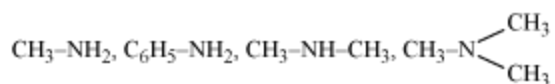


Amines

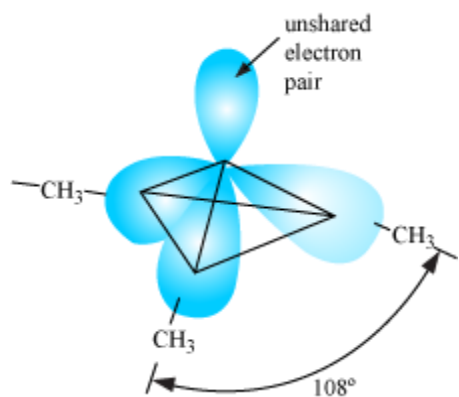
Amines

- 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:



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 NH₃ is replaced by R or Ar, RNH₂ or ArNH₂ is obtained (primary amine, 1°).
- If two H-atoms of NH₃ or one H-atom of RNH₂ are replaced by alkyl or aryl group (R'), R₂NH 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.

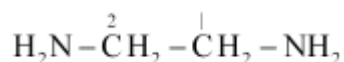
IUPAC System

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

CH_3NH_2 – Methanamine

$\text{CH}_3\text{CH}_2\text{NH}_2$ – Ethanamine

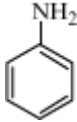
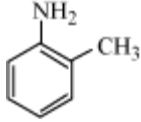
- When more than one amino group is present –
- Suitable prefix such as di-, tri-, etc., is attached to amine.
- 'e' of the suffix of hydrocarbon is retained.
- Positions of $-\text{NH}_2$ group are specified by giving numbers to the parent chain.
- Example:

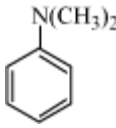


Ethane-1, 2-diamine

- For aryl amines –
- $-\text{NH}_2$ group is directly attached to the benzene ring

- Simplest arylamine: $\text{C}_6\text{H}_5\text{NH}_2$ (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
$\text{CH}_3\text{—CH}_2\text{—NH}_2$	Ethylamine	Ethanamine
$\begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropylamine	Propan-2-amine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_2\text{—CH}_3 \\ \\ \text{H} \end{array}$	Ethylmethylaniline	N-Methylethanamine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_3 \\ \\ \text{CH}_3 \end{array}$	Trimethylamine	N,N-Dimethylmethanamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Aminotoluene

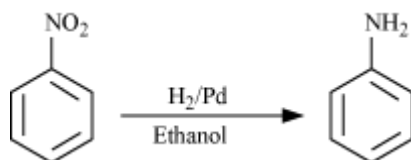
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine
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Methods of Preparation of Amines

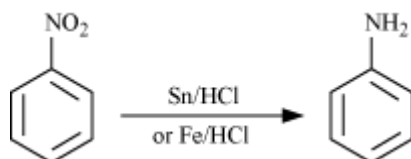
Reduction of Nitro Compounds

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

Example:

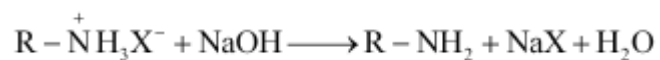
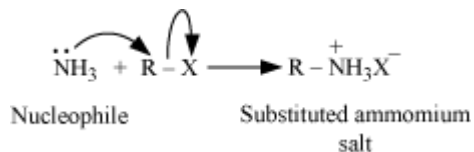


- By reduction with metals in acidic medium

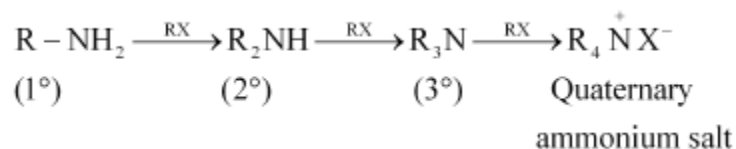


Ammonolysis of Alkyl Halides

- 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.



