



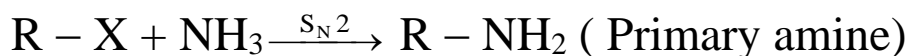
ORGANIC COMPOUNDS CONTAINING NITROGEN

AMINES

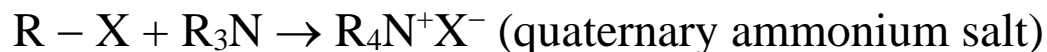
Amines are the derivatives of ammonia obtained by replacement of H atoms by any alkyl or aryl groups.

METHODS OF PREPARATION OF AMINES

(I) By alkylation of NH_3

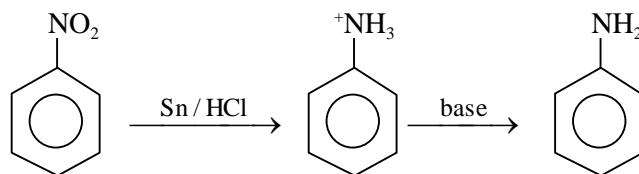


But usually we get a mixture of different amines due to further alkylation.

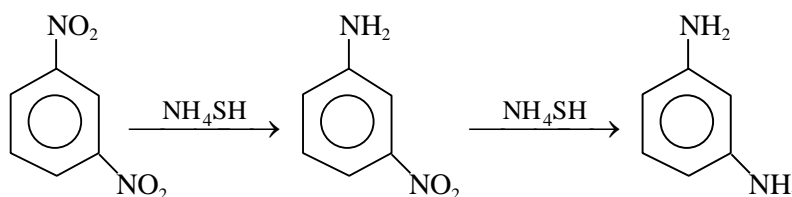




(II) By Reduction of Nitro compounds



If two nitro groups are present at Meta positions to each other, one of them can be reduced by selective reduction. For this purpose we use NH_4SH or $(\text{NH}_4)_2\text{S}$ or H_2S in NH_3 .



(only one NO_2 is reduced at a time)

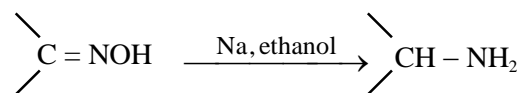
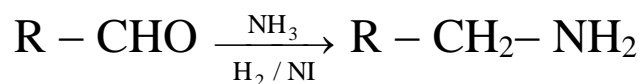
(III) By Reduction of nitriles and isocyanides



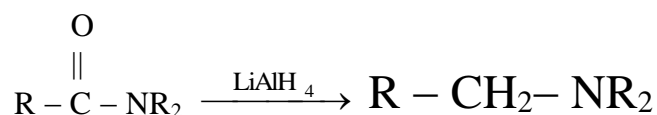
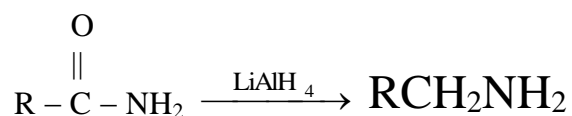
(Primary amine)



Methyl substituted amine

**(IV) By Reduction of oximes****(V) By Reductive amination of carbonyl compounds****(VI) From Amides**

Reduction of amides produces corresponding amines with same number of carbon atoms.



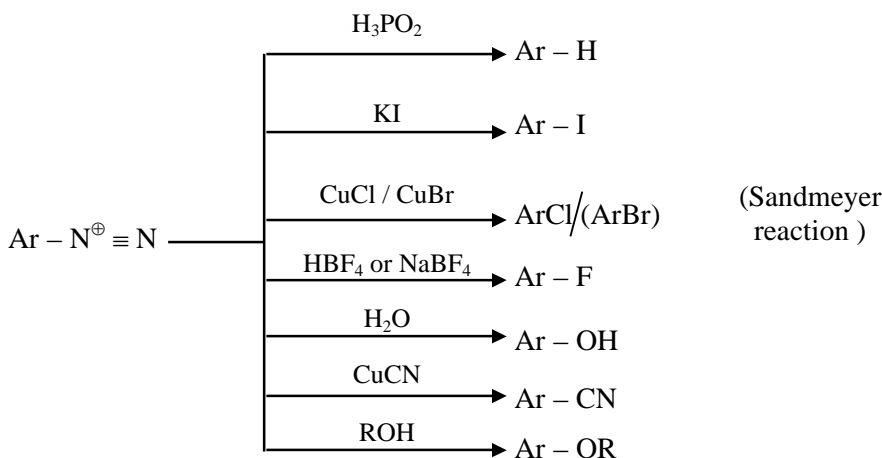
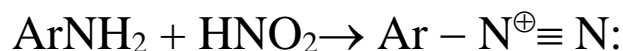
Amines (only primary) can also be prepared by Hoffmann degradation. In this method the



