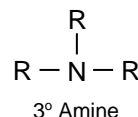
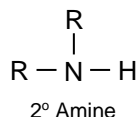
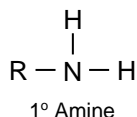
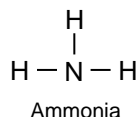


ORGANIC CHEMISTRY- FUNCTIONAL GROUP- 3

AMINES

Amines are alkyl or aryl derivatives of ammonia. Amines are classified into primary, secondary and tertiary amines. If one hydrogen atom of ammonia is replaced, a primary amine results. The substitution of two or three hydrogen atoms leads to secondary and tertiary amines respectively.



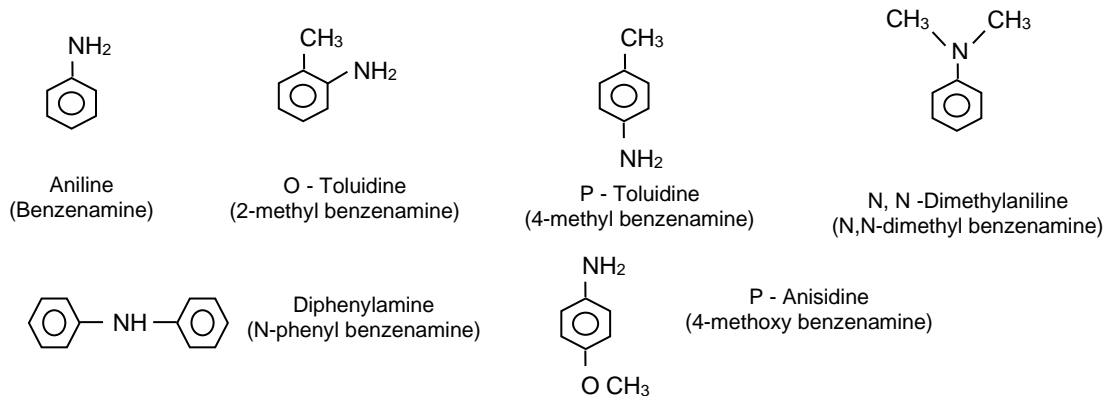
The amines are called '**simple**' when all the alkyl groups are same and '**mixed**' when they are different.

Nomenclature

In common system, amines are named by adding the suffix 'amine' to the corresponding alkyl group. In case of mixed amines, the names of alkyl groups are arranged in alphabetical order.

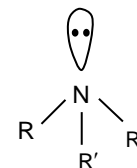
In IUPAC system, they are called aminoalkanes or alkanamines.

Formula	Common name	IUPAC name
$\text{CH}_3 - \text{NH}_2$	Methyl amine	Methanamine
$\text{CH}_3 - \text{CH}_2 - \text{NH}_2$	Ethyl amine	Ethanamine
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{NH}_2 \end{array}$	Iso-Propyl amine	Propan-2-amine
$\text{CH}_3 - \text{NH} - \text{CH}_3$	Dimethyl amine	N-methyl methanamine
$\text{CH}_3 - \text{NH} - \text{C}_2\text{H}_5$	Ethyl methyl amine	N-methyl ethanamine
$\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Tri-methyl amine	N,N-Dimethyl methanamine
$\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array}$	Ethyl methyl propyl amine	N-Ethyl-N-methyl propanamine
$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{NH}_2$	Allylamine	Prop-2-en-1-amine
$\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine



Electronic structure

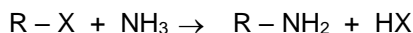
In amines, nitrogen has sp^3 hybridisation. Three of the sp^3 hybrid orbitals overlap with other atoms to form 3 sigma bonds. These sigma bonds are directed to the corners of a tetrahedron. The remaining hybrid orbital contains a lone pair of electron. Therefore amines have pyramidal shapes. Bond angle is around 108° .



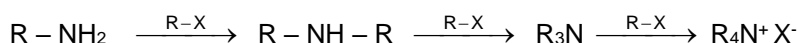
Preparation

(1) From alkyl halides: [By Hofmann's ammonolysis method]

Alkyl halides react with ethanolic solution of ammonia to form primary, secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.



If alkyl halide is in excess, the primary amine formed further reacts with alkyl halides to form 2° and 3° amine and finally quaternary ammonium salt. The reaction is carried out in sealed tube at $373K$.



