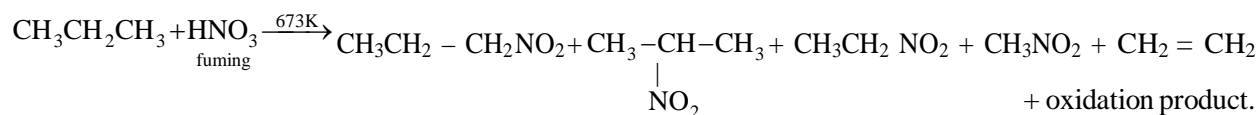
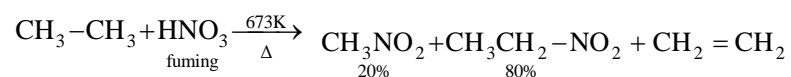
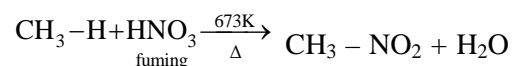
Preparations

1) From Alkyl halides

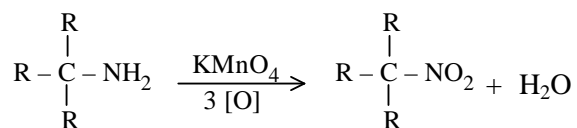


2) From Hydrocarbons

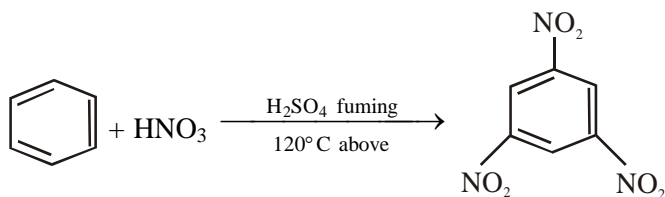
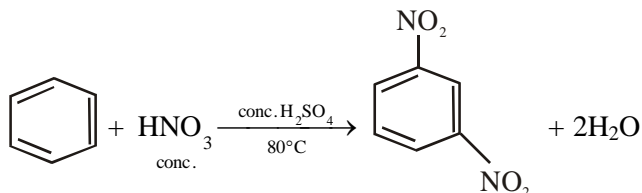
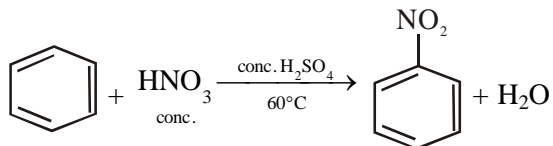
Lower Homologous of alkanes may be converted to nitro alkanes via vapour phase nitration. But here pyrolysis products are more.



They can also be prepared by the oxidation of 1°-amines.

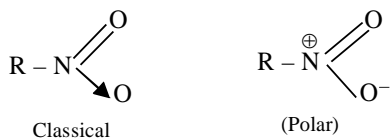


3. Aromatic nitro compounds.

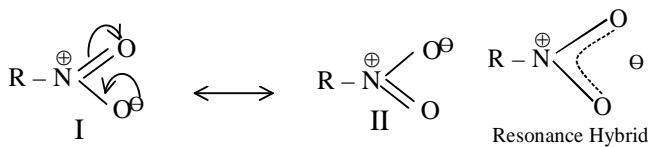


Structure

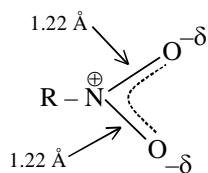
In terms of valence bond theory, the structure of nitroalkanes may be written as



The polar structure is supported by a large dipole moment of the nitro group. Thus nitroalkane is represented as a resonance hybrid of the canonical forms I and II.



The hybrid structure suggests the equivalence of the two nitrogen-oxygen bond as shown in

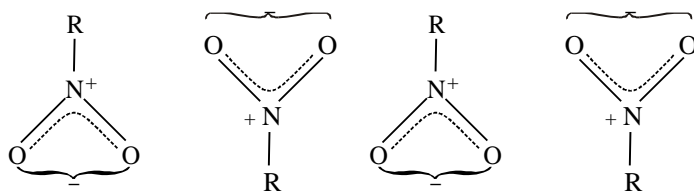


Physical Properties

- 1) The lower nitroalkanes are colourless pleasant smelling liquids at ordinary temperature.
- 2) Nitromethane is about 10 per cent soluble in water but the higher alkanes are practically insoluble. This shows that they are less soluble than alcohols to form hydrogen bonds.
- 3) Since they are polar molecules, nitroalkanes are useful solvents for polar and ionic compounds.
- 4) They have abnormally high boiling points.

e.g.	bp°C		bp°C
Nitromethane, CH ₃ – NO ₂	101	1-Nitropropane, CH ₃ CH ₂ CH ₂ – NO ₂	112
Nitroethane, C ₂ H ₅ – NO ₂	115	2-Nitropropane, (CH ₃) ₂ CH – NO ₂	120

This is explained by the fact that nitroalkanes are highly polar compounds as shown by their high dipole moments (3.6 D). Due to the appreciable electrostatic attraction between the polar molecules, they need a larger amount of energy (heat) in order to separate them.



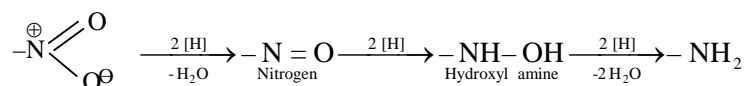
Nitroalkanes have much higher boiling points than the less polar isomeric alkyl nitrites (CH₃ – O – NO, bp – 12°; C₂H₅ – O – NO, bp 17°)

- 5) They are less toxic than isomeric nitrites and aromatic nitro compounds.

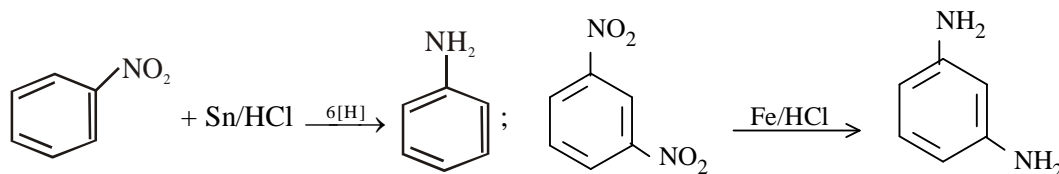
Chemical Properties

1) Reduction

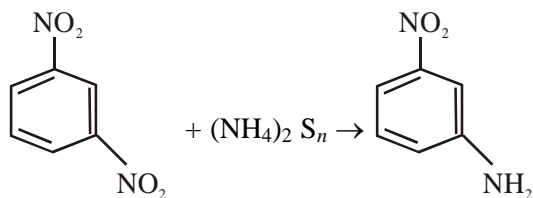
General Reduction : The general reduction sequence can be written as follows :



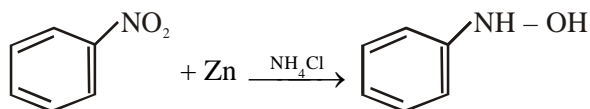
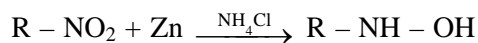
- a) In strongly acidic medium using metals, complete reduction takes place. The metals which may be used are Sn, Zn, or Fe. e.g.



However when ammonium polysulphide is used then selective reduction of one NO₂ group takes place

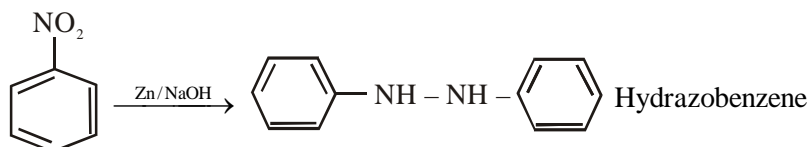
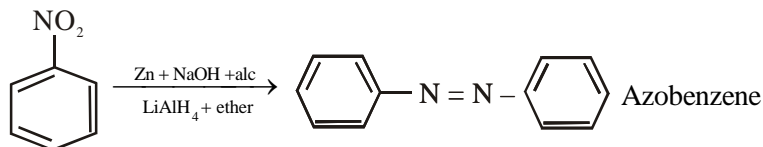
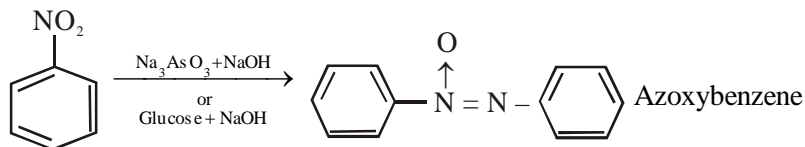


b) In weakly acidic medium

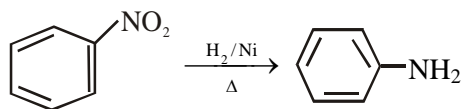
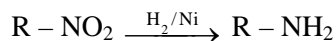


The hydroxylamine when warmed with Tollen's reagent are oxidised to nitrogen compounds and hence hydroxyl amine reduces Tollen's reagent. The hydroxyl amines are also oxidised by per acids to the nitro compounds.