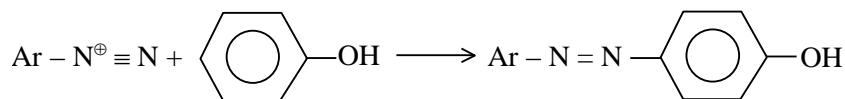
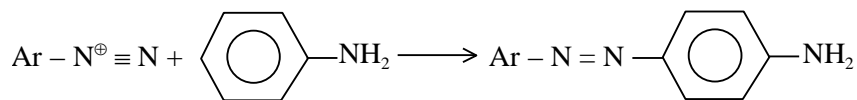
REACTIONS OF AMINES

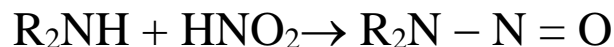
(I) With Nitrous Acid (Distinguishes different amines)

(i) **Primary Amines:** Primary amines react with nitrous acid to produce diazonium ion as follows.



Diazonium ions of aromatic amines also undergo coupling reaction with aromatic rings having a strong activating group to form diazo compounds.



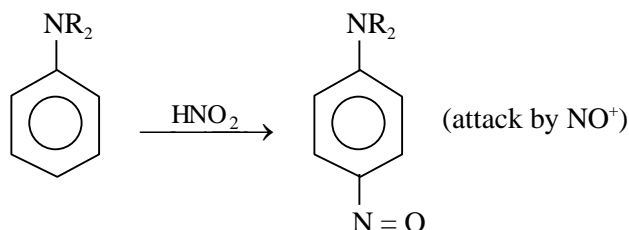
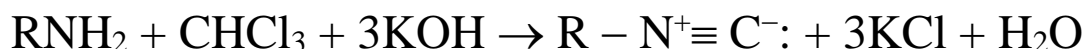
**(ii) Secondary Amines:**

N-Nitrosoamine

(Insoluble in amine)

(iii) Tertiary Amines:

Tertiary amines except N, N-Dialkylaryl amines do not react with HNO_2 .

**(II) Carbylamine Reaction (Only Primary amines)**

an isocyanide

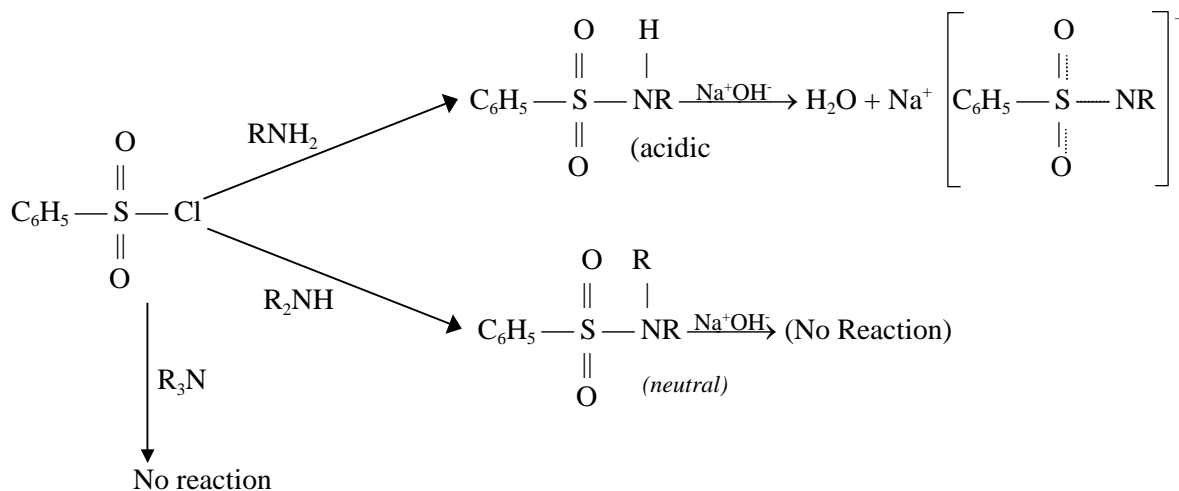
(foul smelling)

