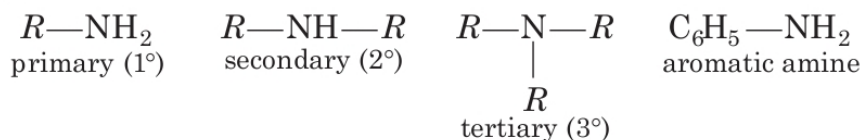
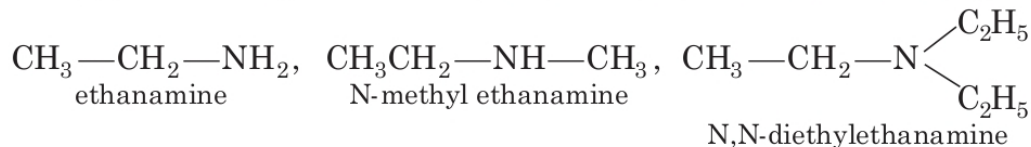


Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH_3 molecule by alkyl/aryl group(s).

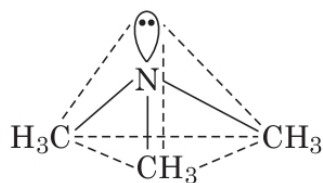


In the IUPAC system, the amines are named as alkanamines, e.g.

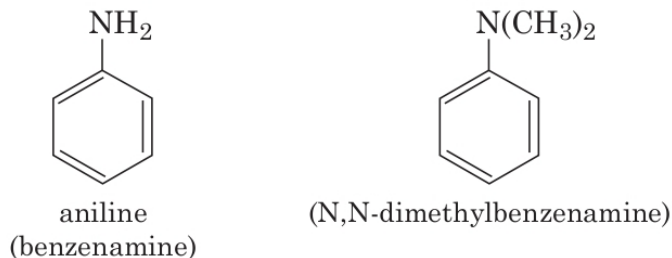


Structure

The nitrogen atom in amine is sp^3 -hybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.

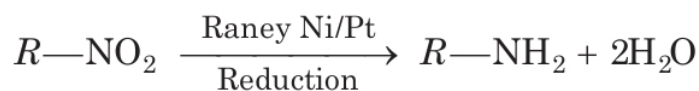


In arylamines, $-\text{NH}_2$ group is directly attached to the benzene ring.

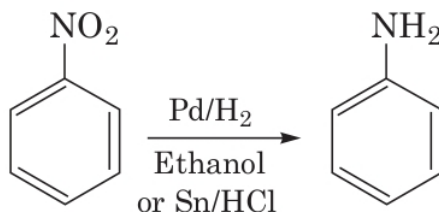


Methods of Preparation of Amines

(i) Reduction of nitro compounds

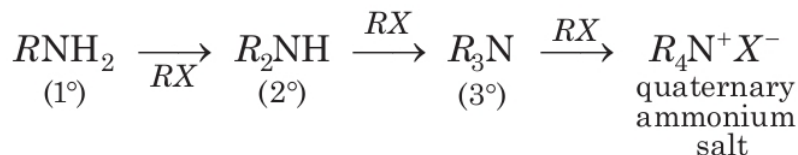
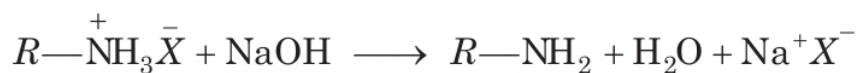
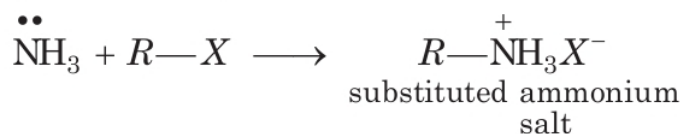


Reduction can take place by Sn/HCl, Ni/H₂, Zn/NaOH, Pd/H₂.



The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amine.

(ii) Ammonolysis of alkyl halides



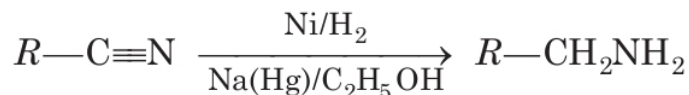
Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking excess of NH₃.

