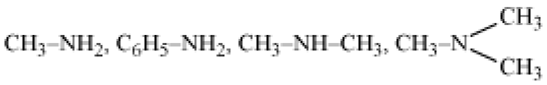
Amines

Amines

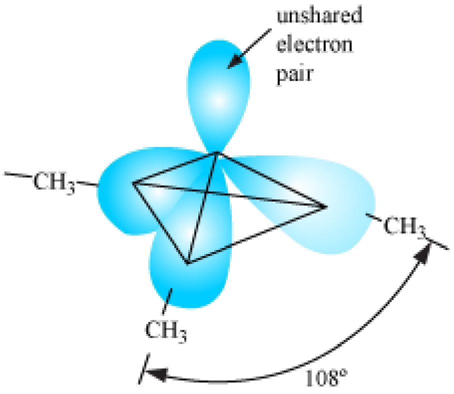
- Derivatives of ammonia
- Obtained by the replacement of one, two or all the three H-atoms of ammonia by alkyl and/or aryl groups
- Example:



$CH_3{-}NH_2$, $C_6H_5{-}NH_2$, $CH_3{-}NH{-}CH_3$, $CH_3{-}N\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$

Structure of Amines

- Nitrogen on amines is *sp*^{3} hybridised.
- Geometry – Pyramidal
- Example: Pyramidal shapes of trimethylamine

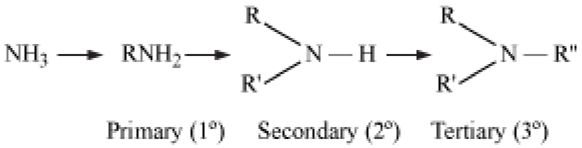


- Bond angle C−N−E (E is C or H) is less than 109.5° due to the presence of unshared pair of electrons. It is 108° in the case of trimethylamine.

Classification

- Classified as primary (1°), secondary (2°), and tertiary (3°)
- If one H-atom of NH_3 is replaced by R or Ar, RNH_2 or $ArNH_2$ is obtained (primary amine, 1°).
- If two H-atoms of NH_3 or one H-atom of RNH_2 are replaced by alkyl or aryl group (R′), R_2NH is obtained (secondary amine, 2°).

- On the replacement of another hydrogen atom by alkyl or aryl group, R_3N is obtained (tertiary amine, 3°).



Nomenclature

Common System

- Aliphatic amine: Named by prefixing alkyl group to amine, i.e., alkylamine.
- Example: Methylamine (CH_3NH_2)
- Secondary and tertiary amines: Prefix di- or tri- is appended before the name of alkyl group when two or more groups are the same.

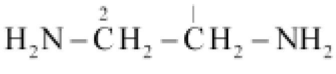
IUPAC System

- Named as **alkanamines**; derived by replacing the 'e' of alkane with the word amine.
- Example:

CH_3NH_2 – Methanamine

$CH_3CH_2NH_2$ – Ethanamine

- When more than one amino group is present –
- Suitable prefix such as di-, tri-, etc., is attached to amine.
- 'e' of the suffix of hydrocarbon is retained.
- Positions of $-NH_2$ group are specified by giving numbers to the parent chain.
- Example:

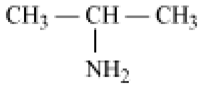
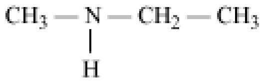
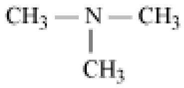
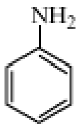
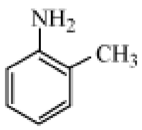


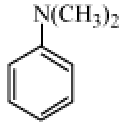
$H_2N-\overset{2}{C}H_2-\overset{1}{C}H_2-NH_2$

Ethane-1, 2-diamine

- For aryl amines –
- $-NH_2$ group is directly attached to the benzene ring

- Simplest arylamine: $C_6H_5NH_2$ (Common name – aniline, IUPAC name – benzenamine)
- While naming arylbenzenes by IUPAC system, the suffix ‘e’ of arene is replaced by ‘amine’.
- Common and IUPAC names of some alkylamine and arylamines are given in the table.