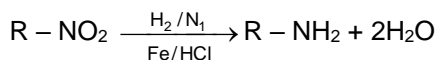
This reaction is a typical example of **nucleophilic substitution reaction**. The ammonium salt can be converted to free amine by treatment with strong base.



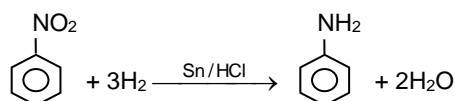
The reactivity of various halides in this method is $R-I > R-Br > R-Cl$

(2) From nitro compounds by reduction.

Nitro compounds can be reduced to primary amines either by using H_2/Pt , Ni or by using Fe/HCl , or Sn/HCl or $LiAlH_4$

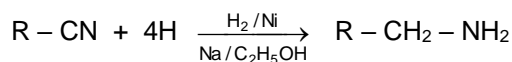


This method is important for the preparation of aromatic primary amines as they cannot be obtained easily from alkyl halides.

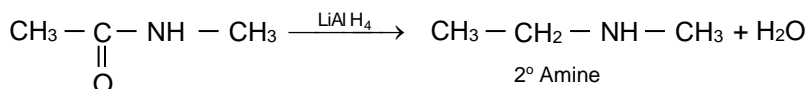
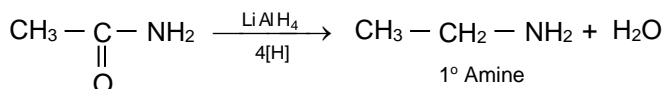


Here Fe/HCl is preferred because $FeCl_2$ formed get hydrolysed to release HCl . Therefore only small amount of HCl is needed.

(3) From Alkyl cyanides on reduction with H_2/Ni , $LiAlH_4$ or Na/C_2H_5-OH give primary amines.

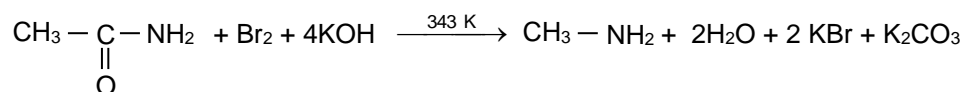


(4) By reduction of **amides** using Na/C_2H_5OH or $LiAlH_4$. Here primary amides give primary amines. Secondary and tertiary amides can give secondary or tertiary amines.



(4) From amides by Hoffmann bromamide degradation reaction

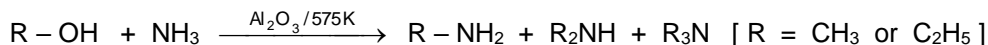
Acid amides on reaction with Br₂ in the presence of alkalis at about 343 K give primary amines.



Here the amine formed by this method has one carbon atom less than the parent compound.

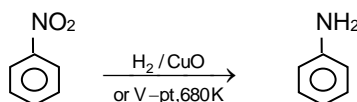
(5) From Alcohols (Industrial method)

Low molecular weight aliphatic amines are manufactured by passing a mixture of an alcohol and ammonia in the vapour phase over heated alumina catalyst. Here a mixture of 1°, 2° and 3° amines are formed.



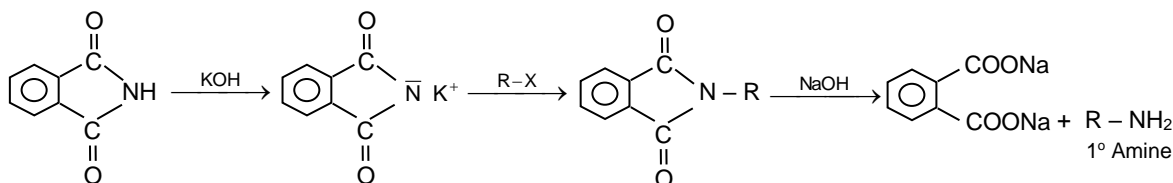
(6) Manufacture of aniline

Aniline is manufactured by vapour phase reduction of nitrobenzene with hydrogen using copper oxide or vanadium-platinum as catalyst.



(7) Gabriel Phthalimide synthesis

In this method, phthalimide is first converted into potassium phthalimide by reaction with KOH. The potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide. It is then hydrolysed to get pure primary amine.



This method cannot be used for the preparation of aromatic amines. This is because aryl halides do not undergo nucleophilic substitution with anion of phthalimide.