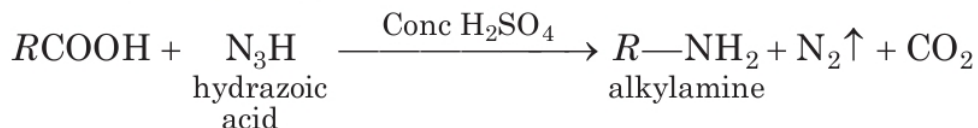
Order of reactivity of halides with amines is RI > RBr > RCl.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

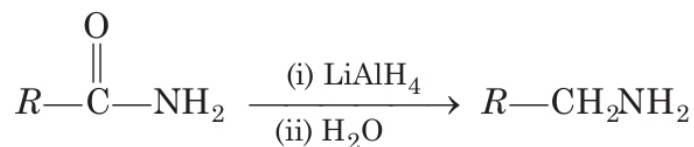


(iv) Schmidt reaction

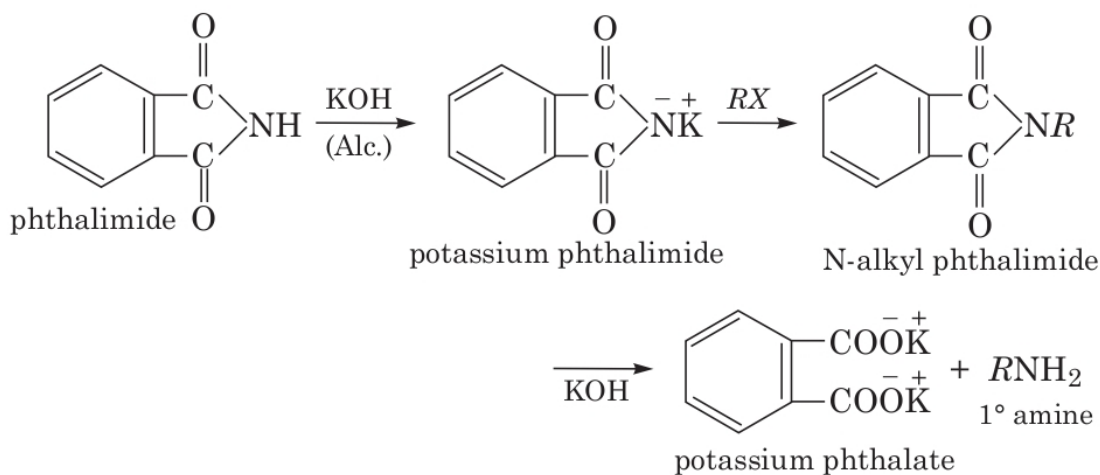


It is a modification of Curtius degradation.

(v) **Reduction of amides**

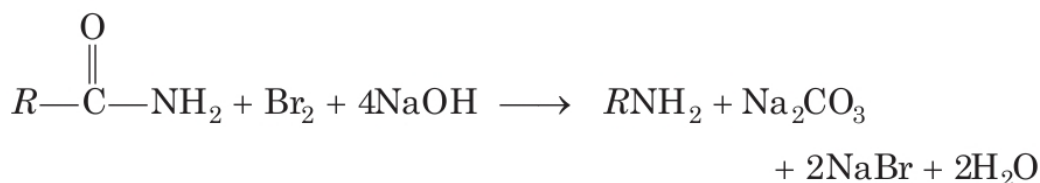


(vi) **Gabriel's phthalimide reaction**



It only produces 1° amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(viii) **Hofmann bromamide degradation reaction**



In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAlH₄/ether.

Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell.
2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
3. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase of hydrophobic alkyl group/chain.
4. Boiling point order is :
primary > secondary > tertiary

5. Tertiary amine does not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

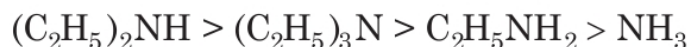
Chemical Properties of Amines

- (i) **Basic Strength of Amines** Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the value of K_b (dissociation constant of base), higher is the basicity of amines. Lesser the value of pK_b , higher is the basicity of amines.

Aliphatic amines (CH_3NH_2) are stronger bases than NH_3 due to the electron releasing $+I$ effect of the alkyl group.

Among aliphatic amines, the order of basic strength in aqueous solution is as follows

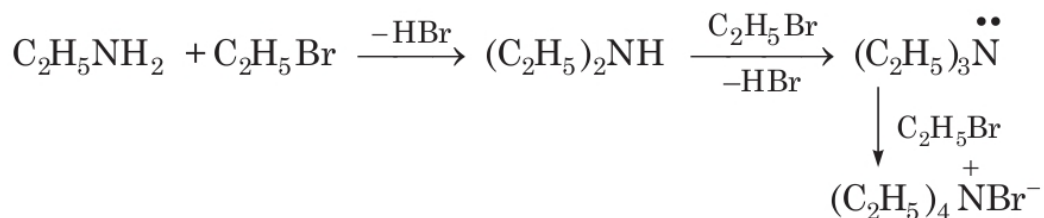


Aromatic amines are weaker bases than aliphatic amines and NH_3 , due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π -electron pairs of the ring.

Electron releasing groups (e.g. $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$ etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like $-\text{NO}_2$, $-\text{X}$, $-\text{CN}$ etc.) tend to decrease the same.

o-substituted aromatic amines are usually weaker bases than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called *ortho* effect and is probably due to steric and electronic factors.