Nucleophilic RNH_2 attacks electrophilic intermediate
[$:CCl_2$]

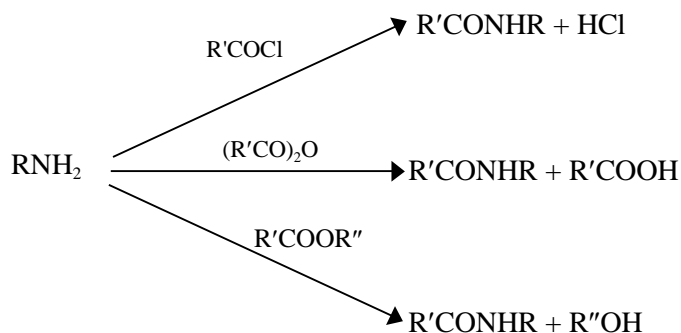
This reaction is used for the detection of primary amines.



(III) Hinsberg's reaction

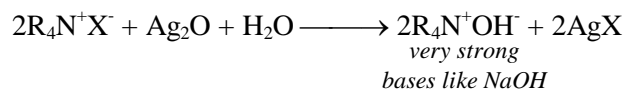


(IV) Reaction with Carboxylic Acid Derivatives



(V) Reactions of Quaternary Ammonium Salts

(i) Formation of 4° Ammonium Hydroxides



(ii) Hofmann Elimination of Quaternary ammonium Hydroxides

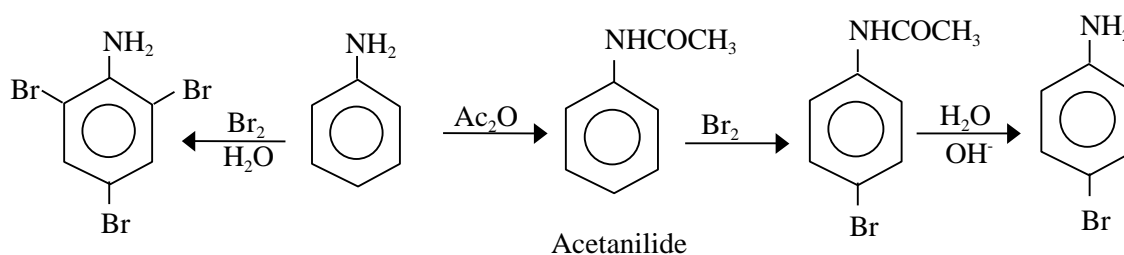


(VI) Ring Reactions of Aromatic Amines

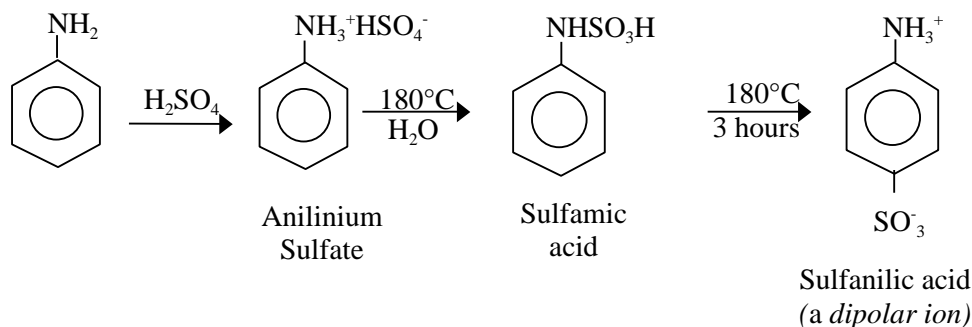
NH_2 , $-\text{NHR}$ and $-\text{NR}_2$ strongly activate the benzene ring toward electrophilic substitution.