Amine	**Common name**	**IUPAC name**
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
 $CH_3-\underset{\underset{NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
 $CH_3-\underset{\underset{H}{\vert}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Aminotoluene

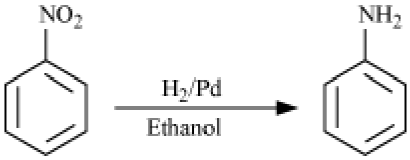
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

Methods of Preparation of Amines

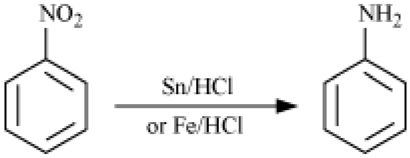
Reduction of Nitro Compounds

- By passing H_2 gas in presence of finely divided Ni, Pd, or Pt

Example:

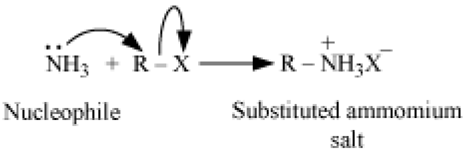


- By reduction with metals in acidic medium



Ammonolysis of Alkyl Halides

- The carbon−halogen (C−X) bond in alkyl or benzyl halides can be easily cleaved by a nucleophile.
- The process of cleavage of C−X bond by ammonia molecule is called **ammonolysis.**
- The reaction is carried out in a sealed tube at 373 K.
- An alkyl or benzyl halide reacts with an ethanolic solution of NH_3 as follows.



$$R-\overset{+}{N}H_3X^- + NaOH \longrightarrow R-NH_2 + NaX + H_2O$$

- Primary amine obtained behaves as a nucleophile and further reacts as

$$\underset{(1°)}{R-NH_2} \xrightarrow{RX} \underset{(2°)}{R_2NH} \xrightarrow{RX} \underset{(3°)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}X^-}$$

- Order of reactivity of halides with amines − RI > RBr > RCl
- Disadvantage − Mixture of primary, secondary, tertiary amines and quaternary ammonium salts is produced.

Reduction of Nitrites

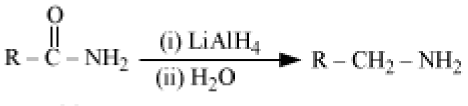
- Reduction of nitrites with $LiAlH_4$

$$\underset{\text{Nitrile}}{R-C\equiv N} \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

- Catalytic hydrogenation of nitriles

$$\underset{\text{Nitrile}}{R-C\equiv N} \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} \longrightarrow R-CH_2-NH_2$$

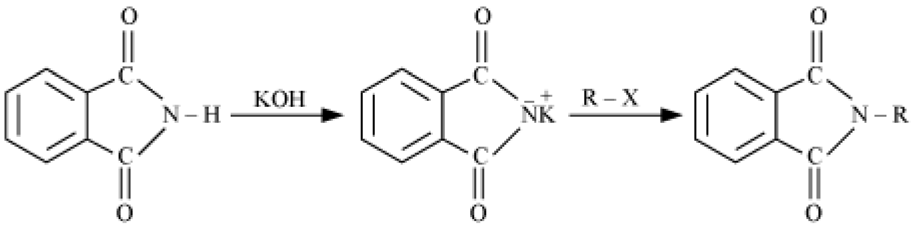
Reduction of Amides



$$\underset{\text{Amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

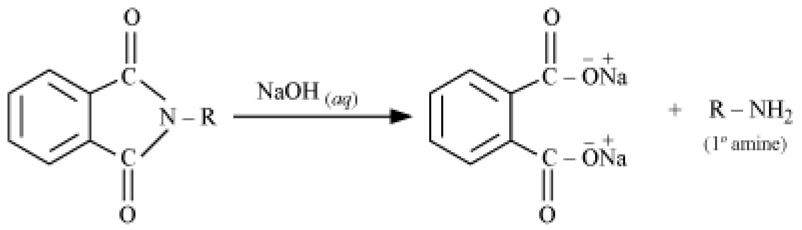
Gabriel Pthalimide Synthesis

- Used for the preparation of primary amine
- Reactions involved in the preparation of primary amine from phthalimide are as follows:



Phthalimide

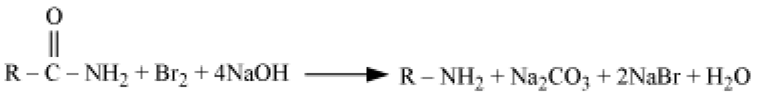
N-Alkylphthalimide



- Aromatic primary amines cannot be prepared by this process.
- Reason – Aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Hoffmann Bromamide Degradation Reaction

- Preparation of primary amines by treating an amide with Br_2 in an aqueous or ethanolic solution of NaOH



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + H_2O$$

- Amine formed contains one carbon less than that present in the amide.