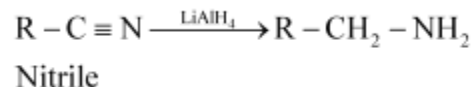
- Primary amine obtained behaves as a nucleophile and further reacts as



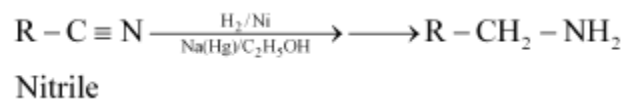
- Order of reactivity of halides with amines – RI > RBr > RCl
- Disadvantage – Mixture of primary, secondary, tertiary amines and quaternary ammonium salts is produced.

Reduction of Nitrites

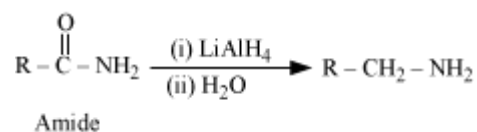
- Reduction of nitriles with LiAlH₄



- Catalytic hydrogenation of nitriles

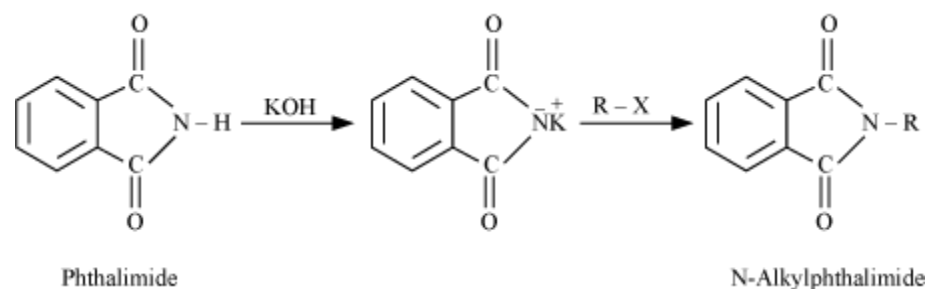


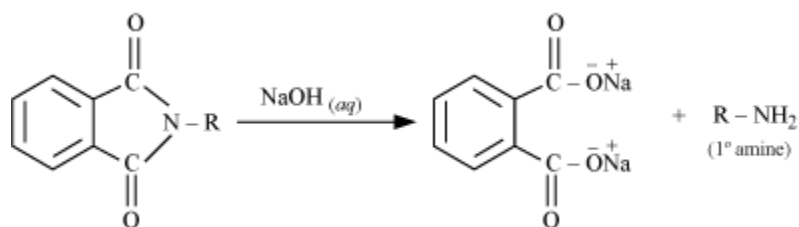
Reduction of Amides



Gabriel Pthalimide Synthesis

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

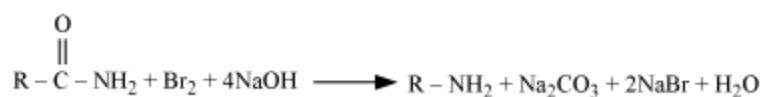




- Aromatic primary amines cannot be prepared by this process.
- Reason – Aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Hoffmann Bromamide Degradation Reaction

- Preparation of primary amines by treating an amide with Br₂ in an aqueous or ethanolic solution of NaOH



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

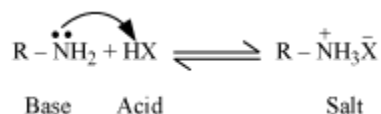
Physical Properties of Amines & Chemical Reaction of Amines - I

- 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

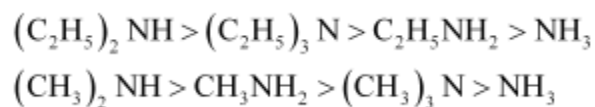
- Amines are basic in nature.