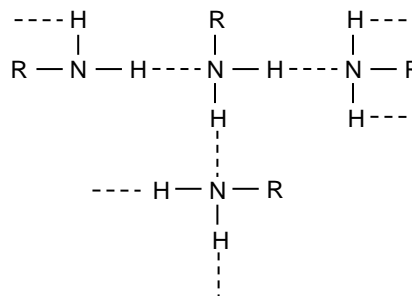
Physical Properties

Ethyl and methyl amines smell like ammonia, higher amines have fishy odours. They are colorless when pure, but get coloured on keeping due to oxidation by air.

Boiling point Amines are polar compounds. All amines except the tertiary amines are capable of forming inter-molecular hydrogen bonds. The inter-molecular hydrogen bond is more in primary than in secondary. Tertiary amines do not have inter-molecular hydrogen bonding due to the absence of H on nitrogen.

The boiling points of isomeric amines is **Primary > Secondary > Tertiary**

As a result amines have higher boiling point than non-polar compounds of comparable molecular masses. However amines have lower boiling points than corresponding alcohols or carboxylic acids. This is because the O – H bond is more polar than N – H bond. Hence hydrogen bonds in alcohols and carboxylic acids are stronger than the hydrogen bonds in amines.



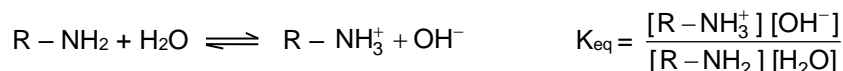
Solubility Aliphatic amines of lower molecular mass are soluble in water. The solubility in water is due to their ability to form hydrogen bonds with water molecules.

The higher amines are soluble in less polar solvents like ethers, alcohols and benzene. Aromatic amines are insoluble in water but soluble in ether, alcohols and benzene.

Chemical Properties

1) Basic character

Due to the presence of a lone pair of electrons on nitrogen, amines are basic in nature. Like ammonia amines are more basic than water and are protonated by water. The basic strength of amines are compared in terms of the equilibrium constant K_b .



Since $[H_2O]$ is constant, it is convenient to incorporate it in to the equilibrium constant. Then the constant obtained is called ***basicity constant***. Each amine has a characteristic K_b . **The larger the value of K_b , the stronger is the base.**

$$K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

But the basic strength is more conveniently expressed in terms of their **pK_b** values ($pK_b = -\log K_b$). ***Smaller the value of pK_b , more is the basic strength of amine.***

I. Alkyl amines are stronger bases than ammonia.

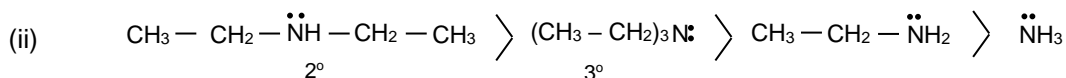
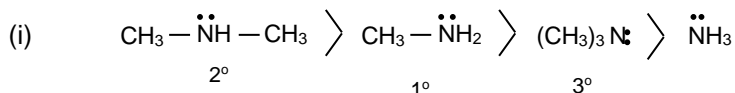
This is due to the electron releasing inductive effect of alkyl groups. Due to electron releasing effect, the electron density on nitrogen increases and the lone pair of nitrogen is more available for sharing.

More over, electron releasing effect of alkyl group, stabilizes the alkyl ammonium ion formed.



II. Basic strength of 1°, 2°, and 3° amines

Among 1°, 2°, and 3° amine the electron releasing effect is maximum in tertiary amines. Thus the basic strength is expected to increase from primary amine to tertiary amine. **But the observed basicity is**



This anomalous behavior is due to (i) Steric effect and (ii) Hydration effect.

(i) Steric effect

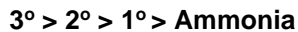
Due to the crowding of alkyl groups on nitrogen atom, the attack of a proton on the amine is hindered. Thus the basic strength is decreased. Crowding of alkyl groups increases from primary to tertiary amines. Consequently basic strength should decrease in the order $1^\circ > 2^\circ > 3^\circ$.

(ii) Hydration effect (solvation effect)

The protonated amines can be hydrated by forming hydrogen bonds with water. Hydration releases energy called hydration energy. Higher the hydration energy, more stable the molecule. Hydration due to hydrogen bond is maximum in primary amine and least in tertiary amine. Therefore basic strength should decrease from $1^\circ > 2^\circ > 3^\circ$.