c) In Alkaline Medium



d) Catalytic Reduction

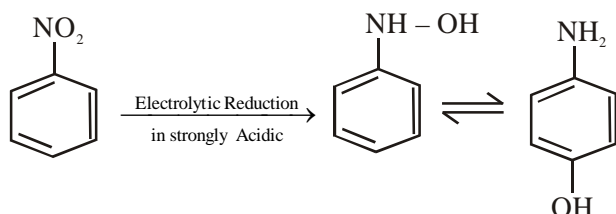


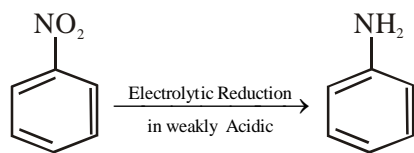
However with excess of hydrogen nitrobenzene can be converted to nitrocyclohexane.

e) Reduction with metal hydrides



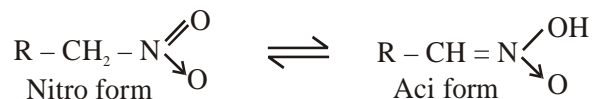
f) Electrolytic Reduction :





2) Tautomerism

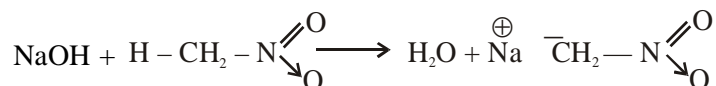
Nitroalkanes containing α -hydrogen atoms show tautomerism



The nitro form is called pseudo acid form whereas the Aci form is nitrolic acid.

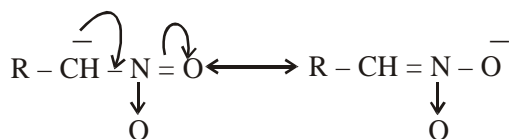
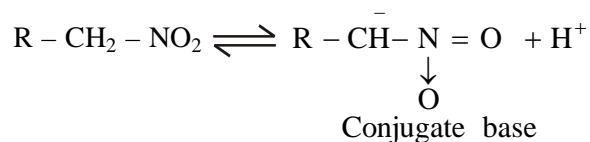
3) Acidic Character

The acidic character of α -H atom in 1° and 2°-nitroalkanes.



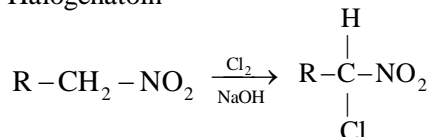
The main reason for the acidic character of 1° and 2° nitroalkanes is

- Hyperconjugating H-atom with NO_2 group
- Helped by strong electron withdrawing $-\text{NO}_2$ group.
- Resonance stabilization of conjugate base

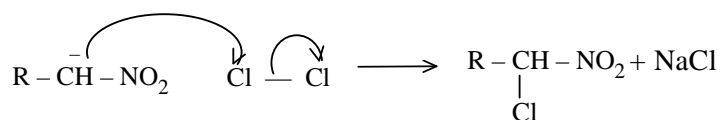
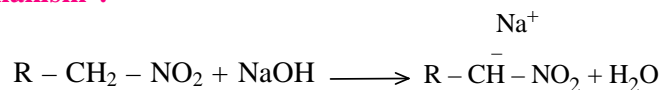


4) Application of acidic character

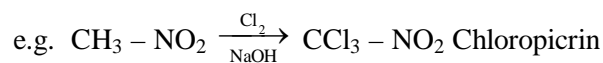
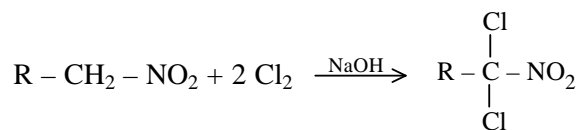
- Halogenation



Mechanism :

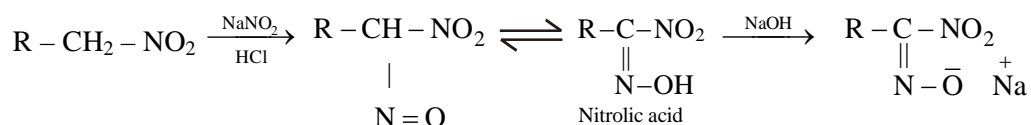


These steps are repeated to get the dichloro nitroalkane i.e.

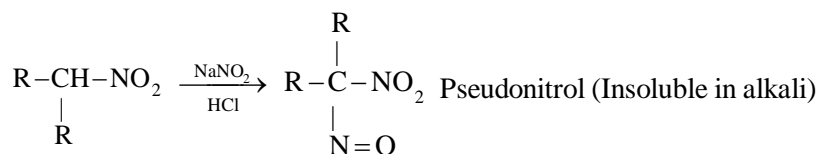


6) Reaction with Nitrous acid (HNO₂)

- i) p-Nitroalkanes give a blue nitroso-nitroalkane which in the presence of NaOH produces a soluble sodium salt having red colouring



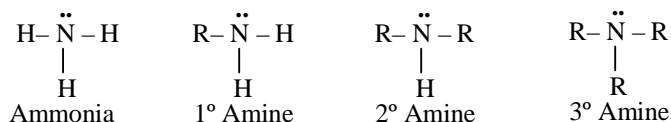
- ii) A secondary nitroalkane gives a blue nitroso derivative which no more contains replaceable H-atom and is therefore insoluble in alkali.



tetra-Nitro compounds do not react with nitrous acid as it does not have any reactive hydrogen atom on the α -carbon atoms.

Amines

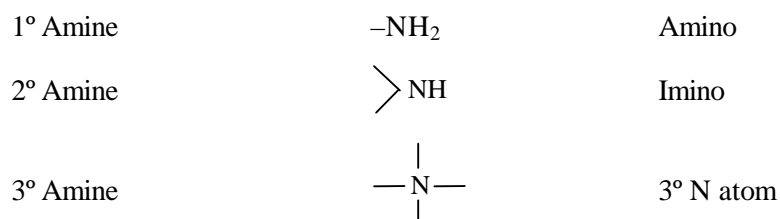
Amines are regarded as derivatives of ammonia, and are classified into 1°, 2° and 3° amines depending upon the number of hydrogen atoms of ammonia replaced by alkyl or aryl groups.



These may be aliphatic or aromatic depending upon the group attached with -NH₂ group.



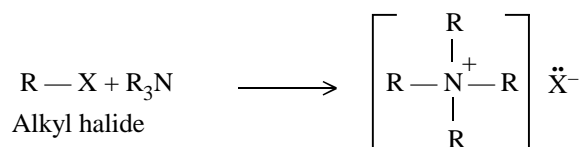
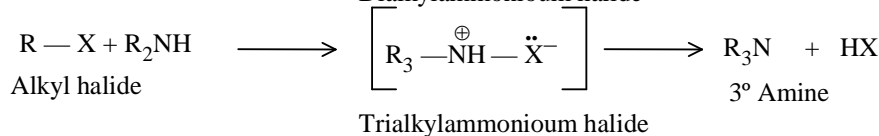
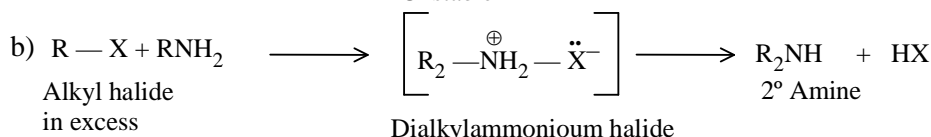
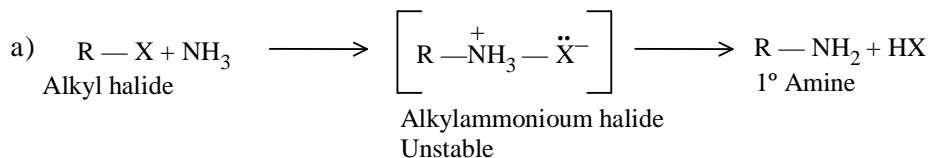
The functional groups present in amines are :-



Methods of preparation :

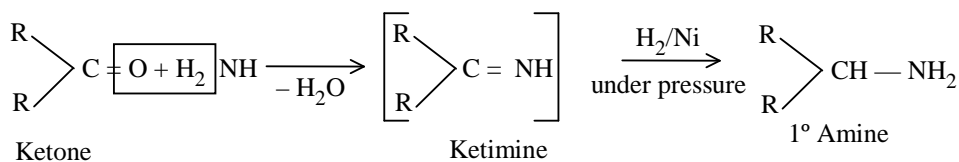
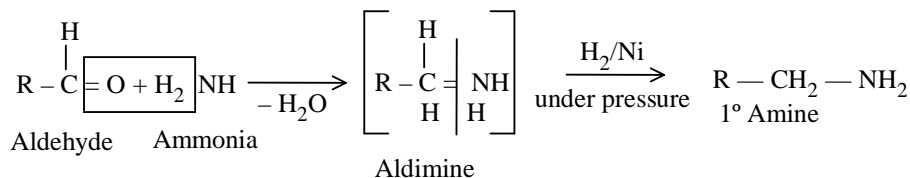
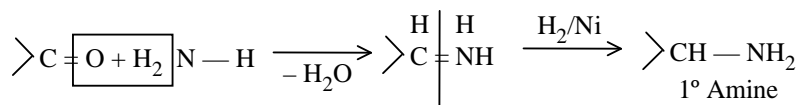
(1) From alkyl halides (Hoffmann's ammonolysis).