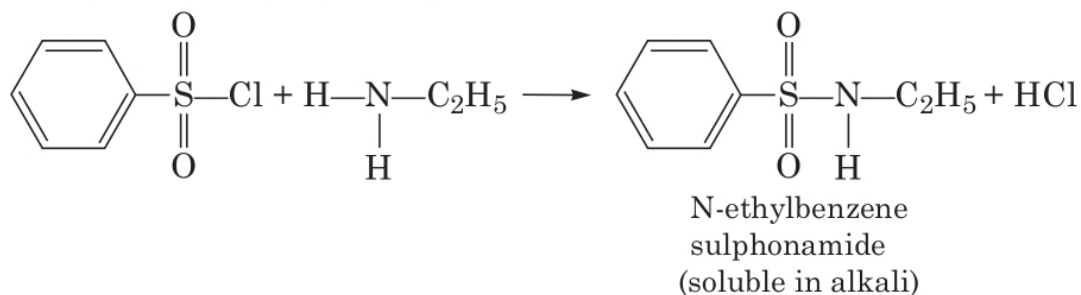
- (ii) **Alkylation** All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.



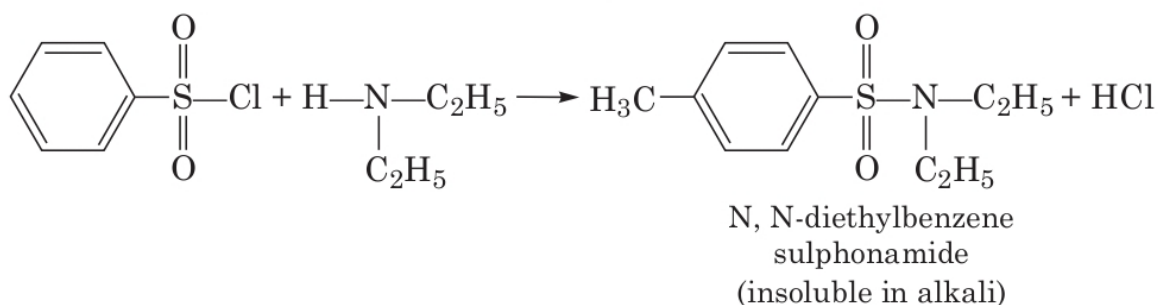
But secondary and tertiary amines react with nitrous acid in different manner. Methyl amine gives dimethyl ether with HNO_2 .

(vii) **Reaction with aryl sulphonyl chloride** [Hinsberg reagent]

The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonamide.

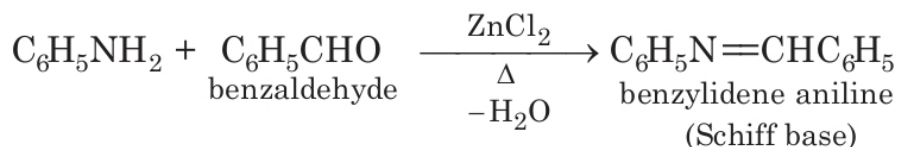


The reaction of benzenesulphonyl chloride with secondary amine yields N,N-diethyl benzene sulphonamide.



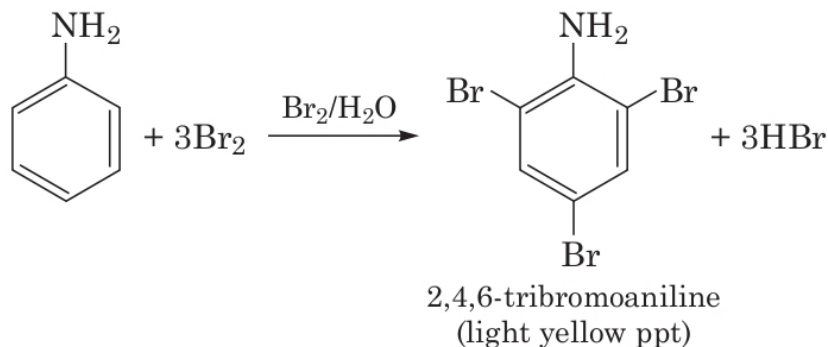
Tertiary amines does not react with benzenesulphonyl chloride.

(viii) **Reaction with aldehydes** Schiff base is obtained.