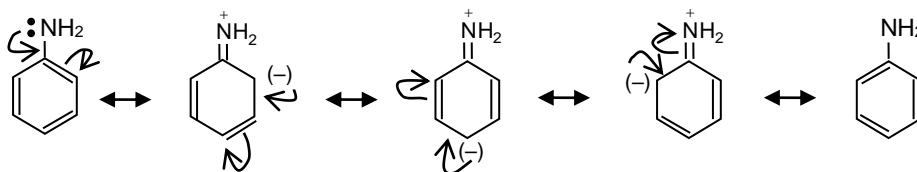
Thus in 3° amine, hydration is least and steric hindrance and + I effect are maximum. In 1° amines, steric effect and + I effect are minimum and hydration effect is maximum. **The resultant of all these effects make the secondary amines more basic than primary or tertiary amines.**

But in gas phase and in non-polar solvents like chlorobenzene the solvent effect is missing. Therefore the order of basic strength is



III. Aromatic amines such as aniline are less basic than ammonia

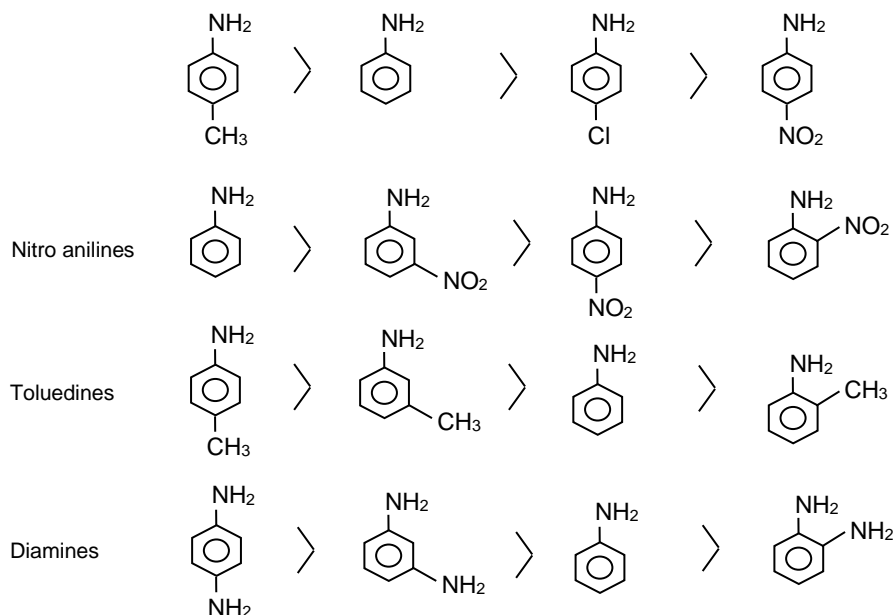
This is because in aniline the lone pair of electrons on nitrogen undergoes delocalization with the π electrons of benzene ring. Thus aniline is a hybrid of the following resonating structures. Thus the availability of the lone pair of electrons on the nitrogen is decreased.



Effect of substituents on basic character

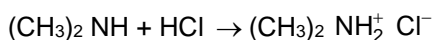
The presence of electron releasing groups such as $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{NH}_2$ etc at the para position increases the basic strength.

The presence of electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{X}$ etc at the para position decrease the basic strength.



1) Salt formation

Due to the basic nature, amines readily dissolve in acids to form salts.



2) Reaction with metal ions

$$\text{AgCl} + 2 \text{CH}_3\text{NH}_2 \rightarrow [\text{Ag}(\text{CH}_3\text{NH}_2)_2]^+ \text{Cl}^-$$
$$\text{CuSO}_4 + 4 \text{CH}_3\text{NH}_2 \rightarrow [\text{Cu}(\text{CH}_3\text{NH}_2)_4]^{2+} \text{SO}_4^{2-}$$