(i) Halogenation

For monohalogenation, $-\text{NH}_2$ is first acetylated, because $\text{CH}_3\text{CONH}-$ is only moderately activating



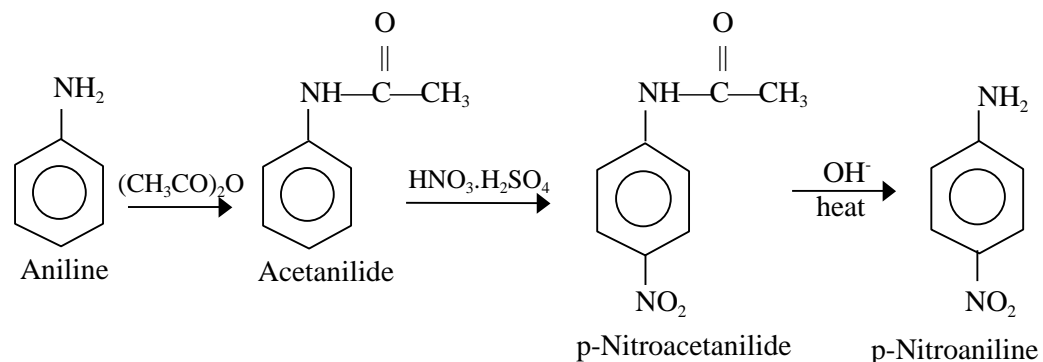
(ii) Sulfonation



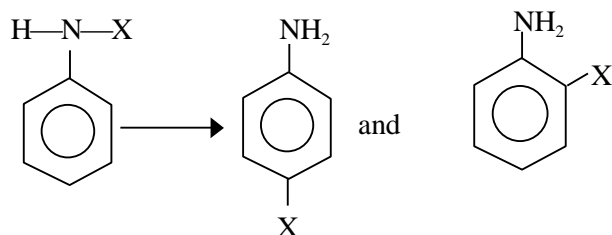


(iii) Nitration

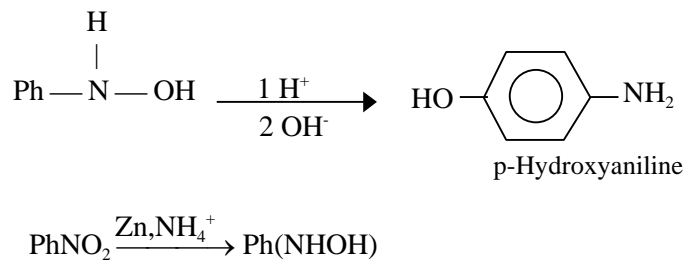
To prevent oxidation by HNO_3 and meta substitution of $\text{C}_6\text{H}_5\text{NH}_3^+$, amines are first acetylated.