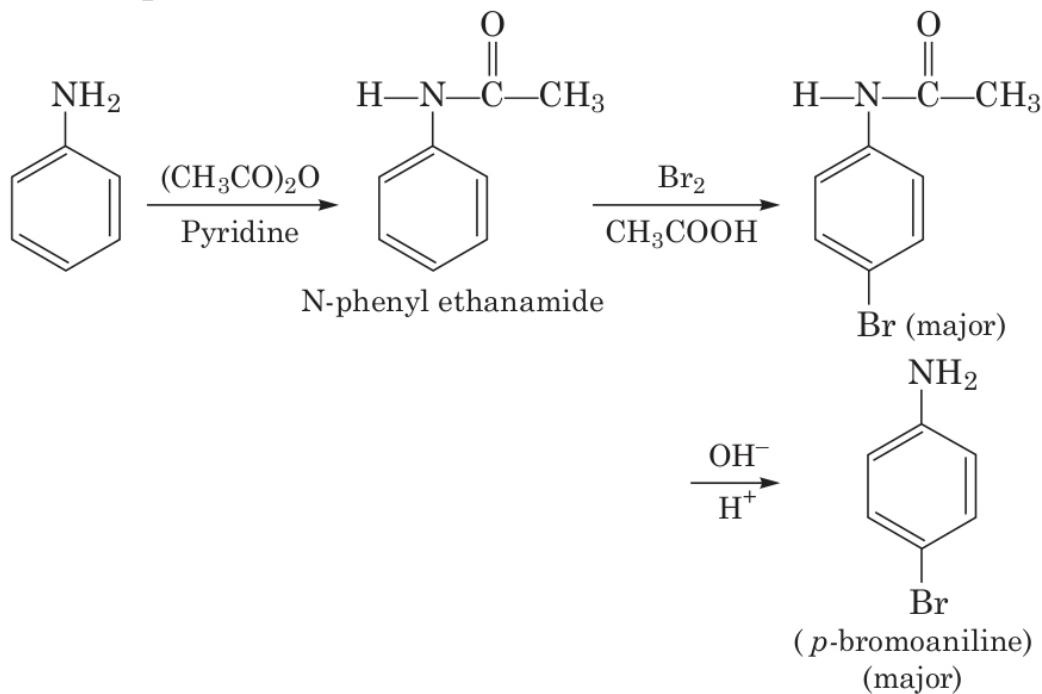


(ix) **Electrophilic substitution reactions** Aniline is *ortho* and *para* directing towards electrophilic substitution reaction due to high electron density at *ortho* and *para*-positions.

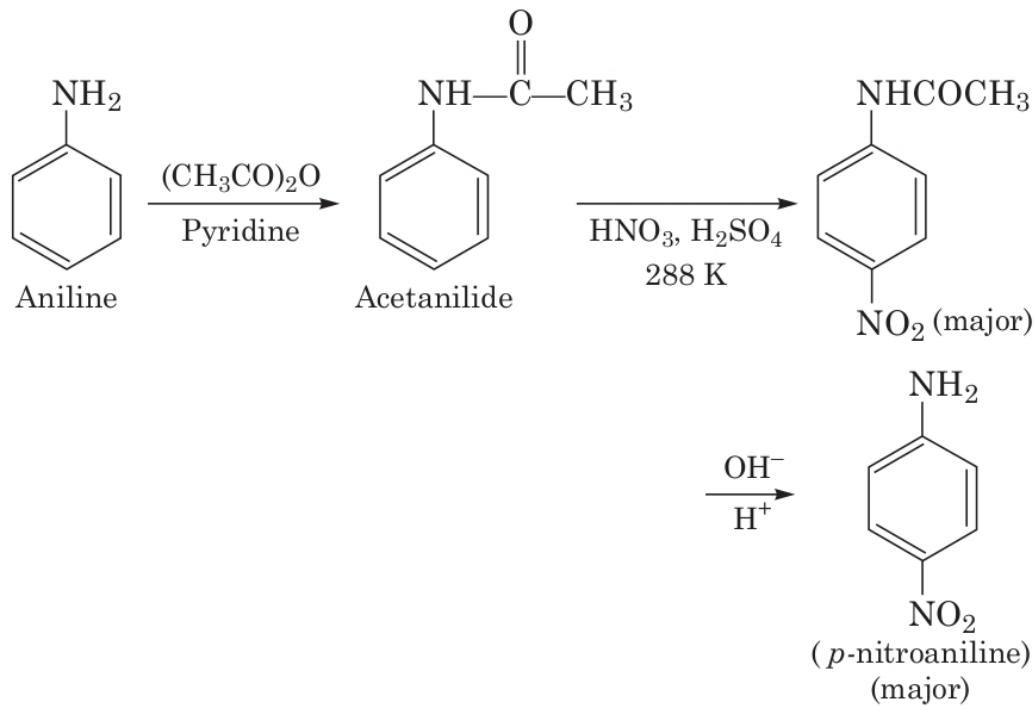
(a) **Bromination**



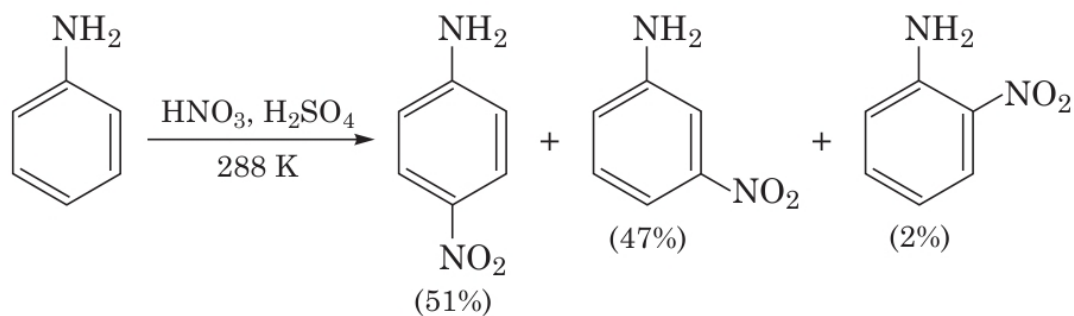
To prepare monosubstituted derivative, activating effect of $-\text{NH}_2$ group must be controlled. It can be done by protecting the $-\text{NH}_2$ group by acetylation with acetic anhydride.