Deep blue solution

$$\text{R-NH}_2 \xrightarrow[\text{-HX}]{\text{R-X}} \underset{\text{2}^\circ \text{Amine}}{\text{R}_2\text{NH}} \xrightarrow[\text{-HX}]{\text{R-X}} \underset{\text{3}^\circ \text{Amine}}{\text{R}_3\text{N}} \xrightarrow[\text{-HX}]{\text{RX}} \underset{\text{Tetraalkylammoniumhalide}}{\text{R}_4\text{N}^+\text{X}^-}$$
$$\text{C}_2\text{H}_5-\text{NH}_2 + \text{CH}_3-\text{COCl} \xrightarrow{\text{base}} \text{C}_2\text{H}_5-\text{NH}-\text{CO}-\text{CH}_3 + \text{HCl}$$
$$\text{C}_2\text{H}_5-\ddot{\text{N}}(\text{H})-\text{H} + \begin{array}{c} \text{CH}_3 \\ | \\ \text{C}-\text{Cl} \\ || \\ \text{O} \end{array} \xrightarrow{\text{base}} \begin{array}{c} \text{H} \quad \text{CH}_3 \\ | \quad | \\ \text{C}_2\text{H}_5-\text{N}^+-\text{C}-\text{Cl} \\ | \quad | \\ \text{H} \quad \text{O}^- \end{array} \longrightarrow \begin{array}{c} \text{C}_2\text{H}_5-\text{N}-\text{C}-\text{CH}_3 \\ | \quad || \\ \text{H} \quad \text{O} \end{array} + \text{HCl}$$
$$\text{C}_6\text{H}_5-\text{NH}_2 + \text{C}_6\text{H}_5-\text{COCl} \xrightarrow{\text{Pyridine or NaOH}} \text{C}_6\text{H}_5-\text{NH}-\text{CO}-\text{C}_6\text{H}_5 + \text{HCl}$$
$$\text{R}-\text{NH}_2 + \text{O}=\underset{\text{H}}{\underset{|}{\text{C}}}-\text{R} \longrightarrow \text{R}-\underset{\text{H}}{\underset{|}{\text{N}}}=\underset{\text{H}}{\underset{|}{\text{C}}}-\text{R} + \text{H}_2\text{O}$$

Schif's base

$$\text{C}_6\text{H}_5 - \text{NH}_2 + \text{O} = \underset{\text{H}}{\text{C}} - \text{C}_6\text{H}_5 \longrightarrow \text{C}_6\text{H}_5 - \text{N} = \underset{\text{H}}{\text{C}} - \text{C}_6\text{H}_5 + \text{H}_2\text{O}$$

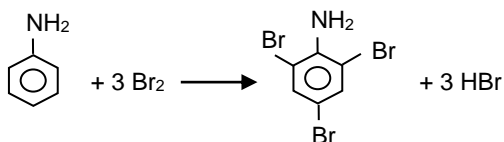
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8. Ring substitution of aromatic amines

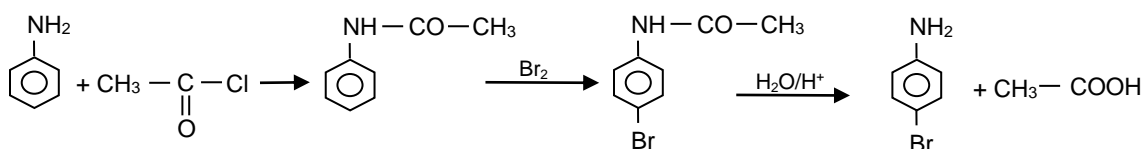
The amine group in aromatic amines is an electron donating group. Hence it increases the electron density at the ortho and para positions. Hence the electrophilic substitution takes place at the ortho and para positions.

(a) Halogenation

Aniline readily reacts with excess bromine to give 2, 4, 6 - tri bromoaniline.

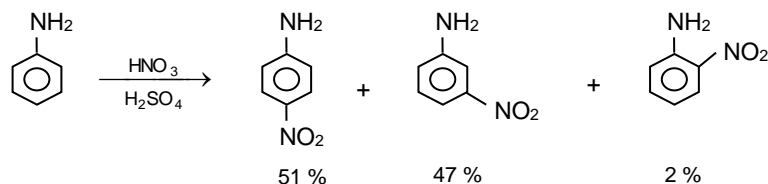


To get a mono bromo compound, the amino group is acetylated before bromination.