(VII) Aniline-X Rearrangements

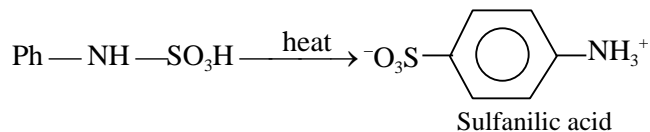


(i) Phenylhydroxylamines





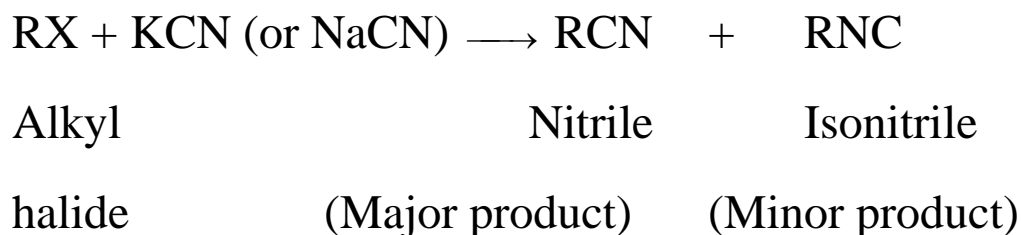
(ii) Sulfamic Acid



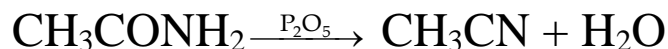
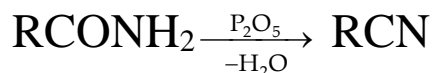
ALKYL CYANIDES

Methods of Preparation

(i) From alkyl halides: The alkyl cyanides is prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



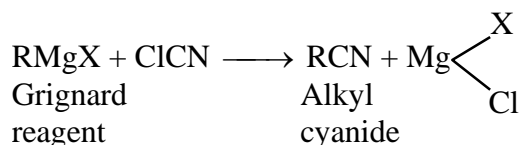
(ii) From acid amides: Pure nitriles are obtained by dehydration of acid amides with phosphorus pentoxide. Amides are distilled with phosphorus pentoxide, P_2O_5 .



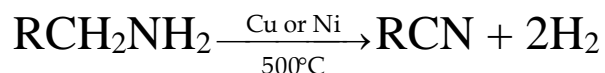
Acetamide	Methyl cyanide	
	Salt	



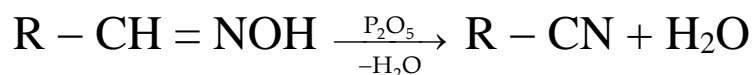
(iii) From Grignard reagent: Grignard reagent reacts with cyanogenchloride to form alkyl cyanides.



(iv) From primary amines: Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.



(v) From oximes: Aldoxime are converted into alkyl cyanides when distilled with phosphorus pentoxide or acetic anhydride.



Aldoxime

Alkyl cyanide

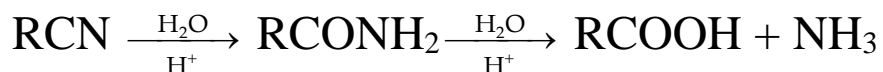
GENERAL PHYSICAL PROPERTIES OF ALKYL CYANIDES

These are neutral substances .They are soluble in water and organic solvents.

GENERAL CHEMICAL PROPERTIES OF ALKYL CYANIDES

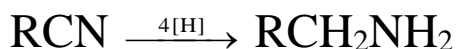


(I) Hydrolysis: Alkyl cyanides are hydrolysed by both acids and alkalis. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.



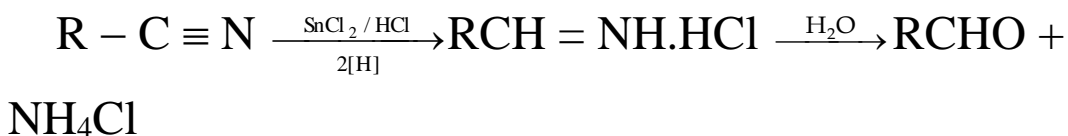
Alkyl Amide cyanide

(II) Reduction: When reduced with hydrogen in presence of Pt or Ni, or LiAlH_4 (lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.