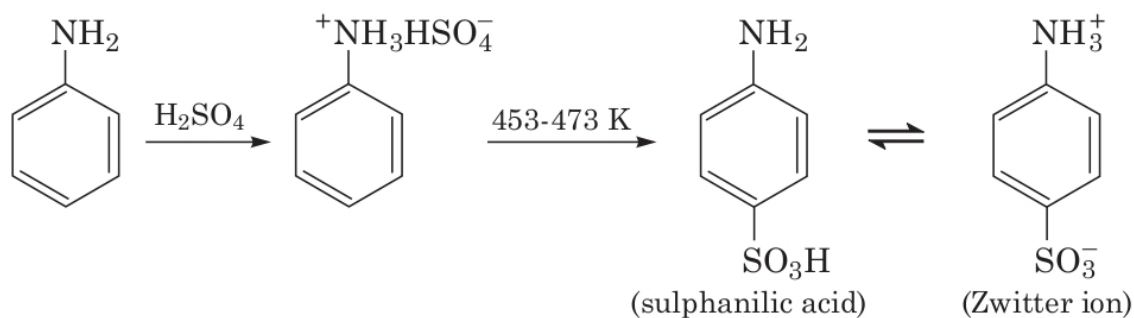
(b) **Nitration** Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strong acidic medium, aniline is protonated as anilinium ion which is *meta* directing so it gives *meta* product also.



(c) **Sulphonation** On sulphonation, aniline gives sulphanilic acid, as the major product.



(d) Aniline does not undergo **Friedel-Crafts** reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence, behave like a strong deactivating group for further chemical reaction.

(x) **Oxidation** Use of different oxidising agents gives different products. e.g.

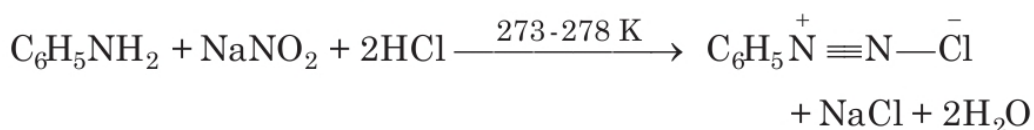
Oxidising agent	Product
Acidified KMnO_4 (or $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{CuSO}_4 + \text{dil. acid}$)	Aniline black (a dye)
Chromic acid ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4$)	<i>p</i> -benzoquinone
Caro's acid (H_2SO_5)	nitrobenzene and nitrosobenzene
Conc. nitric acid	decomposes

Separation of Mixture of Amines (1°, 2° and 3°)

- (a) **Fractional distillation** This method is based on the boiling points of amines and is used satisfactorily in industry.
- (b) **Hofmann's method** Diethyloxalate is called Hofmann's reagent with which mixture of amines is treated.
1° amine forms solid dialkyl oxamide $(\text{CONHR})_2$.
2° amine forms liquid dialkyl oxamic ester $(\text{CONR}_2 - \text{COOC}_2\text{H}_5)$
3° amines do not react.
- (c) **Hinsberg's method** see chemical reactions on Page 448.

Benzene Diazonium Chloride $(\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-)$

Preparation (Diazotisation reaction)



The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

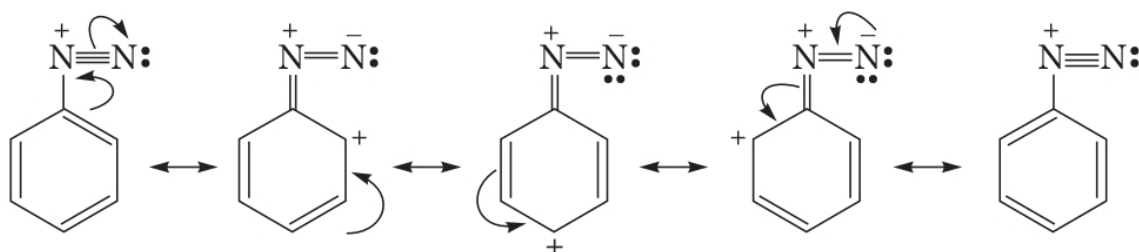
┌ Diazonium salts are prepared and used in aqueous solutions because
in solid state, they explode. ┘