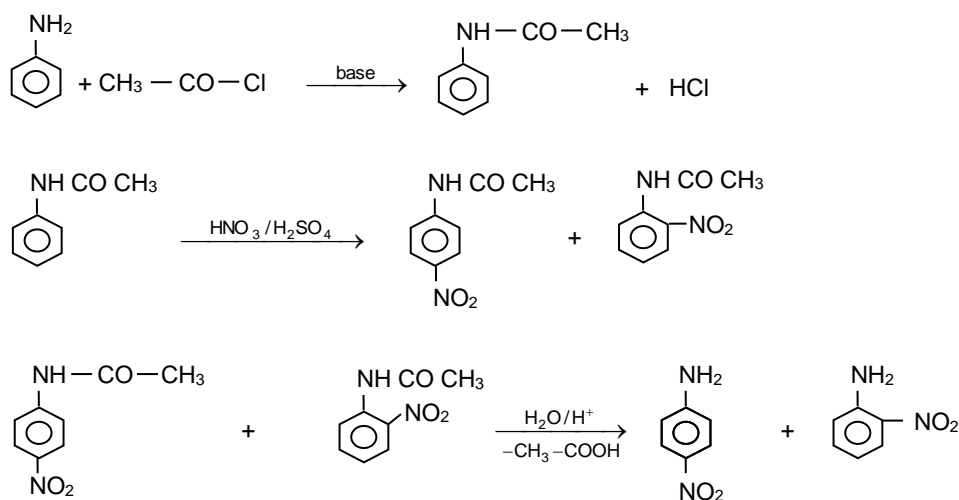


(b) Nitration

Direct treatment of aniline with HNO₃ leads to the formation of complex tarry oxidation products. More over in strongly acidic medium aniline get protonated to m-directing and deactivating ⁺NH₃ group. Therefore nitration of aniline, unexpectedly gives 47% m-nitroaniline.

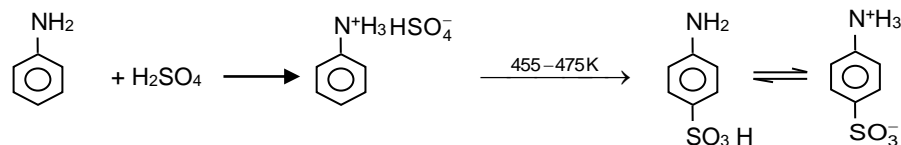


Therefore, before nitration, aniline is first acetylated to protect the -NH₂ group. Acetanilide on treatment with HNO₃ / H₂SO₄, gives ortho and para nitro acetanilide. This on hydrolysis give ortho and para nitro aniline.



(c) Sulphonation

Aniline on treatment with con H_2SO_4 form the salt, **anilinium hydrogen sulphate**. This on heating gives sulphanilic acid.



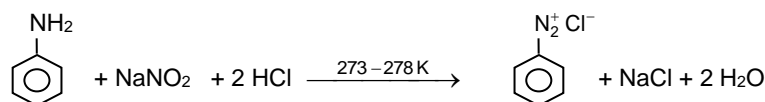
Sulphanilic acid is an important intermediate in the manufacture of dyes and drugs. Sulpha drugs like sulphathiazole and sulphadiazine are made from sulphanilic acid.

Aniline does not give Friedel-Crafts reaction. This is because AlCl_3 , the catalyst used in this reaction is a Lewis acid and it forms a salt with $-\text{NH}_2$ group. Thus N of aniline acquires positive charge and hence acts as a strong deactivating group.

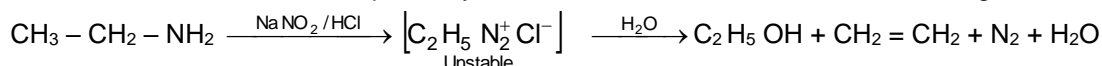
9. Reaction with nitrous acid

(a) With primary amines

Aromatic primary amines react with HNO_2 to give **diazonium** salts at low temperature. (273-278K).



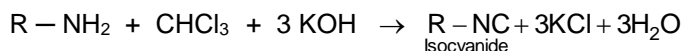
Aliphatic primary amines react with nitrous acid to form diazonium salts. However the aliphatic diazonium salts are unstable and decompose to yield mixture of alcohols and alkenes, and N_2 gas is evolved.



Test for amines

(1) Carbylamine test [Isocyanide Test]

When a primary amine is treated with chloroform and alkali, a carbylamine or isocyanide with a characteristic foul smell is formed. This is a test for primary amines. 2° and 3° amines do not show this reaction.

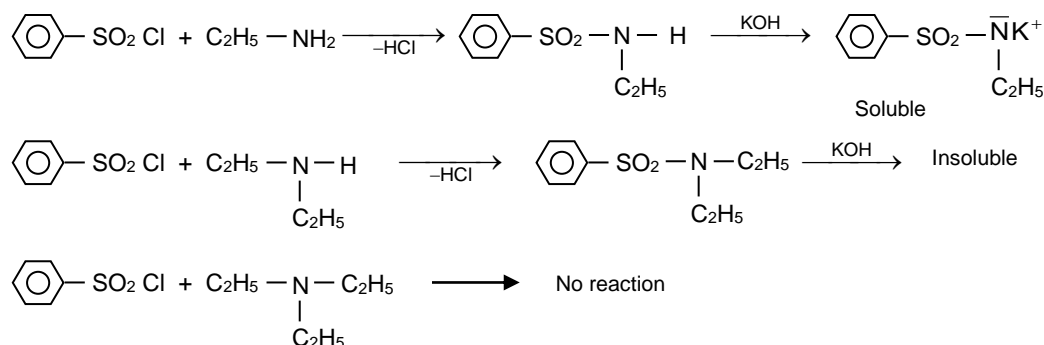


2) Hinsberg's test [Reaction with benzene sulphonyl chloride]