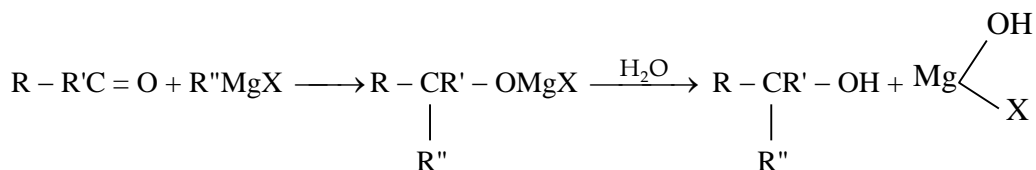
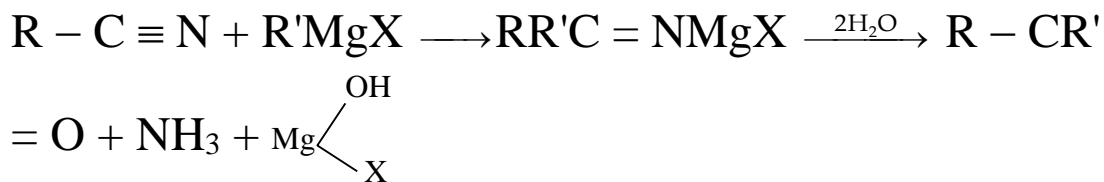
Alkyl cyanide Primary amine

However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).

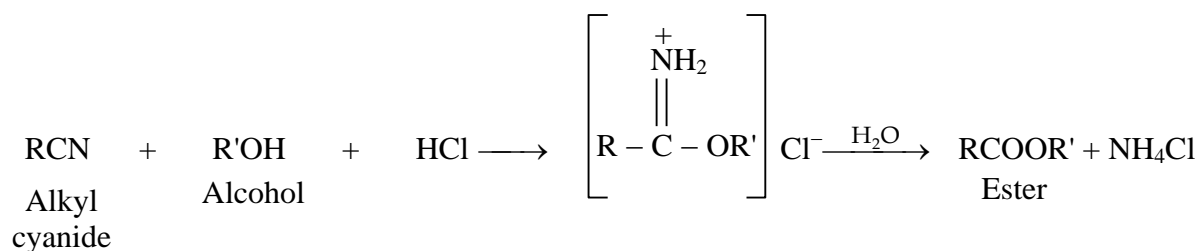


Imine hydrochloride Aldehyde

(III) Reaction with Grignard reagent: With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



(IV) Alcoholysis: When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dry HCl, an imido ester is formed, which on hydrolysis with water forms ether.

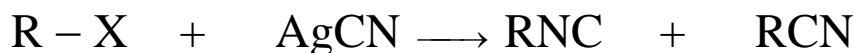


Uses: Alkyl cyanides are important intermediate in the laboratory synthesis of a large number of compounds like acids, amides, esters, amines etc.

ALKYL ISOCYANIDES

Methods of Preparation

(i) From alkyl halides: The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.



Alkyl halide Isocyanide Cyanide

(Isonitrile) (Nitrile)

Main product Minor product

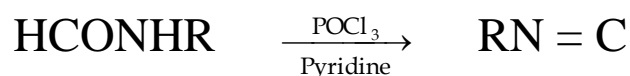
(ii) From primary amines: (Carbylamine reaction) Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.



Primary amine Chloroform Isocyanide

(iii) From N-alkyl formamides:

N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides



N-alkyl formamide Isocyanide

GENERAL PHYSICAL PROPERTIES OF ALKYL ISO CYANIDES

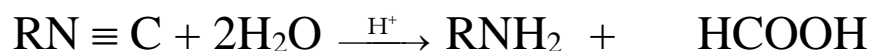
- (I) Alkyl isocyanides are colourless, unpleasant smelling liquids.
- (II) The boiling points of isonitriles are higher than corresponding alkyl cyanides.



- (III) They are insoluble in water but freely soluble in organic solvents
- (IV) Isonitriles are much more poisonous than isomeric cyanides.

GENERAL CHEMICAL PROPERTIES OF ALKYL ISOCYANIDES

- (I) **Hydrolysis:** Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.



Alkyl isocyanide Primary amine Formic acid

- (II) **Reduction:** When reduced with nascent hydrogen or hydrogen in presence of nickel, isocyanides form secondary amines containing methyl as one of the alkyl groups.



Alkyl isocyanide Secondary amine

- (III) **Action of heat:** When treated for some time at 250°C, a small amount of isonitrile changes into isomeric nitrile.