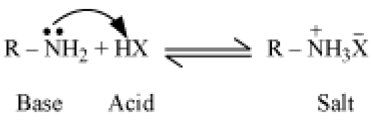
Physical Properties of Amines & Chemical Reaction of Amines - I

- Lower aliphatic amines are gases with fishy odour.
- Primary amines with three or more carbon atoms are liquid.
- Higher ones are solid.
- Aniline and other arylamines are colourless, but get coloured on storage due to atmospheric oxidation.
- Lower aliphatic amines are soluble in water.
- Reason: Form H-bonds with water molecules
- Solubility decreases with increase in molar mass.
- Higher amines are insoluble in water.
- Amines are soluble in organic solvents like alcohol, ether and benzene.
- Order of boiling points of isomeric amines is

Primary > Secondary > Tertiary

Chemical Reactions

- Amines are basic in nature.



$$\underset{\text{Base}}{R-\ddot{N}H_2} + \underset{\text{Acid}}{HX} \rightleftharpoons \underset{\text{Salt}}{R-\overset{+}{N}H_3\overset{-}{X}}$$

- Order of basicity of amines in the gaseous phase:

  Tertiary amine > Secondary amine > Primary amine > NH_3

- Order of basic strength in the case of methyl-substituted and ethyl-substituted amines is as follows:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

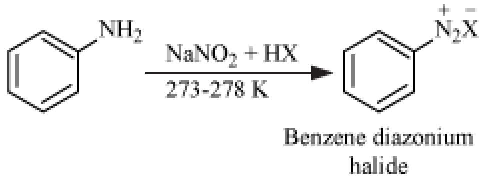
- In the case of substituted aniline:
- Electron-releasing groups like $-OCH_3$, $-CH_3$ increase basic strength
- Electron-withdrawing groups such as $-NO_2$, $-SO_3$, $-COOH$, $-X$ decrease basic strength.

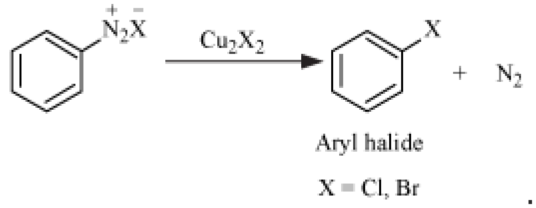
  Let us go through the given video to see the basicity of the simplest aromatic amine, aniline.

- **Alkylation**

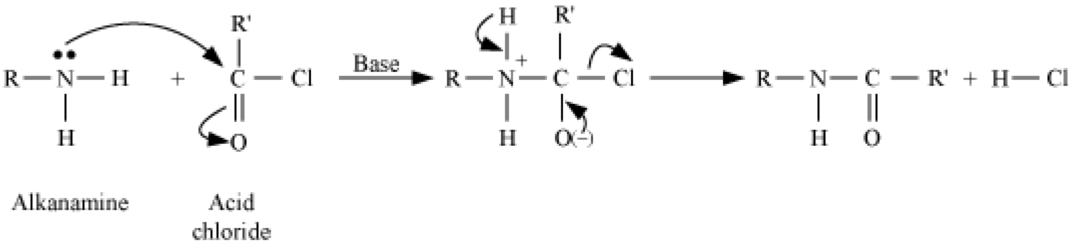
  Amines undergo alkylation on reaction with alkyl halides.