Benzenesulphonyl chloride [$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$], also known as **Hinsberg's reagent** reacts with primary and secondary amines to form **sulphonamides**.

- (1) Primary amine react with benzenesulphonyl chloride to form N-ethylbenzenesulphonamide. It contains an acidic hydrogen on N and hence it is soluble in aqueous KOH.
- (2) Secondary amine react with benzenesulphonyl chloride to form N,N-diethylbenzenesulphonamide. It does not contain any acidic hydrogen attached to N atom. Hence it is insoluble in KOH solution.
- (3) A tertiary amine does not react with benzene sulphonyl chloride.

This test helps to distinguish between primary, secondary and tertiary amines.



Uses of amines

- 1) Lower aliphatic amines are used as solvents.
- 2) Aromatic amines are used in the manufacture of dyes, indicators and drugs.
- 3) In laboratory, aromatic primary amines are converted into a variety of compounds via diazonium salts.
- 4) Aniline is used as antioxidant in the manufacture of rubber.
- 5) Amines are also used in petroleum refining and manufacture of detergents.

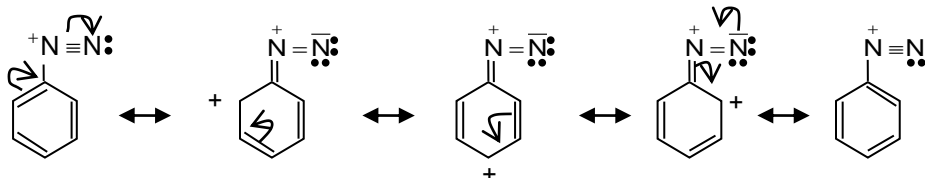
DIAZONIUM SALTS

Aromatic primary amines react with nitrous acid to form a class of compounds called **diazonium salts**. They have the general formula **Ar N₂⁺ X⁻**. Where X⁻ ion may be anion such as Cl⁻, Br⁻, HSO₄⁻ etc. The N₂⁺ group is (⁺N≡N) and is called **diazonium group**.

They are named by adding the word diazonium to the name of the aromatic compound followed by the name of the anion.

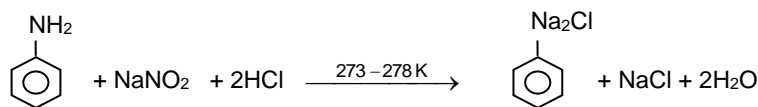


Stability: Primary aliphatic amines form **alkyl diazonium salts** which are highly unstable. But primary aromatic amines form **arene diazonium salts** which are stable. The stability of **arene diazonium salts** can be explained on the basis of resonance.



Method of preparation (Diazotisation)

The primary aromatic amines react with nitrous acid at low temperature (273 - 278K) to give aromatic diazonium salts. This reaction is known as diazotisation. Nitrous acid is unstable and therefore it is prepared in situ by the reaction of sodium nitrite and dilute HCl.



Reactions of diazonium salts

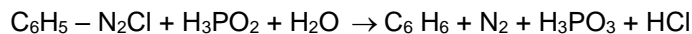
Reactions of diazonium salts can be classified into two types.

- (1) **Replacement reactions** and (2) **Coupling reactions**

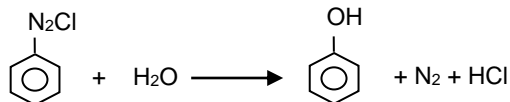
(1) Replacement reactions

In replacement reactions, the nitrogen is lost as N₂ gas and a different group is introduced in its place.

- (i) **Replacement by hydrogen:** This is done by treatment with hypophosphorus acid (phosphinic acid) or ethanol.