- 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:



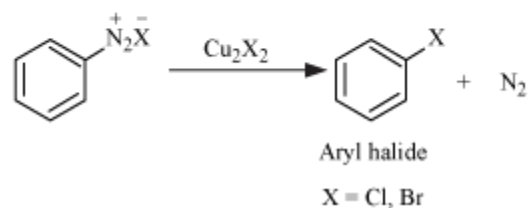
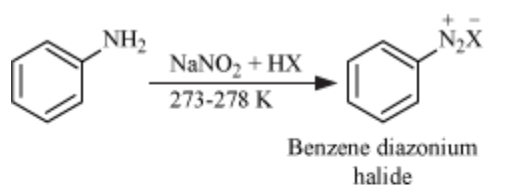
- In the case of substituted aniline:
- Electron-releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength
- Electron-withdrawing groups such as $-\text{NO}_2$, $-\text{SO}_3$, $-\text{COOH}$, $-\text{X}$ decrease basic strength.

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

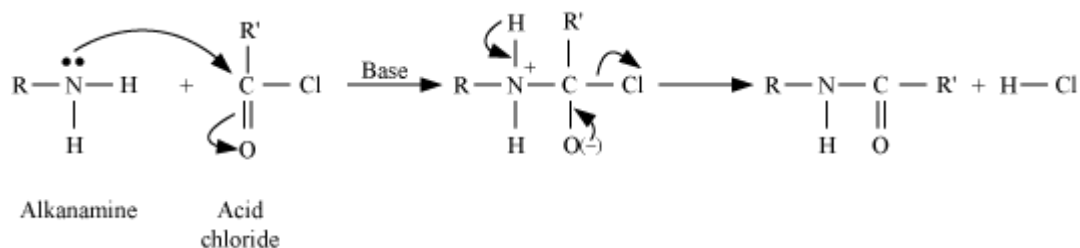
- Alkylation**

Amines undergo alkylation on reaction with alkyl halides.

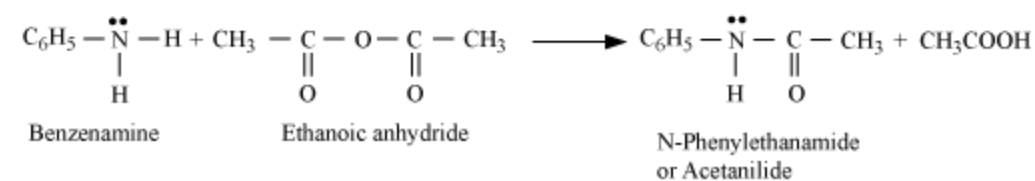
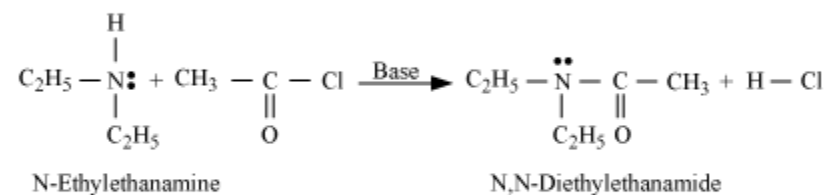
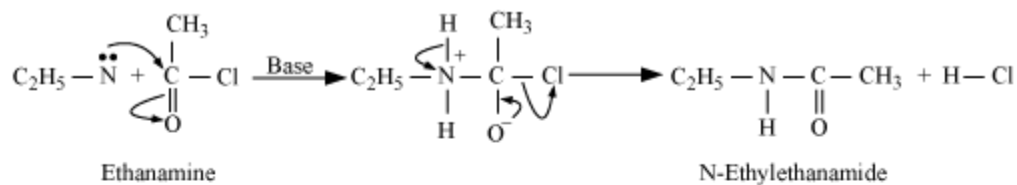
-
- Sandmeyer's reaction