On heating alkyl halides with alc. NH_3 in a sealed tube at 100°C , a mixture of 1° , 2° , 3° amines and quaternary ammonium salt is formed.

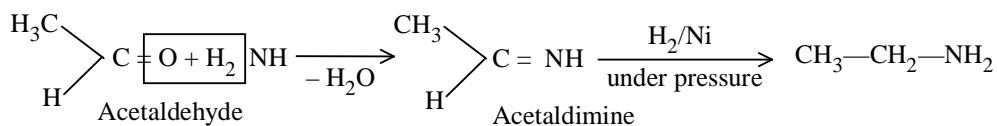


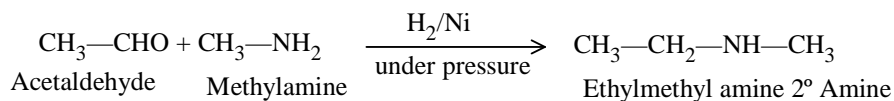
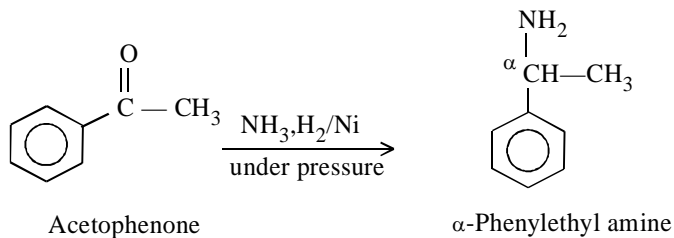
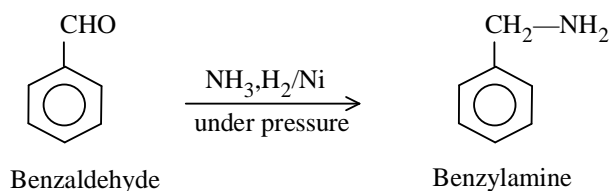
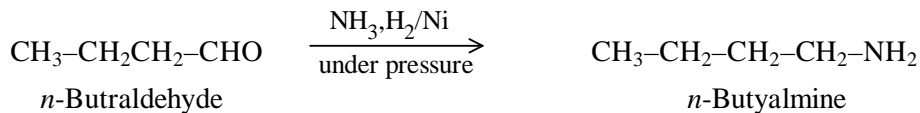
Quaternary ammonium salt (Tetraalkyl ammonium halide)

(2) **By reductive amination.** On treating carbonyl compounds (>C=O) (aldehydes and ketones) with NH_3 , followed by treatment with H_2 in presence of Ni under pressure, 1° amine is formed. This reaction is known as reductive amination.

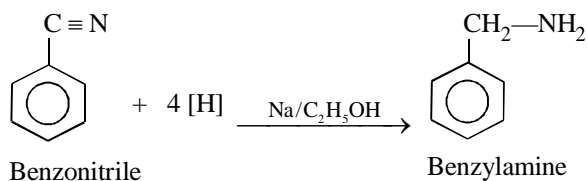
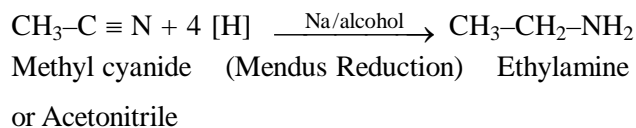
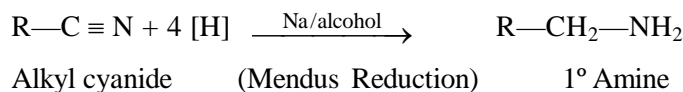
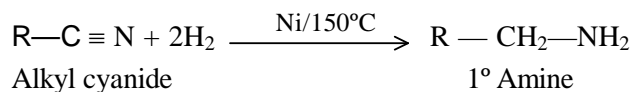


e.g.

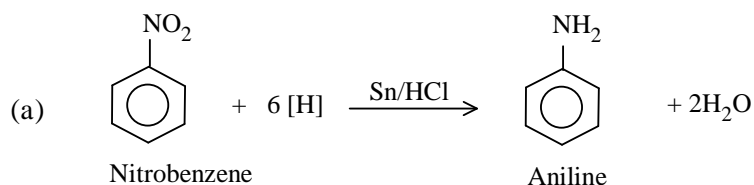




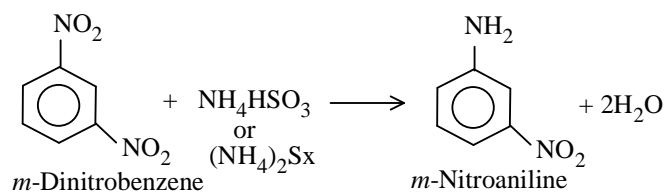
(3) By reduction of acid nitriles.



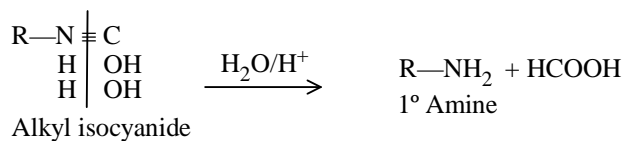
(4) By the reduction of nitro compounds.



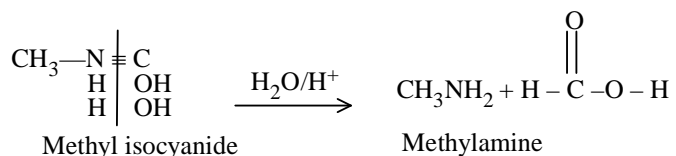
(b) **Selective reduction.**



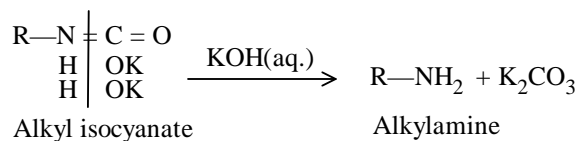
(5) **By hydrolysis of isocyanides (Complete hydrolysis with dilute acids)**



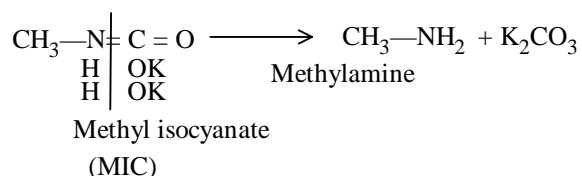
e.g.



(6) **From isocyanates.**

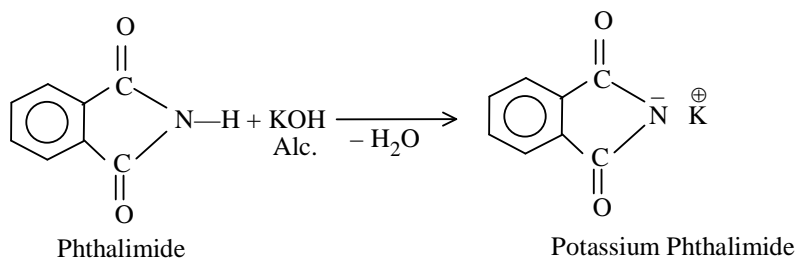


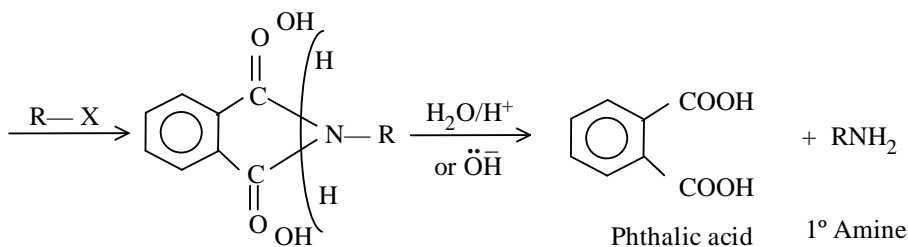
e.g.



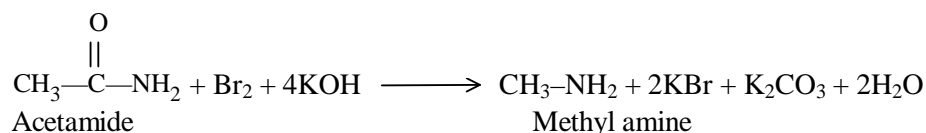
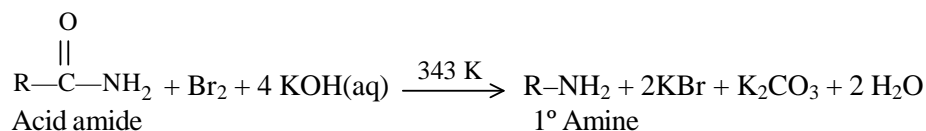
(7) **By Gabriel's phthalimide synthesis.**

This reaction can be employed to synthesize either aliphatic 1° amine or aralkyl amine such as benzylamine. But aniline cannot be prepared by this method.