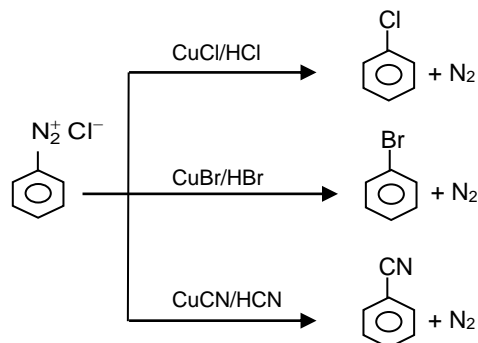


(ii) **Replacement by –OH** This involves warming of the diazonium salt with water.

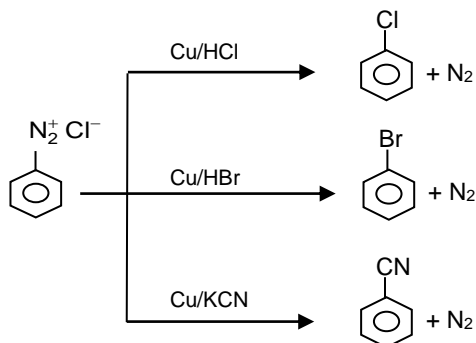


(iii) **Replacement by –Cl, –Br, or –CN (Sandmayer's reaction)**

The diazonium group is replaced by –Cl, –Br or –CN group respectively. When an aqueous solution of benzene diazonium chloride is warmed with CuCl and HCl, CuBr and HBr, or CuCN and KCN. This reaction is known as **Sandmayer's reaction**.

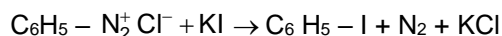


Gatterman modified Sandmayer's reaction by warming the diazonium salt solution with copper powder in the presence of the corresponding halogen acid.

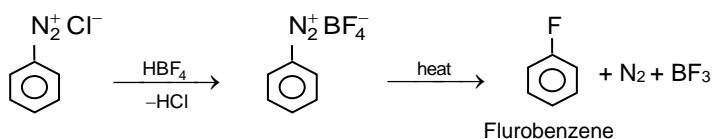


This reaction is called **Gattermann reaction**.

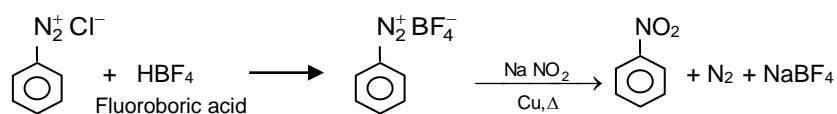
(iv) **Replacement by iodine**



(v) **Replacement by fluorine [Balz Shiemann reaction]**



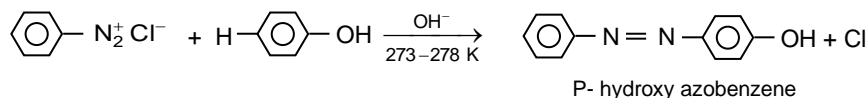
(vi) **Replacement by –NO₂ group:**



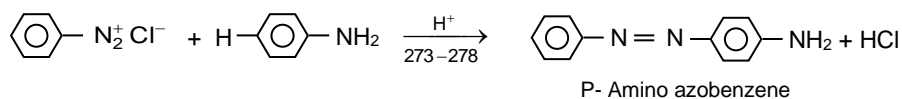
(II) Coupling reactions

Diazonium salts react with electron rich aromatic compounds such as phenols and amines to form azo compounds. Azo compounds are coloured and are used as dyes and indicators.

(i) Reaction with phenol

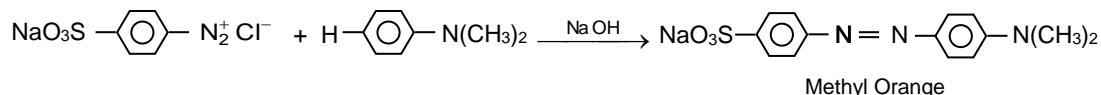


(ii) Reaction with aniline



(iii) Methyl orange:

The acid-base indicator methyl orange is obtained by coupling of diazonium salt of sulphanilic acid and N, N-dimethyl aniline.



Importance of diazonium salts

1. Aryl fluorides and iodides cannot be prepared by direct halogenation. But they can be prepared from diazonium salts.
2. The cyano compounds cannot be obtained by nucleophilic substitution of chlorobenzene. But they can be easily obtained from diazonium salt.
3. Diazonium salts are also useful in for introduction of $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{NO}_2$ etc in benzene ring.