-
- Sandmeyer’s reaction

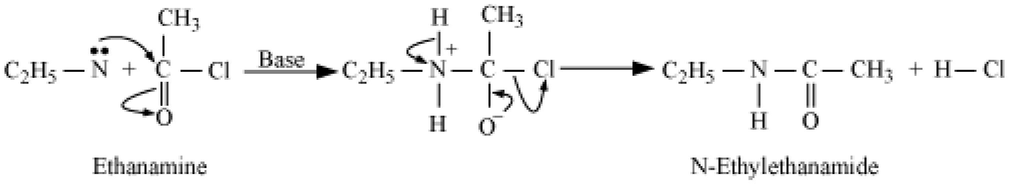


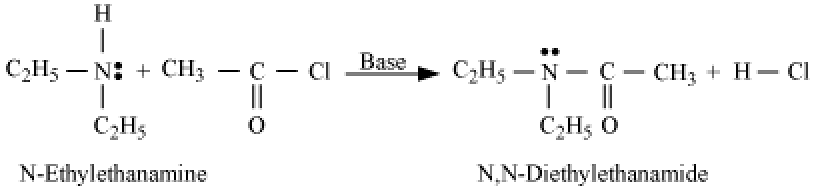


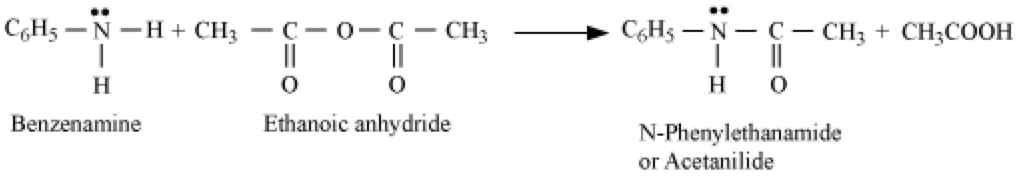
- **Acylation**



- Example:







Benzoylation – Reaction of amines with benzoyl chloride (C_6H_5COCl)

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{N-methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

Chemical Reactions of Amines - II

Carbylamine Reaction

$$\text{Aliphatic/Aromatic primary amines} + CHCl_3 + KOH \xrightarrow{\text{Heat}} \underset{\text{(foul smelling)}}{\text{Isocyanides or carbylamines}}$$

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Alkyl}\\\text{isocyanide}}}{R-NC} + 3KCl + 3H_2O$$

- Known as carbylamine reaction or isocyanide test
- Used as a test for primary amines
- 2° and 3° amines do not show this test

Reaction with Nitrous Acid

$HNO_2$is prepared *in situ*from a mineral acid (HCl) and sodium nitrite ($NaNO_2$).

- Primary aliphatic amines

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{Diazonium salt}}{\left[R-\overset{+}{N}_2\overset{-}{Cl}\right]} \xrightarrow{H_2O} \underset{\text{Alcohol}}{R-OH} + N_2 + HCl$$

- Aromatic amines

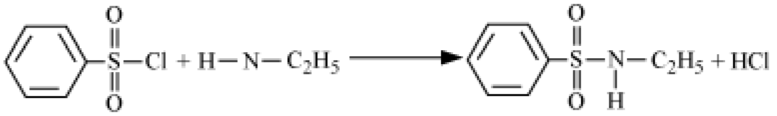
$$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow[273-278\text{ K}]{NaNO_2+2HCl} \underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

- Secondary and tertiary amines react differently with HNO_2.

Reaction with arylsulphonyl chloride

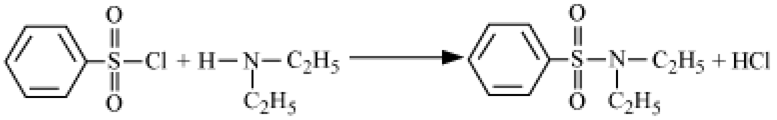
- Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) (known as Hinsberg's reagent) reacts with 1° and 2° amines to form sulphonamides.

- With primary (1°) amine



N – Ethylbenzenesulphonamide
(soluble in alkali)

- With secondary (2°) amine

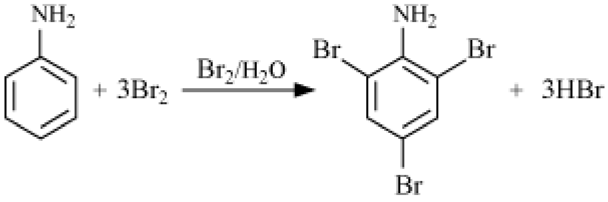


N, N – Diethylbenzenesulphonamide
(insoluble in alkali)

- No reaction with tertiary (3°) amines
- This reaction is used for the distinction of 1°, 2° and 3° amines.