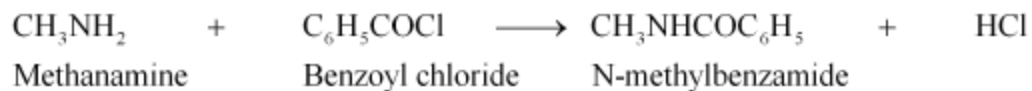
- Acylation**



- Example:**



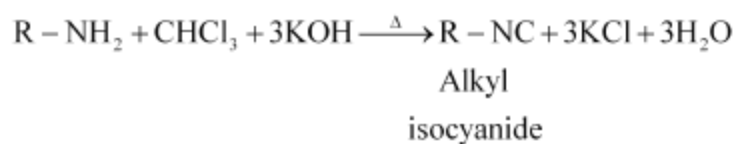
Benzoylation – Reaction of amines with benzoyl chloride (C₆H₅COCl)



Chemical Reactions of Amines - II

Carbylamine Reaction

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

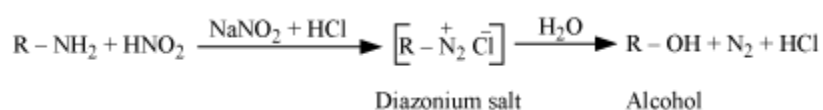


- Known as carbylamine reaction or isocyanide test
- Used as a test for primary amines
- 2° and 3° amines do not show this test

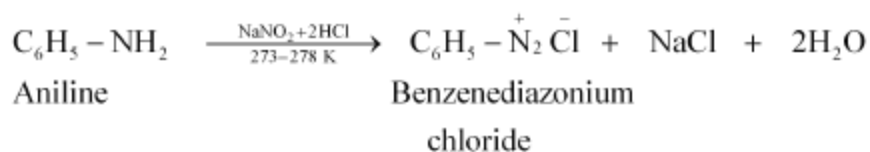
Reaction with Nitrous Acid

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

- Primary aliphatic amines



- Aromatic amines

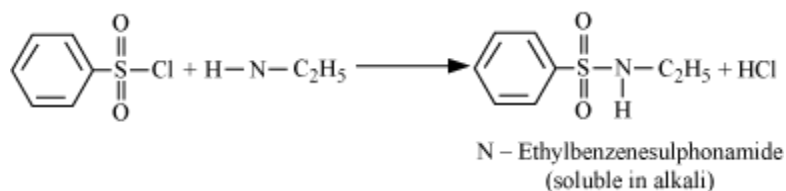


- Secondary and tertiary amines react differently with HNO_2 .

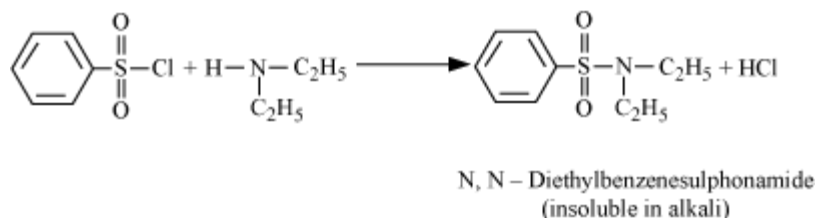
Reaction with arylsulphonyl chloride

- Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) (known as Hinsberg's reagent) reacts with 1° and 2° amines to form sulphonamides.