Physical Properties

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

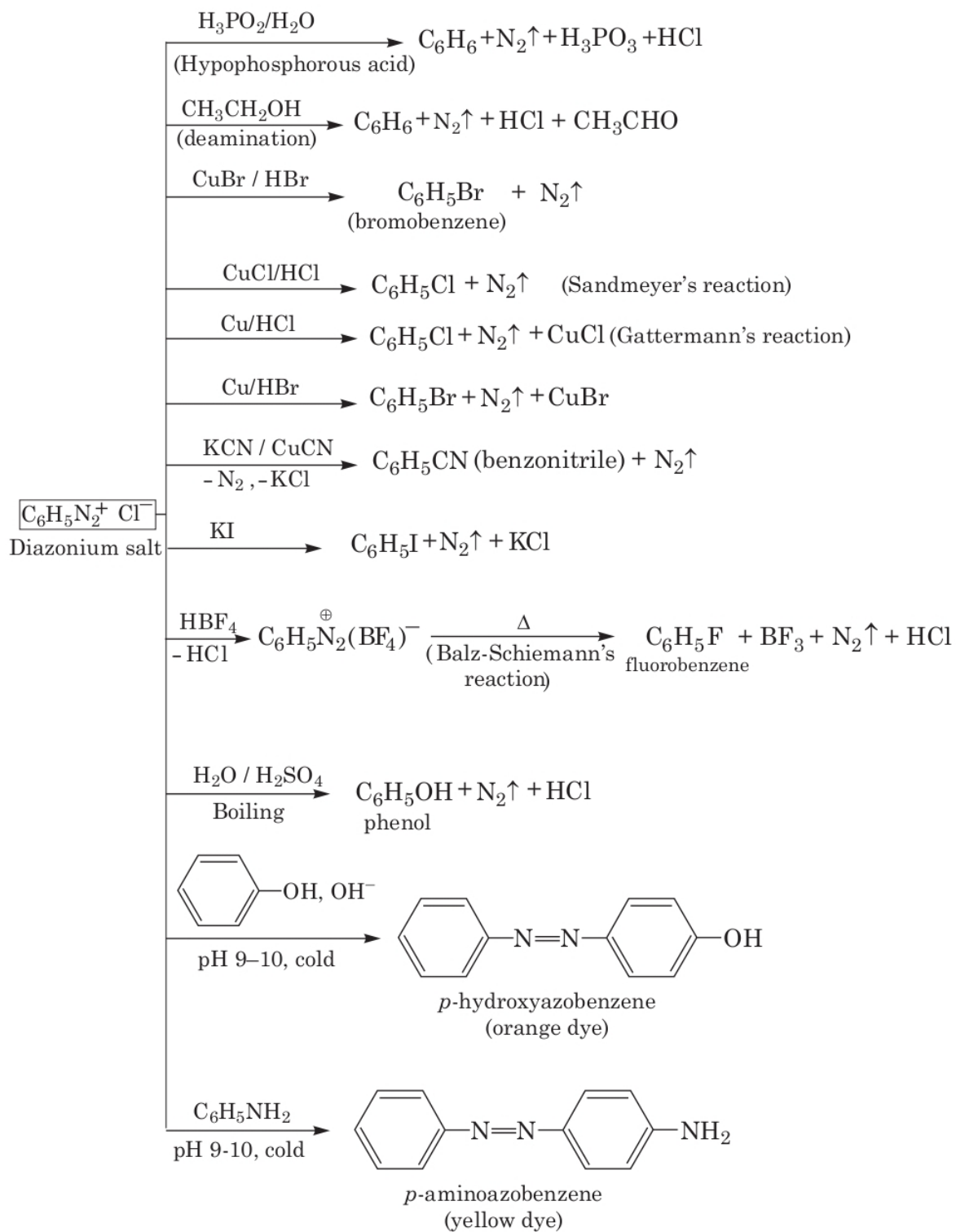
Stability of Arenediazonium salts

It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:



Various resonating structures of arenediazonium ion

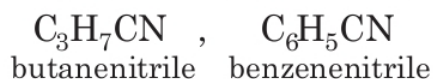
Chemical Properties



Alkyl Cyanides (RCN)

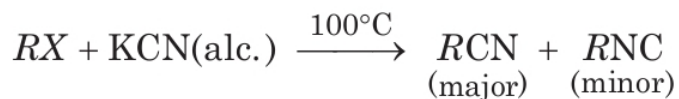
These compounds have formula RCN . These are the derivatives of HCN .

According to IUPAC system, cyanides are named as 'alkanenitrile', e.g.