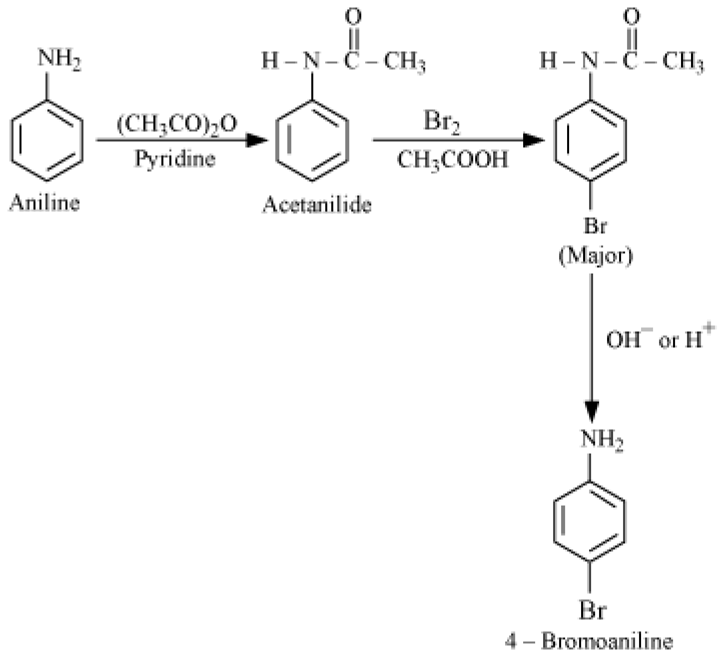
Electrophilic Substitution Reactions

- Aniline is a resonance hybrid of five structures.
- −NH_2 group is a powerful *ortho* and *para* directing group.
- **Bromination**



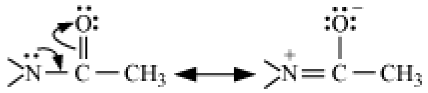
Aniline 2,4,6-Tribromoaniline.

- Electrophilic substitution reaction of aromatic amines is of very high reactivity − tends to occur both at *ortho* and *para* positions. To prepare monosubstituted aniline, −NH_2 group is protected by acetylation with acetic anhydride; then the desired substitution is carried out, followed by hydrolysis.

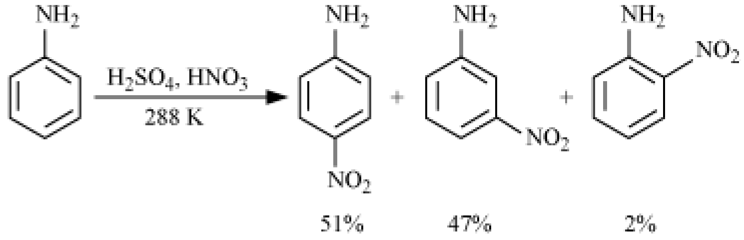


Activating effect of $-NHCOCH_3$is less than that of the amino group.

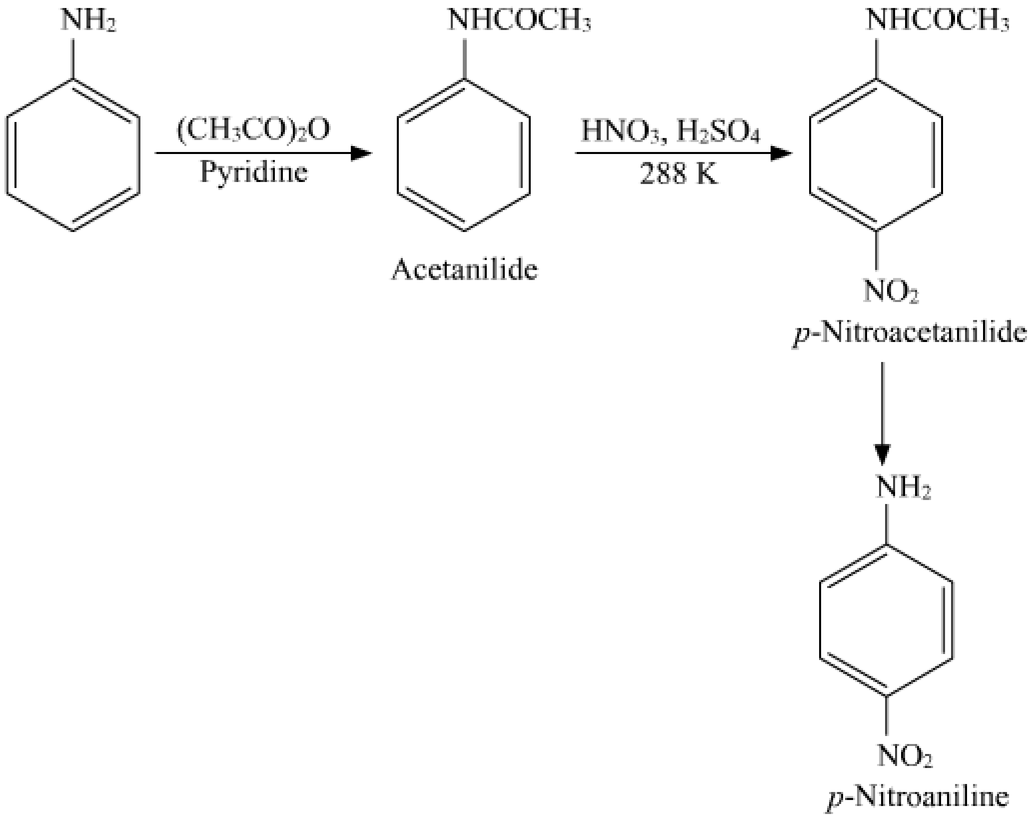
Reason – Lone pair is less available on nitrogen for donation to the benzene ring by resonance.