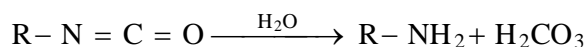
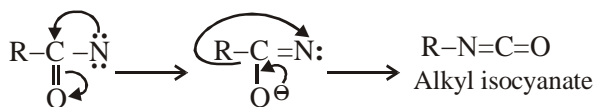
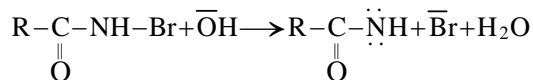
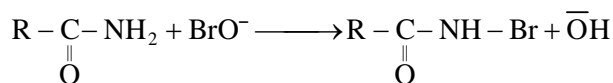




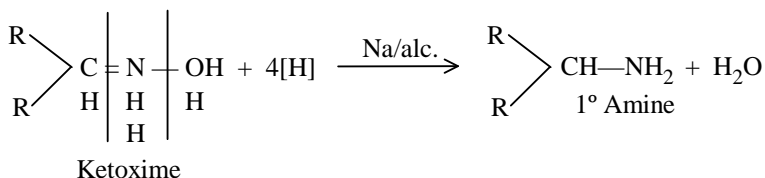
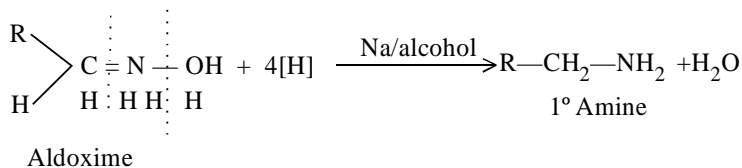
- (8) **By Hoffmann's bromamide degradation reaction.** On treating acid amides (aliphatic or aromatic) with liquid aqueous solution of alkali at 343 K a primary amines containing lesser number of carbon atoms is obtained. This reaction is employed for stepping down the series. This is also called as Hoffmann's rearrangement.



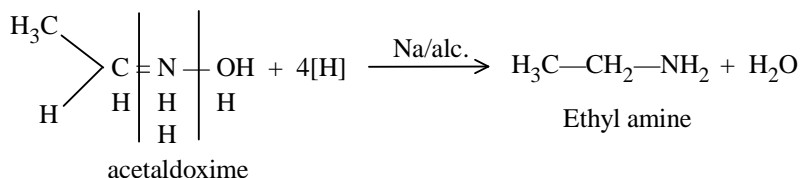
Mechanism



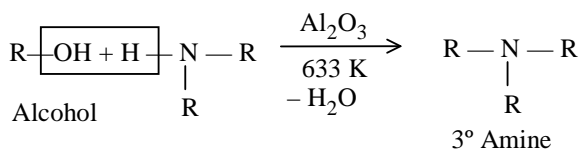
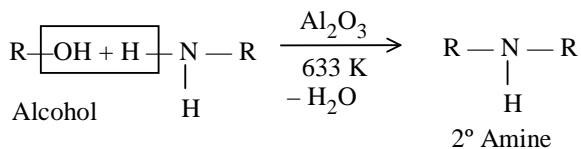
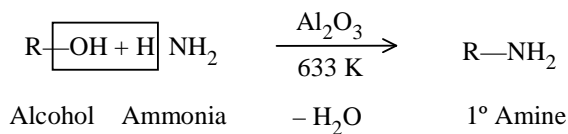
- (9) **By reduction of aldoxime.** Primary amines can be prepared by reduction of oximes of aldehydes and ketones with lithium aluminium hydride or with sodium/alcohol.



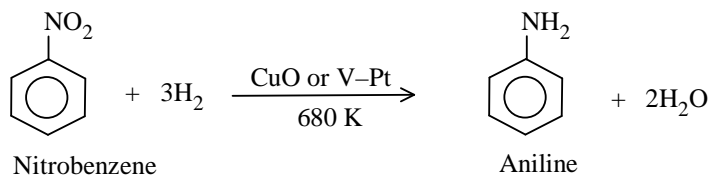
e.g.



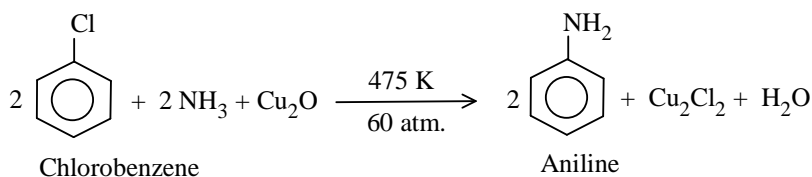
(10) From alcohols (Industrial method for aliphatic amines generally).



(11) From Nitro-derivatives (Industrial method for aromatic amines generally).

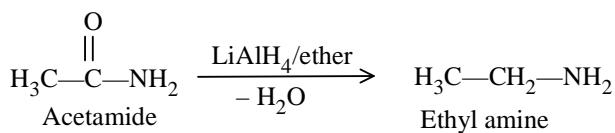
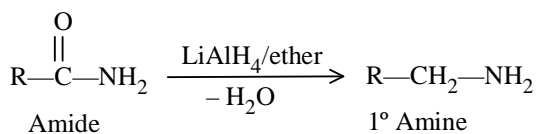


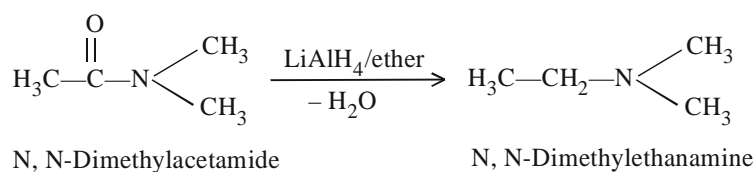
(12) From chlorobenzene.



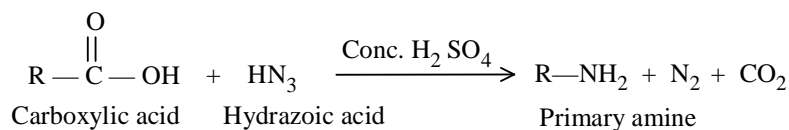
This is called as **Dow's process**.

(13) From amides : Primary, secondary and tertiary amines can be prepared by reduction of the corresponding amides with lithium aluminium hydride.

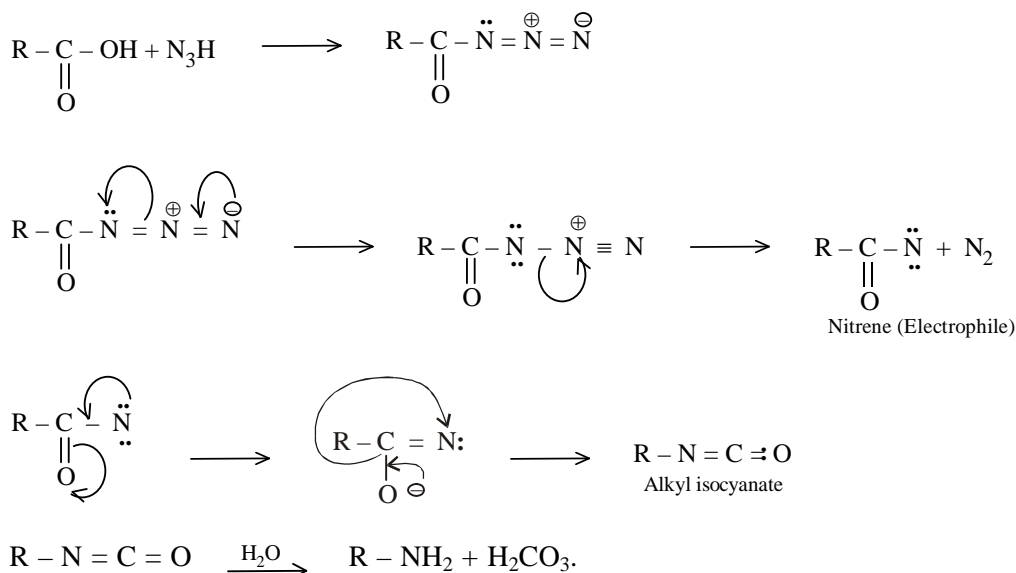




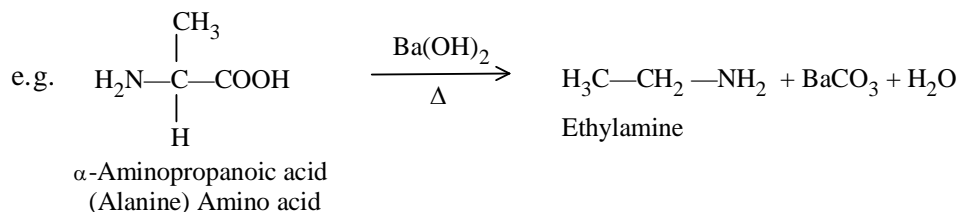
(14) **Schmidt reaction.** The carboxylic acid on treatment with hydrazoic acid in the presence of H^+ ions forms primary amines and the reaction is known as **Schmidt reaction**.



Mechanism :



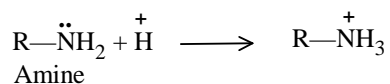
(15) **From α -amino Carboxylic acids.** All α -amino carboxylic acids on decarboxylation in the presence of Barium hydroxide gives 1° -amine.

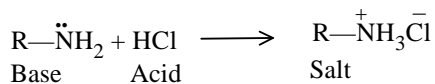


Chemical Properties :

1. Basic nature of amines. All amines are basic in nature. Their basic nature can be proved by the following observations.