- With primary (1°) amine



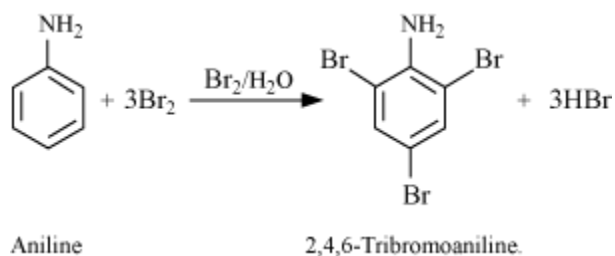
- With secondary (2°) amine



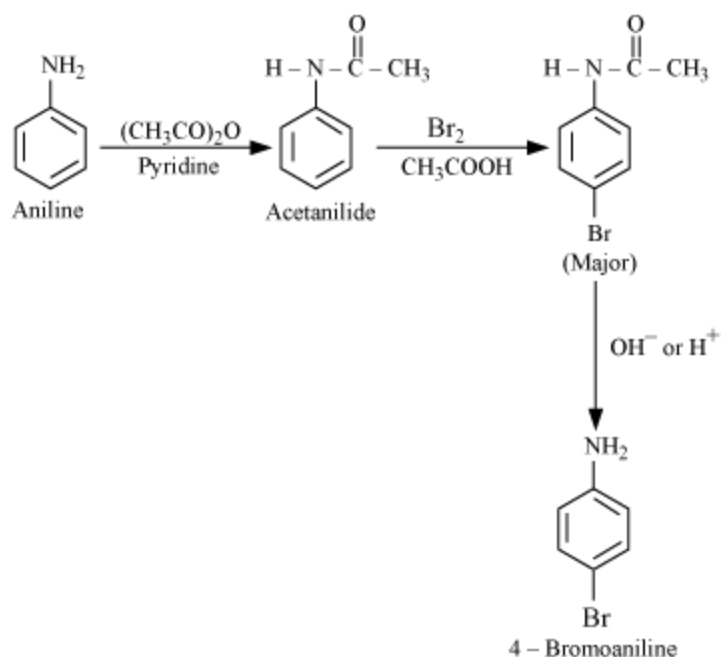
- No reaction with tertiary (3°) amines
- This reaction is used for the distinction of 1° , 2° and 3° amines.

Electrophilic Substitution Reactions

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



- 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.

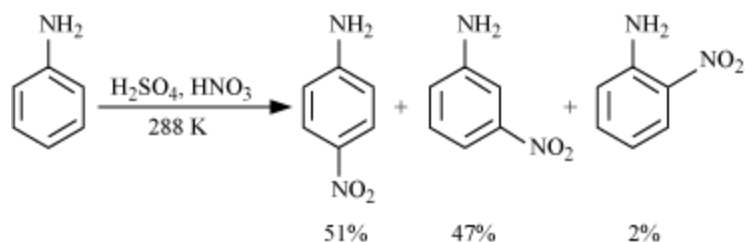


Activating effect of $-\text{NHCOCH}_3$ is less than that of the amino group.

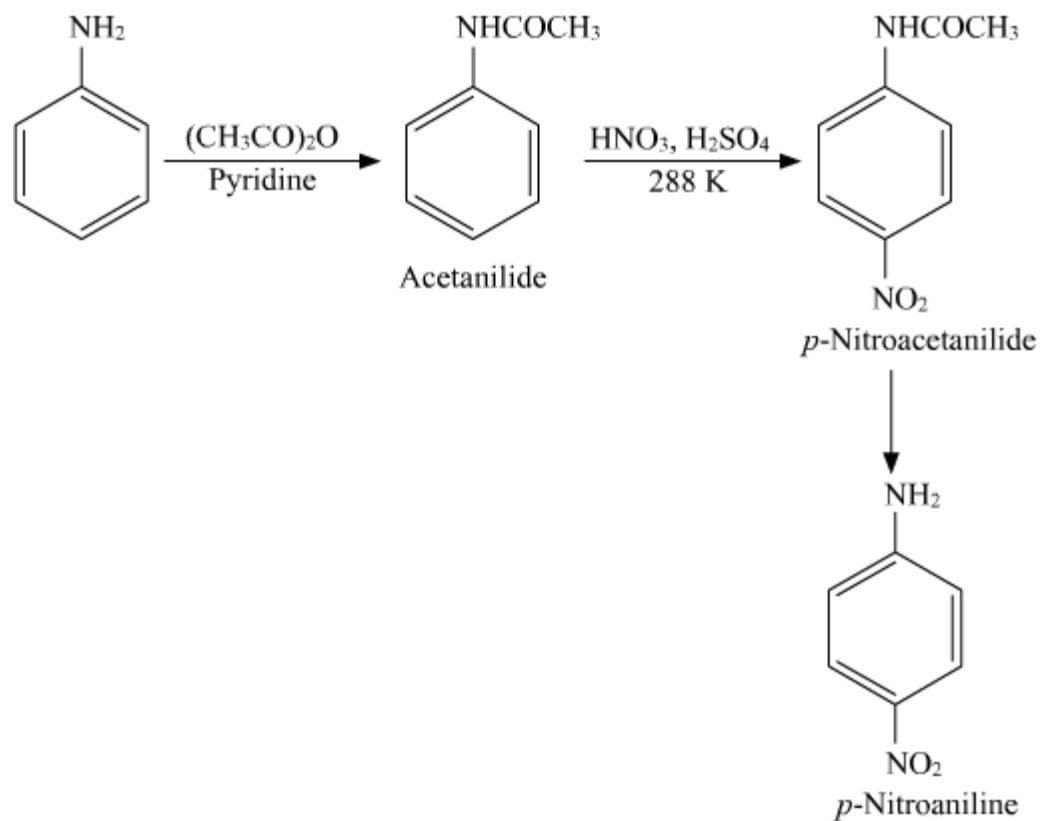
Reason – Lone pair is less available on nitrogen for donation to the benzene ring by resonance.