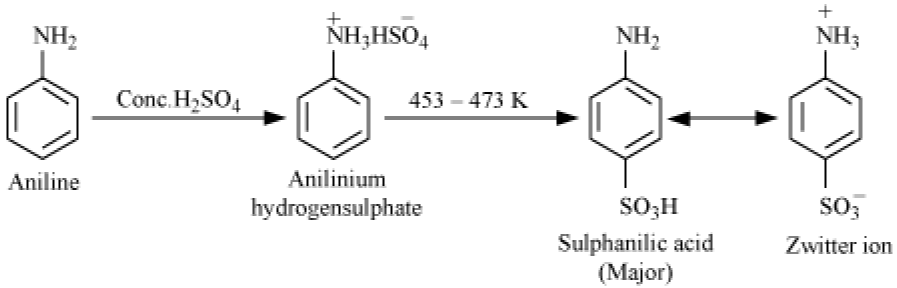
- **Nitration**



- In strong acidic medium, anilinium ion is formed, which is *meta* directing. Hence, significant amount of *meta* derivative is also formed along with *ortho* and *para* isomers.
- By protecting $-NH_2$ group by acetylation reaction, *para* isomer can be obtained as the major product.



- **Sulphonation**



Diazonium Salts

- General formula = $R\overset{+}{N}_2X^-$

  R → An aryl group

  X^- ion → Cl^-, Br^-, HSO_4^-, BF_4^-, etc.

$\overset{+}{N}_2$ group → Diazonium group

- Examples:

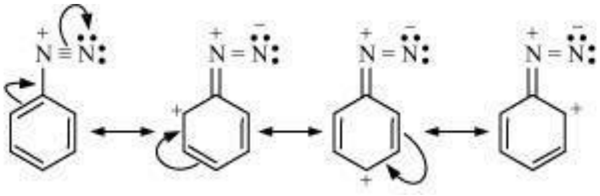
  $C_6H_5\overset{+}{N}_2Cl^-$ → Benzenediazonium chloride

  $C_6H_5\overset{+}{N}_2HSO_4^-$ → Benzenediazonium hydrogen sulphate

- Primary aliphatic amines form unstable alkyldiazonium salts.

  Primary aromatic amines form stable arenediazonium salts, which are stable for a short time in solution (at 273 − 278 K).

  Stability of arenediazonium salts can be explained on the basis of resonance.



Preparation

$$\underset{\text{Aniline}}{C_6H_5NH_2} + NaNO_2 + 2HCl \xrightarrow{273-278\text{ K}} \underset{\substack{\text{Benzendiazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + NaCl + 2H_2O$$

- HNO_2 is produced in the reaction by the reaction of $NaNO_2$ and HCl.

- The conversion of primary aromatic amines into diazonium salts is called diazotisation.