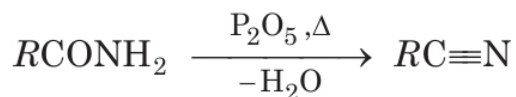


Methods of Preparation

(i) From alkyl halides



(ii) From acid amides

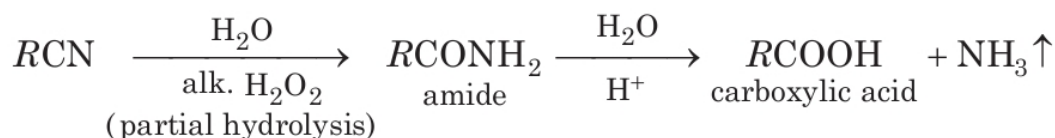


Physical Properties

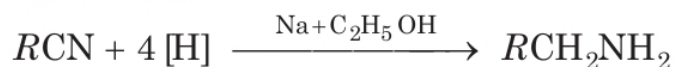
1. These are neutral compound with pleasant odour, similar to bitter almonds.
2. These are soluble in water as well as organic solvents.
3. These are poisonous but less than HCN .

Chemical Properties

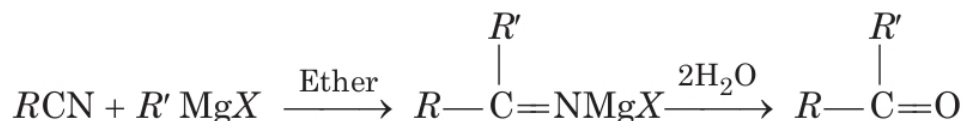
1. Hydrolysis



2. Reduction



3. Reaction with Grignard's reagent



Alkyl Isocyanides (RNC)

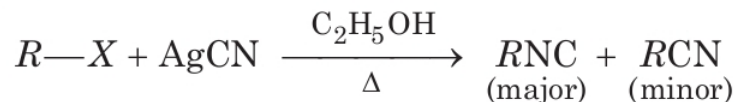
According to IUPAC system, these are named as 'alkane isonitrile'.

e.g. CH_3NC methyl isonitrile

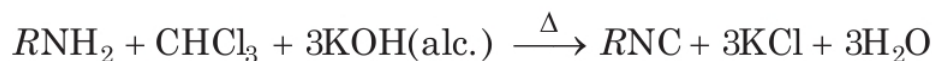
$\text{C}_6\text{H}_5\text{NC}$ benzene isonitrile

Methods of Preparation

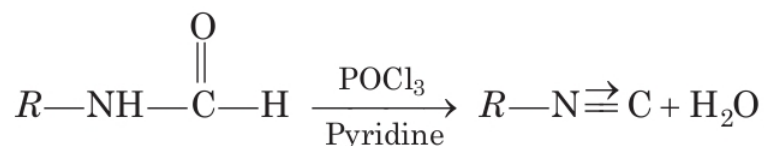
1. From alkyl halides



2. Carbylamine reaction



3. From N-alkyl formamide

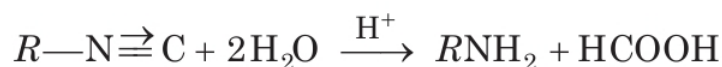


Physical Properties

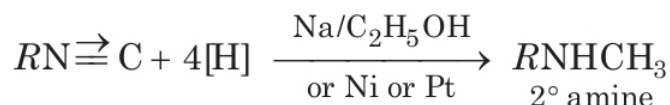
1. These are colourless unpleasant smelling liquids.
2. These are soluble in organic solvents but insoluble in water.

Chemical Properties

1. Hydrolysis



2. Reduction



3. **Addition reaction** Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.



4. **Isomerisation** At 250°C, it isomerises to nitrile.



Nitro Compounds

These are obtained by replacing one H of hydrocarbon by —NO_2 group.

These are named according to IUPAC system as 'nitro alkane'.

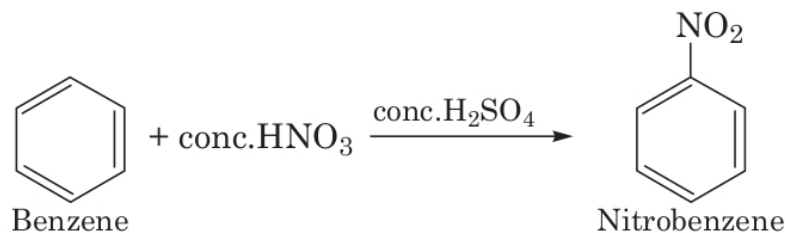
Methods of Preparation

1. From alkyl halides



2. Nitration

Nitrating mixture is conc. HNO_3 + conc. H_2SO_4 .



Physical Properties

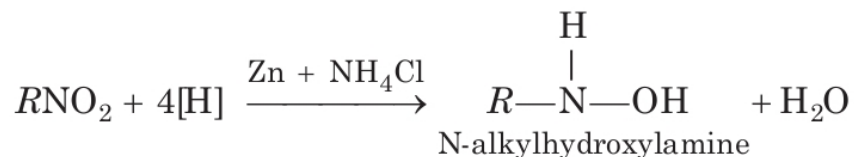
1. These are colourless pleasant smelling liquids.
2. Their boiling point are much higher than isomeric alkyl nitriles.
3. These are less soluble in water but readily soluble in organic solvents.