- These turn red litmus blue.
- A lone pair of electrons is available on N atom for sharing with a proton, therefore, they are basic in nature.

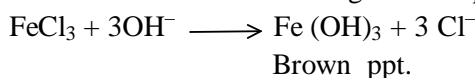
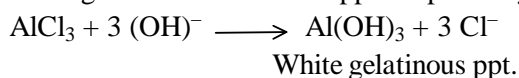




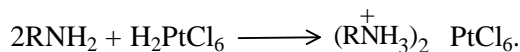
(iii) Amines give OH^- ions in aqueous solution.



The presence of hydroxide ions can be tested in laboratory by adding AlCl_3 or FeCl_3 solution with which they form white gelatinous and brown ppt. respectively.



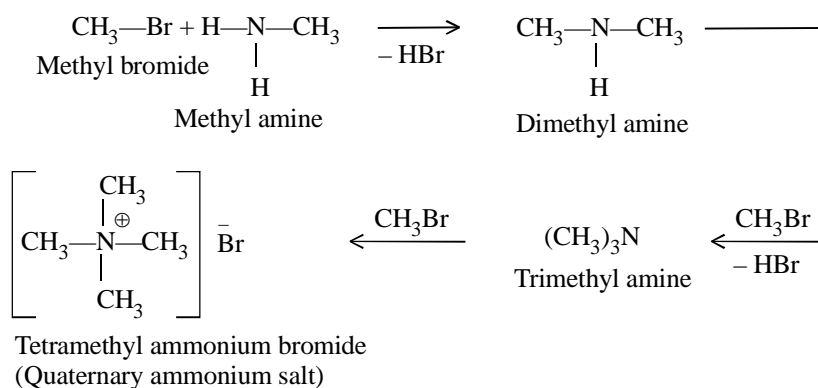
(iv) Amines react with chloroplatinic acid (H_2PtCl_6) to form insoluble salts called Chloroplatinates.



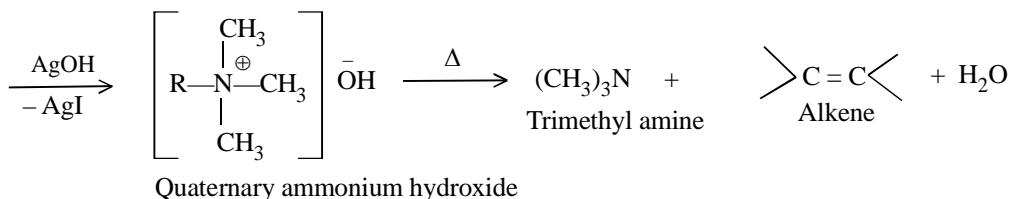
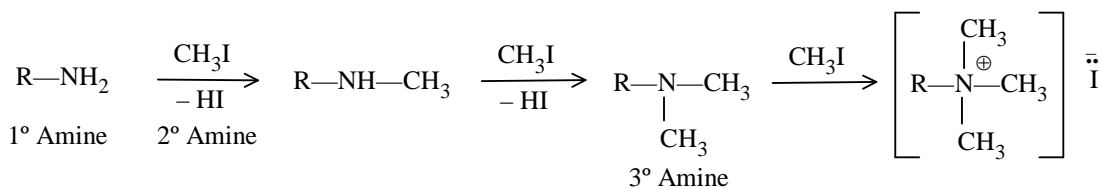
This is the method used for determining the equivalent weight of an amine. (Platinichloride Method).

2. Alkylation. All the three types of amines undergo alkylation when treated with alkyl halide.

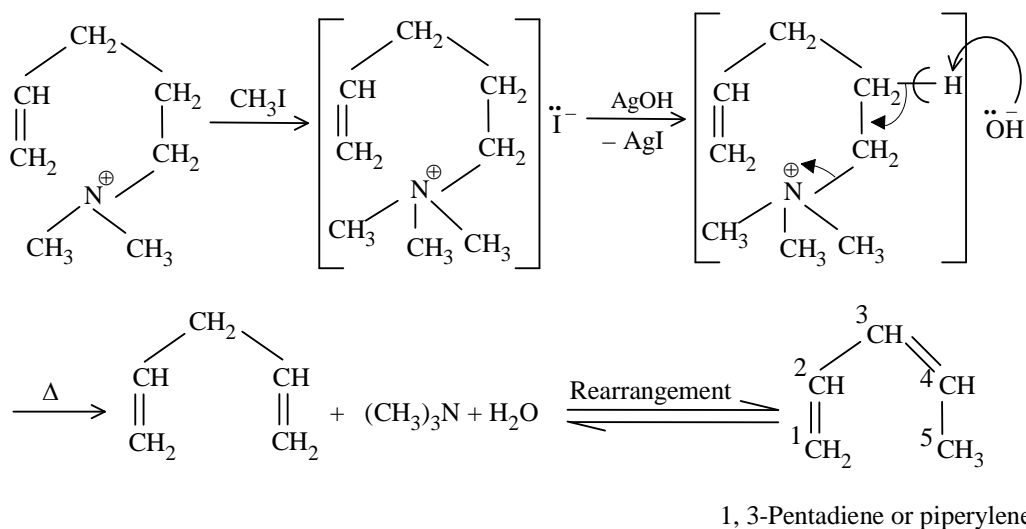
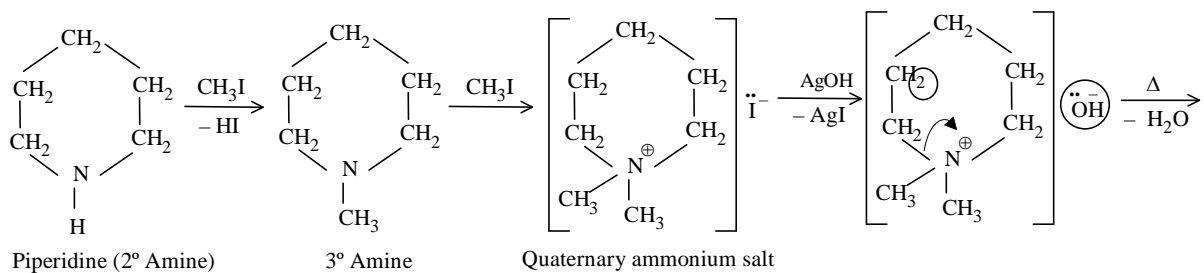
(a) **Aliphatic amines.**



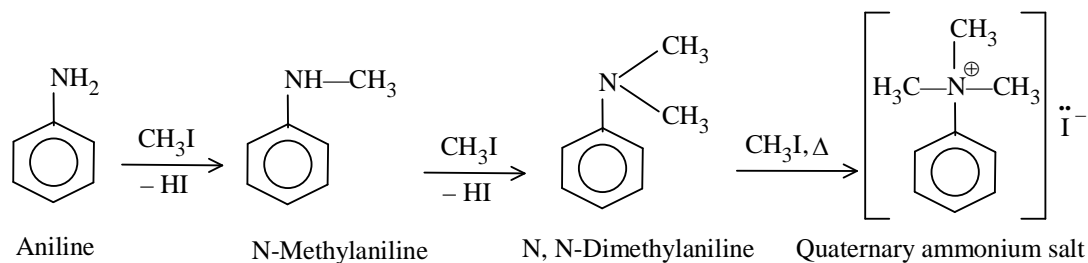
Exhaustive alkylation and Hoffmann elimination. The reaction of amines with excess of alkyl halide to form a quaternary ammonium salt is known as exhaustive alkylation and if the alkyl group is methyl, then it is known as exhaustive methylation. The exhaustive methylation of amine followed by treatment with moist silver oxide ($\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{AgOH}$) and subsequent heating to form alkene is known as **Hoffmann elimination**.



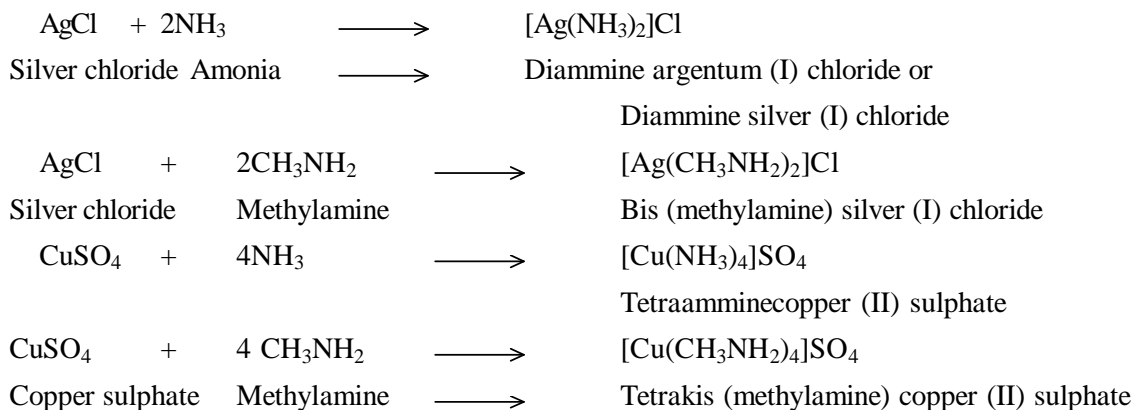
Importance of Hoffmann elimination. This reaction can be used to determine the structure of amines especially in complex molecules such as **alkaloids**.