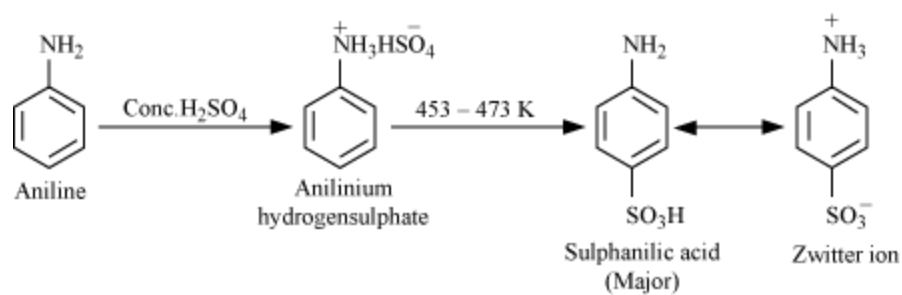
• Nitration



- 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 $-\text{NH}_2$ group by acetylation reaction, *para* isomer can be obtained as the major product.



- Sulphonation**



Diazonium Salts

- General formula = $\text{R} \text{N}_2^+ \text{X}^-$

$\text{R} \rightarrow$ An aryl group

X^- ion $\rightarrow \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{BF}_4^-$, etc.

N_2^+ group $\rightarrow$ Diazonium group

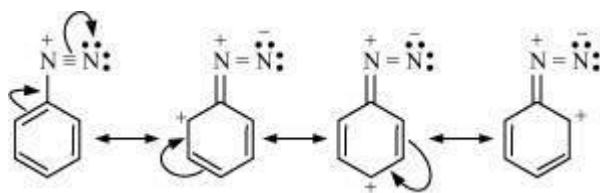
- Examples:



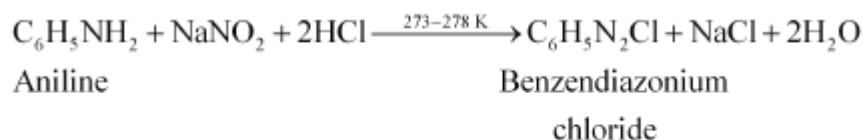
- Primary aliphatic amines form unstable alkyldiazonium salts.