Chemical Properties

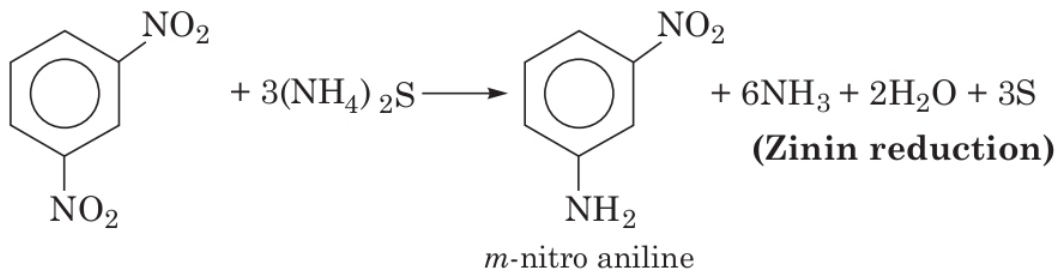
1. **Reduction** With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.



If neutral reducing agent like Zn dust + NH_4Cl is used, hydroxylamines are obtained as major product.



In the presence of $(\text{NH}_4)_2\text{S}$ or Na_2S , selective reduction takes place.

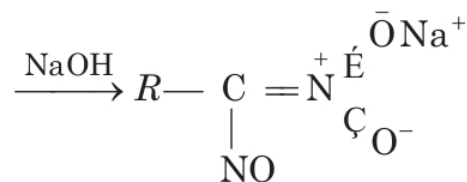
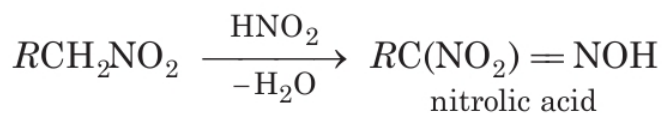


Nitrobenzene gives different products with different reagents and in different mediums.

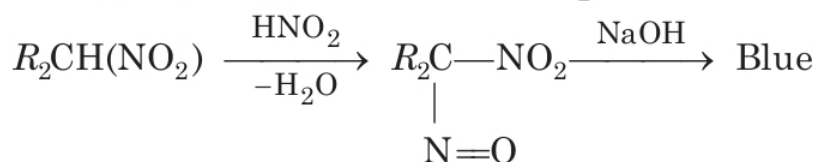
Medium	Reagent	Product
Acid	Sn/HCl	aniline
Neutral	Zn/NH ₄ Cl	N-phenyl hydroxylamine
	Na ₃ AsO ₃ /NaOH	azoxybenzene $\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5\text{N} = \text{NC}_6\text{H}_5) \end{array}$
Alkaline	Zn/NaOH, CH ₃ OH	azobenzene
	Zn/NaOH, C ₂ H ₅ OH	hydrazobenzene
Metallic hydride	LiAlH ₄	aniline
Electrolytic	dil. H ₂ SO ₄	<i>p</i> -aminophenol

2. Action of HNO₂

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

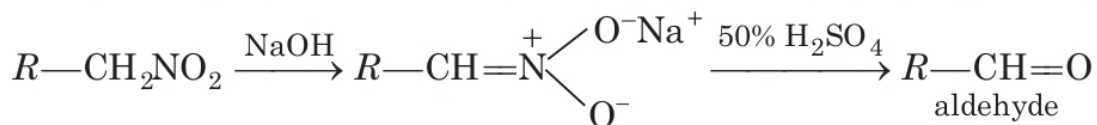


2° nitroalkanes give pseudo nitrol with HNO₂.

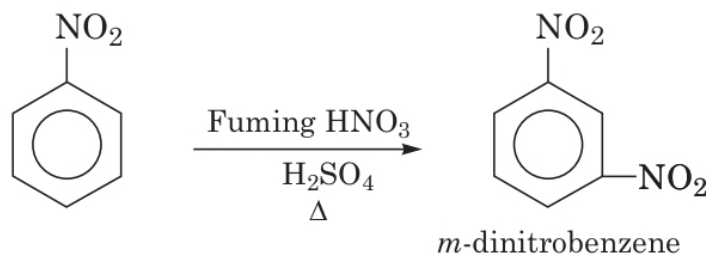


3° nitroalkanes does not react with HNO₂.

3. **Nef carbonyl synthesis** Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H₂SO₄ at room temperature. This reaction is called Nef carbonyl synthesis.



4. **Electrophilic substitution** On nitration, nitrobenzene gives *m*-dinitrobenzene (as —NO₂ is a *m*-directing group and strongly deactivating).



It does not give Friedel-Craft's alkylation.

5. **Nucleophilic substitution reaction** —NO₂ group activates the ring towards nucleophilic substitution.