(b) Aromatic amines.

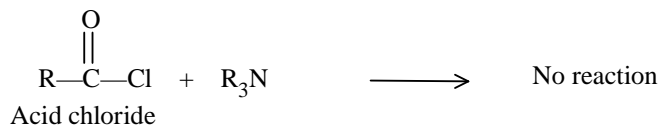
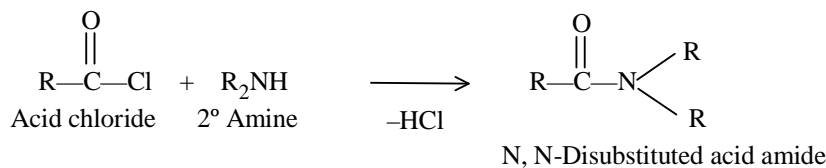
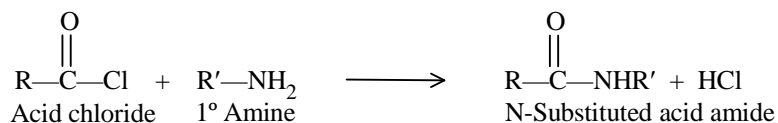


3. Reaction with metal ions. Amines form co-ordination compounds with metal ions such as Ag^+ , Cu^{+2} etc.

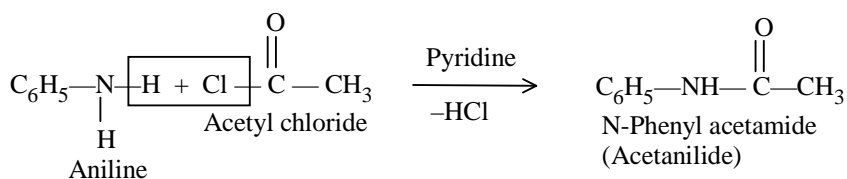


4. Acylation

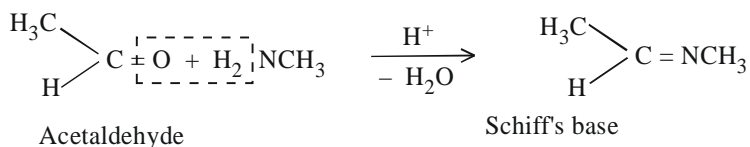
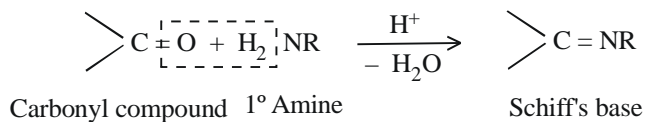
(a) Aliphatic amines.



(b) Aromatic amines.

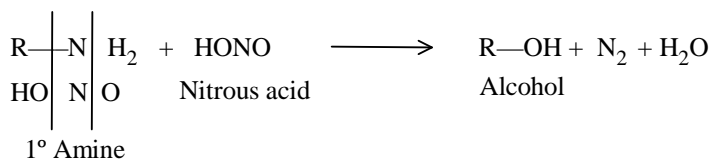
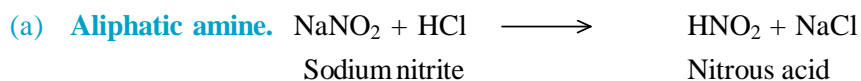


5. **Reaction with aldehydes and ketones.** Aldehydes and ketones react with primary amines to form Schiff's bases.

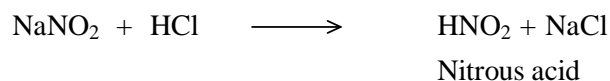


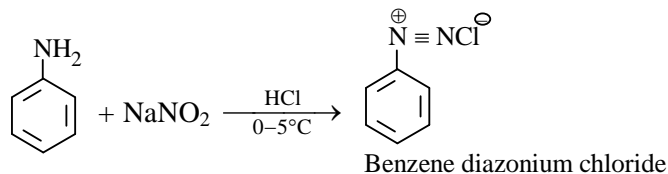
6. **Reaction with nitrous acid.** All amines react with nitrous acid to give different products. Since nitrous acid is an unstable molecule, therefore, it is always produced in situ.

(i) Primary amine

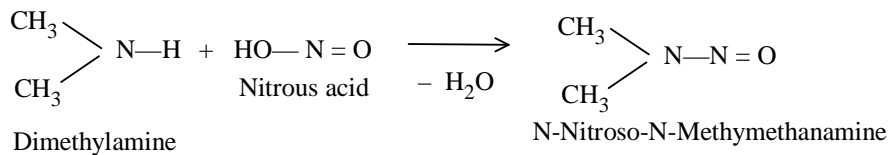


(b) Aromatic amine.

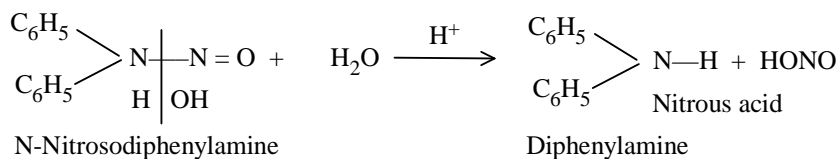




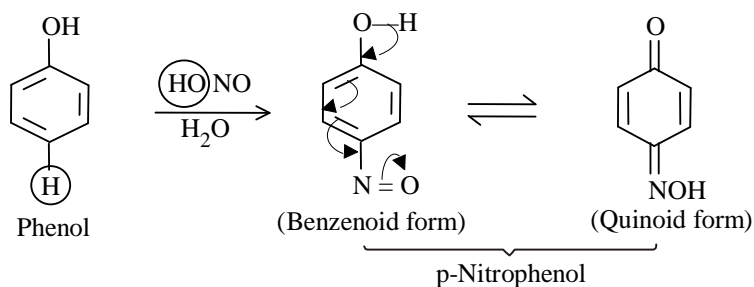
(ii) **Secondary amine.** Both aliphatic and aromatic amines forms nitrosoamines*



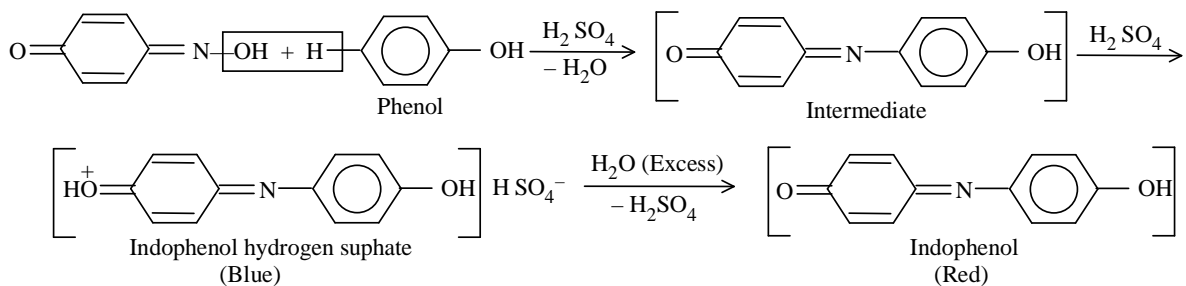
Nitrosoamine formed above, on treatment with acid such as H_2SO_4 , gives the original 2° amine and nitrous acid.



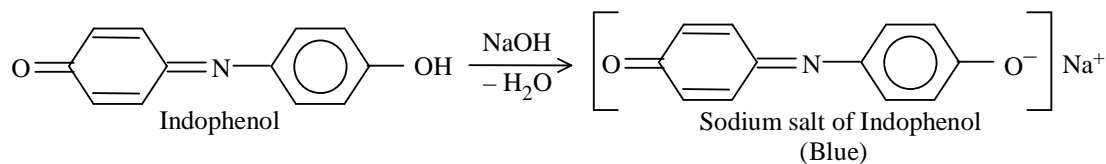
Nitrous acid react with phenol to form p-Nitrosophenol which is tautomeric with monoxime of quinone.



Quinoid form of p-Nitrosophenol then condenses with another molecule of phenol to give indophenol hydrogen sulphate (blue) which on dilution changes to indophenol (red).

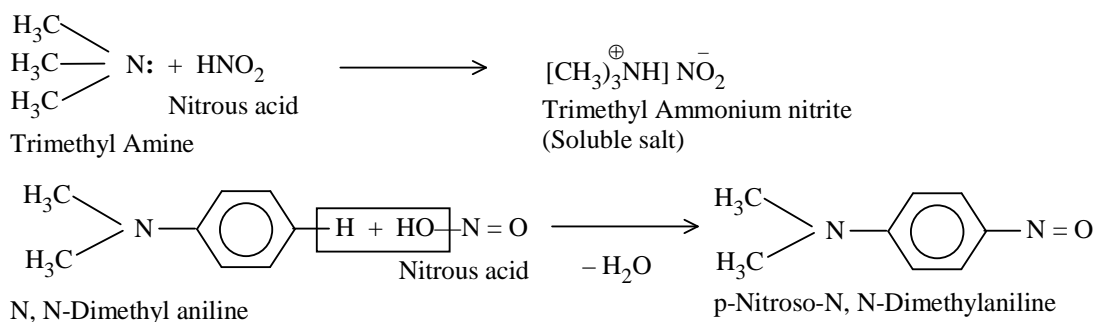


with excess of NaOH , sodium salt of Indophenol is produced which is blue in colour.