Physical properties

- Colourless crystalline solid

- Readily soluble in water

- Stable in cold, but reacts with water when warmed

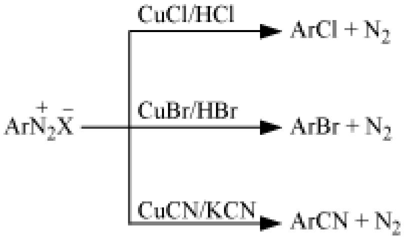
- Decomposes easily in dry state

- Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

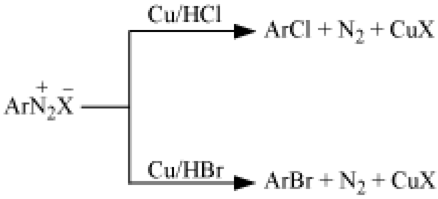
Chemical Reactions

Reaction Involving Displacement of Nitrogen

- $\overset{+}{N}_2$ group is a good leaving group and escapes from the reaction mixture as a gas.
- Replacement by halide or cyanide ion
- **Sandmeyer reaction**



- **Gatterman reaction**



- Replacement by iodide ion

$$Ar\overset{+}{N}_2Cl^- + KI \longrightarrow ArI + KCl + N_2$$

$$C_6H_5\overset{+}{N}_2Cl^- + KI \longrightarrow \underset{\text{Iodobenzene}}{C_6H_5I + KCl} + N_2$$

- Replacement by fluoride ion

$$Ar\overset{+}{N}_2Cl^- + \underset{\text{Fluoroboric acid}}{HBF_4} \longrightarrow Ar - \overset{+}{N}_2BrF_4^- \xrightarrow{\text{Heat}} Ar - F + BF_3 + N_2$$

- Replacement by Hydrogen atom

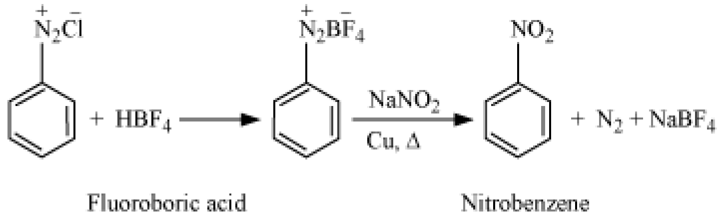
$$Ar\overset{+}{N}_2Cl^- + \underset{\text{Hypophosphorus acid}}{H_3PO_2} + H_2O \longrightarrow \underset{\text{Arene}}{ArH} + N_2 + \underset{\text{Phosphorus acid}}{H_3PO_3} + HCl$$

$$Ar\overset{+}{N}_2Cl + \underset{\text{Ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Arene}}{ArH} + N_2 + \underset{\text{Ethanol}}{CH_3CHO} + HCl$$

- Replacement by hydroxyl group

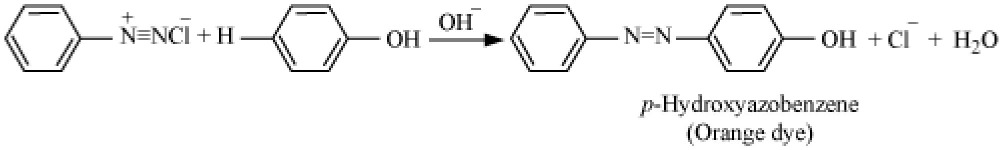
$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_2O \xrightarrow{283K} ArOH + N_2 + HCl$$

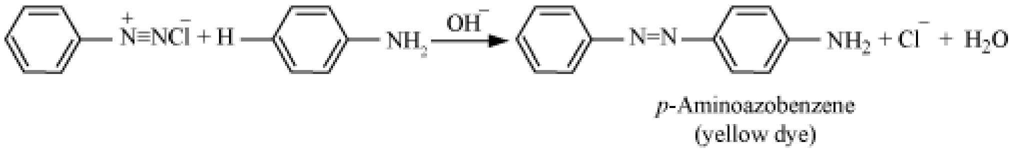
- Replacement by $-NO_2$ group



Reactions Involving Retention of Diazo Group

- Coupling reactions
- Azo products are obtained, which have an extended conjugated system. Both the aromatic rings are joined through the $-N=N-$ bond.





- It is an example of electrophilic substitution reaction.

Importance of Diazonium Salts in synthesis of aromatic compounds

- Substituted aromatic compounds can easily be prepared by the replacement of diazo group, which cannot be obtained by direct substitution in benzene or substituted benzene.

- − F, −Cl, −Br, −I, −CN, −OH, $-ON_2$ groups can be introduced into the aromatic ring.