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



- 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

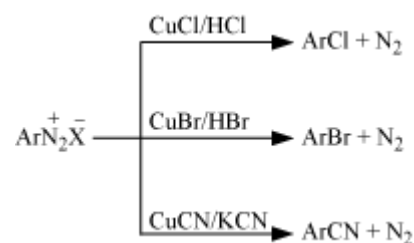
- Colourless crystalline solid
- Readily soluble in water
- Stable in cold, but reacts with water when warmed
- Decomposes easily in dry state

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

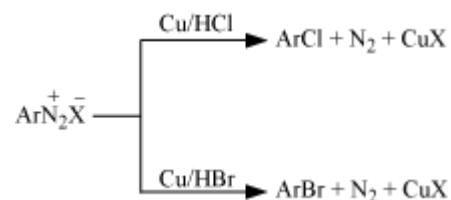
Chemical Reactions

Reaction Involving Displacement of Nitrogen

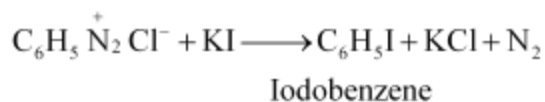
- N_2^+ group is a good leaving group and escapes from the reaction mixture as a gas.
- Replacement by halide or cyanide ion
- **Sandmeyer reaction**



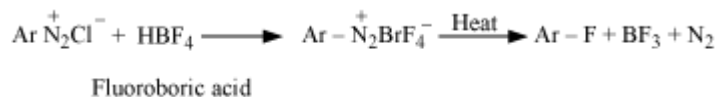
- **Gatterman reaction**



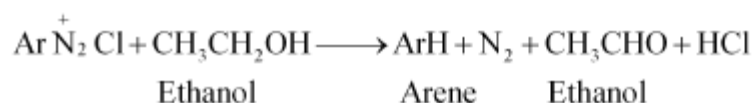
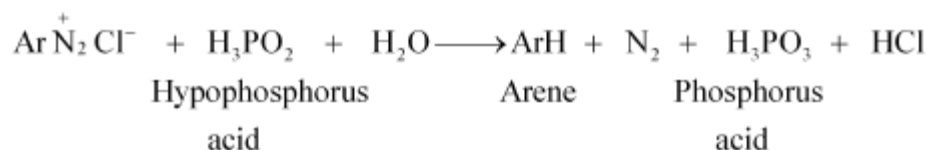
- Replacement by iodide ion



- Replacement by fluoride ion



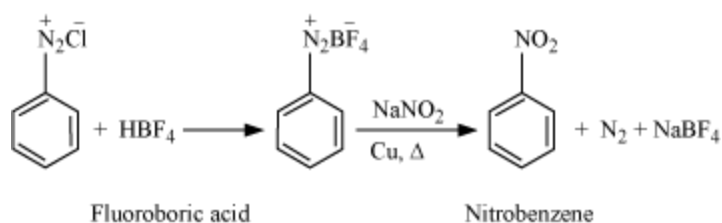
- Replacement by Hydrogen atom



- Replacement by hydroxyl group

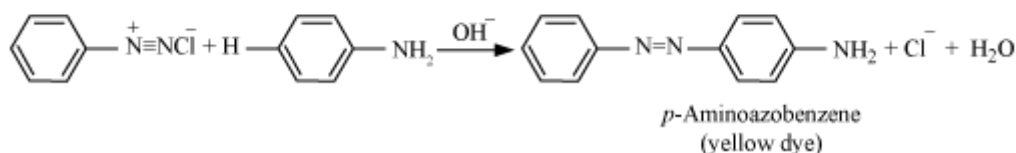
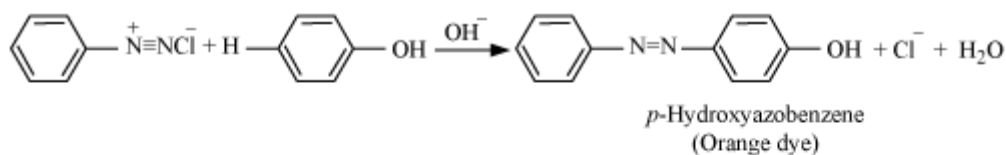


- Replacement by -NO₂ group



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, –ON₂ groups can be introduced into the aromatic ring.