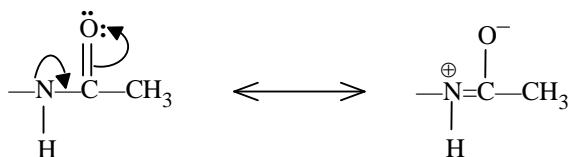
This is what is called the Liberman nitroso reaction.

(iii) **Tertiary amine.**



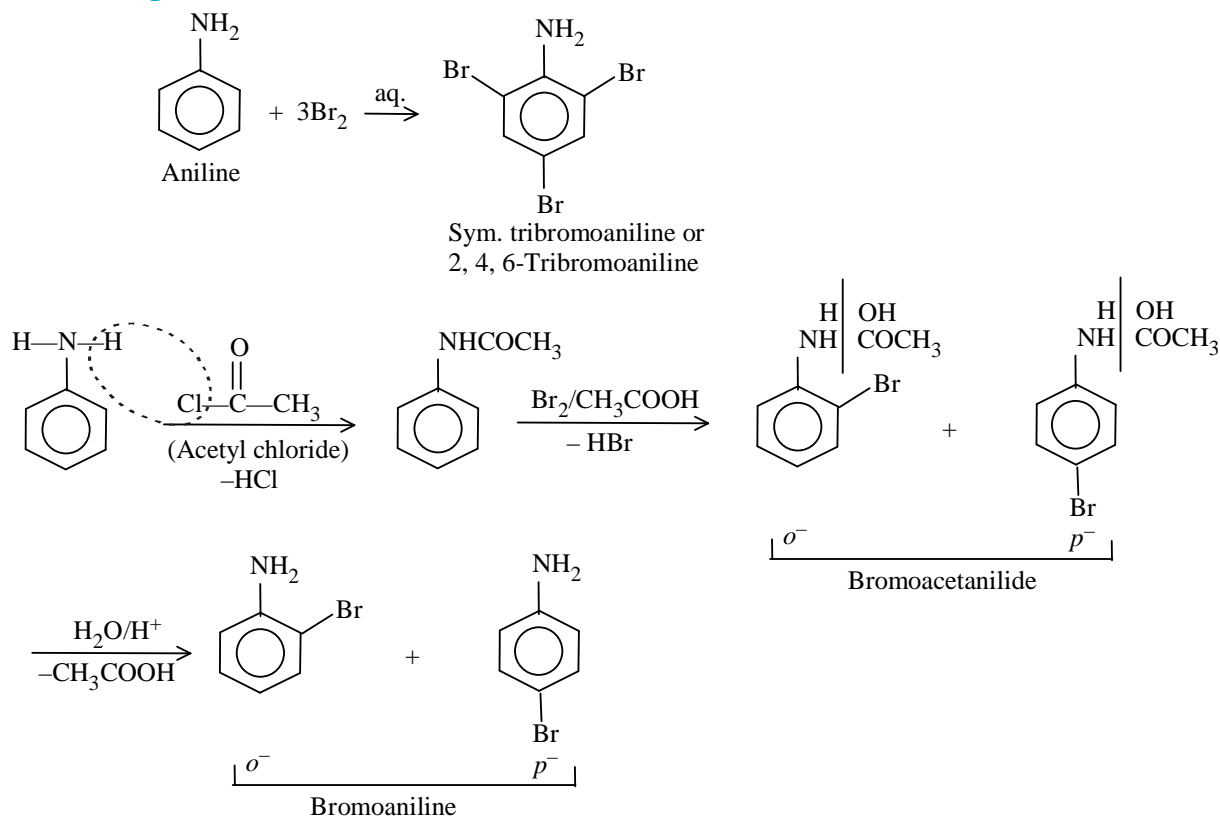
7. **Electrophillic substitution reactions (Reactions due to benzene nucleus).** Aniline undergoes electrophilic substitution reactions, more readily than benzene, because, amino group increases electron density on benzene ring, therefore, attack of electrophile takes place at a faster rate in aniline than in benzene. Electron density increases more at o- and p-positions, therefore, $-\text{NH}_2$ group is o- and p-directing in nature.

$-\text{NH}_2$ group activates the ring so much that the reaction always proceeds to tri-substituted stage (2, 4, 6-stage) even in the absence of catalyst. But sometimes we require monosubstitution product, then, in order to get monosubstituted product, activating power of $-\text{NH}_2$ group is reduced by changing it into acyl derivatives. Acyl group being electron withdrawing in nature decreases electron density on N atom of amines.

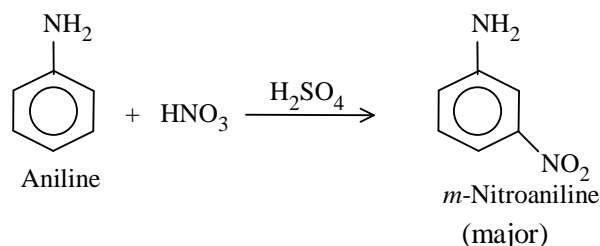


This is called as protection of amino group.

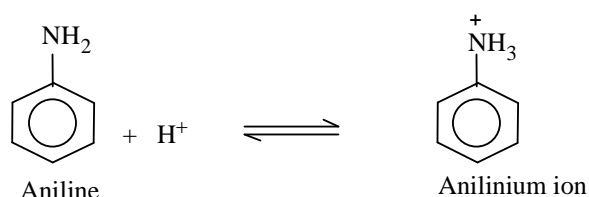
(i) **Halogenation.**



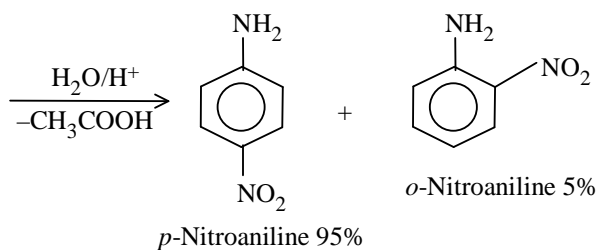
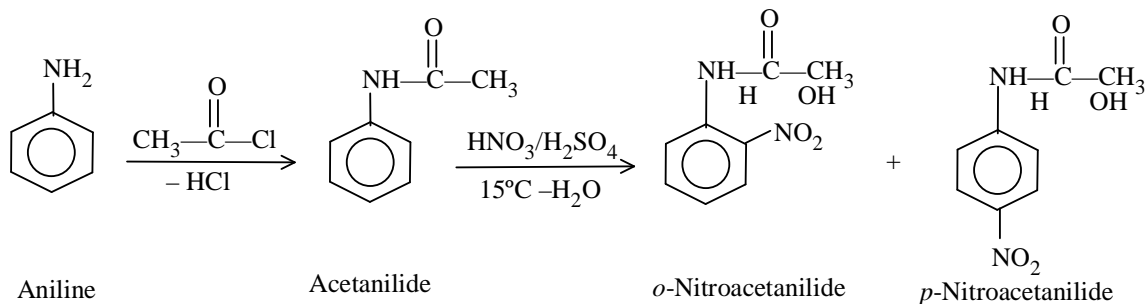
- (ii) **Nitration.** HNO_3 is a strong oxidising agent as well as a nitrating agent also. Therefore, if we add HNO_3 straight away to aniline, a tarry (sticky) oxidation product (a small amount of *m*-Nitroaniline) is also formed.



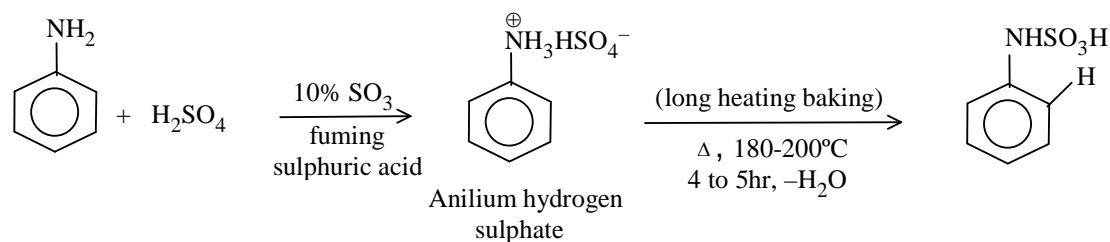
Undoubtedly $-\text{NH}_2$ group is ortho and para directing but in acidic medium like HNO_3 and H_2SO_4 it becomes meta directing as $-\text{NH}_2$ combines with H^+ ion to form anilinium ion ($\text{C}_6\text{H}_5 - \text{NH}_3^+$) The NH_3^+ group being electron withdrawing in nature is *m*-directing in nature.

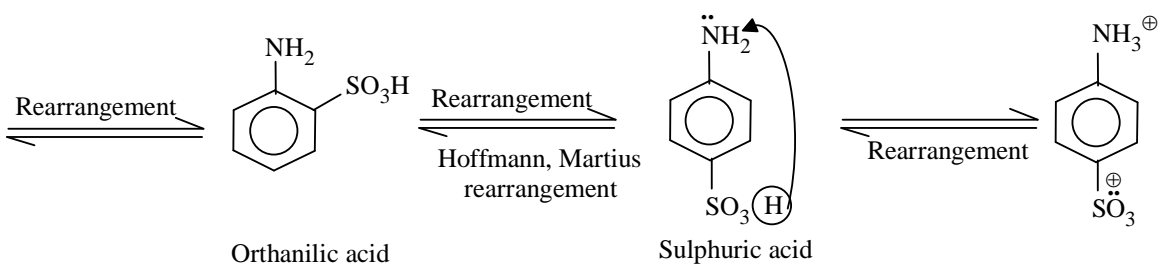


To avoid the formation of *m*-Nitroaniline nitration is never done directly. Instead it is done in steps as follow :

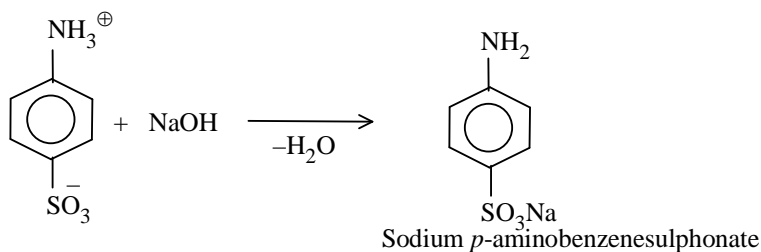


- (iii) **Sulphonation.**



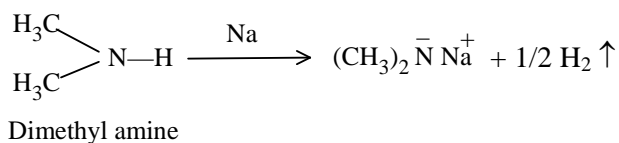
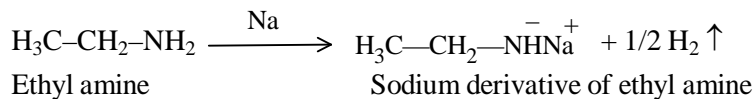


Sulphanilic acid exist as Zwitter ion which is amphoteric in nature i.e., it can behave as an acid as well as a base. Sulphanilic acid is insoluble in water, acids and organic solvents but is soluble in alkalis due to formation of sodium salts.

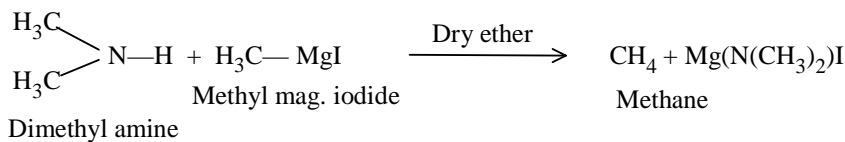
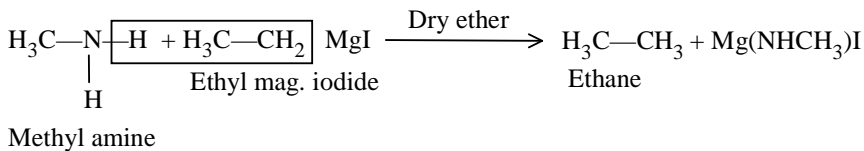
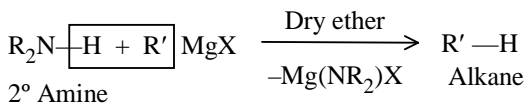
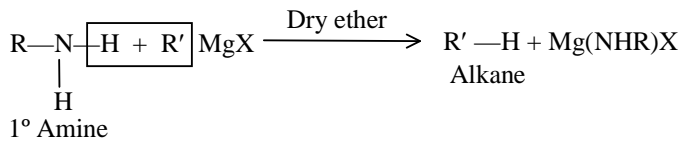


8. Miscellaneous reactions.

- (i) **Reaction with Sodium.** 1° and 2° amines evolves H_2 gas with sodium. This indicates acidic nature of amines.

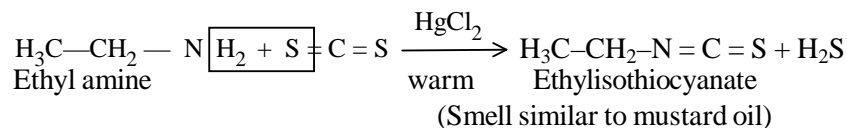
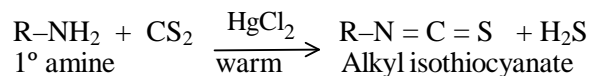


- (ii) **Reaction with Grignard's reagent.** Primary and secondary amines react with Grignard's reagent to form alkanes.



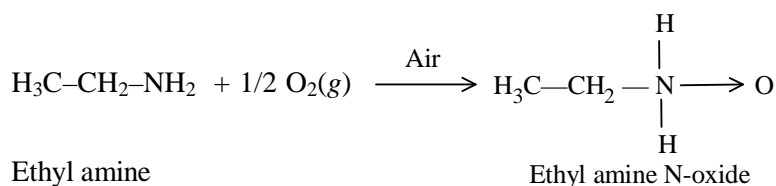
(iii) **Reaction with carbon disulphide.**

(a) **Aliphatic amines.**

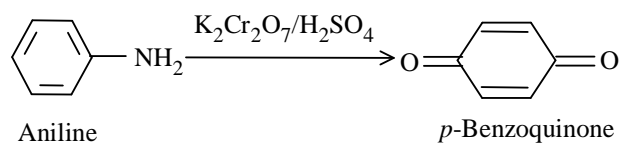


This reaction is known as **Hoffmann's mustard oil reaction.**

(iv) **Oxidation.** Aliphatic amines are slowly oxidised by air to give N-oxides.



Under controlled conditions, oxidation of aniline with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ gives *p*-Benzoquinone.



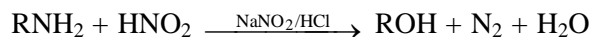
Aniline give different colours by using different oxidising agents.

Oxidising agent	Colour produced
Bleaching powder	Deep violet
$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Conc. H}_2\text{SO}_4$	Intense blue
$\text{K}_2\text{Cr}_2\text{O}_7 + \text{CuSO}_4 + \text{dil. H}_2\text{SO}_4$	Aniline black dye

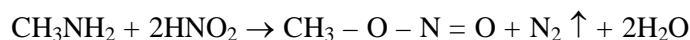
Distinction between primary, secondary and tertiary amines

1. Nitrous acid test.

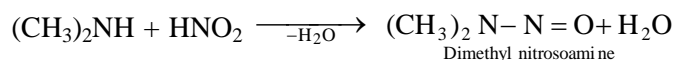
Primary amines: Alcohols are produced with the liberation of N_2 .



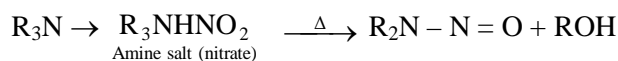
CH_3NH_2 is an exception to this reaction.



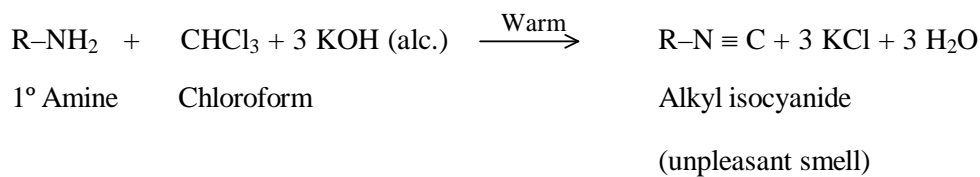
Secondary amines: They produce nitrosoamines which is a reddish yellow oily compound.



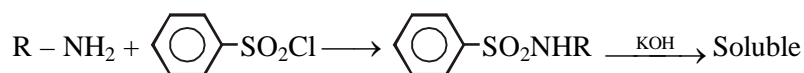
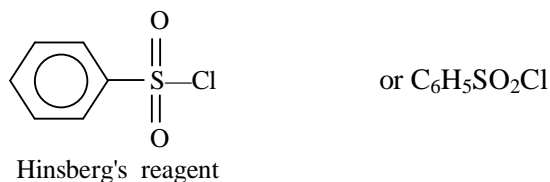
Tertiary amines: These dissolve in cold HNO_2 and form unstable nitrate salt with no visible sign of evolution of N_2 or any yellow colour. These salts on heating give nitrosoamine and alcohol.



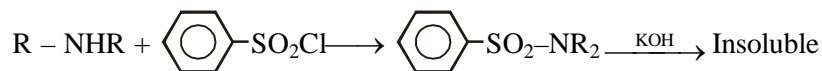
2. **Carbylamine test.** This test is given by primary amines only (both aliphatic and aromatic).



3. **Hinsberg's test.** Benzene sulphonyl chloride is called as Hinsberg's reagent.



1° amine



2° amine

3° amine do not react with benzene sulphonyl chloride

4. **Hoffmann's method.** In this method the amine mixture is treated with diethyl oxalate which gives a solid oxamide with a primary amine, a liquid oxamic ester with a secondary amine while tertiary amine does not react.

