

## Amines

### Amines:

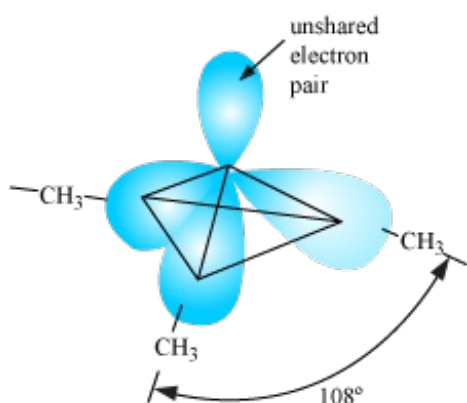
- (i) Derivatives of ammonia
- (ii) Obtained by the replacement of one, two or all the three H-atoms of ammonia by alkyl and/or aryl group

### (iii) Structure of Amines

Nitrogen on amines is  $sp^3$  hybridised.

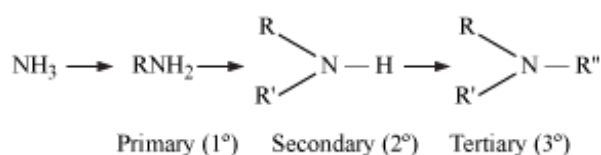
Geometry – Pyramidal

Example: Pyramidal shapes of trimethylamine



**Classification:** Primary (1°), secondary (2°) and tertiary (3°)

- (i) If one H-atom of  $\text{NH}_3$  is replaced by R or Ar,  $\text{RNH}_2$  or  $\text{ArNH}_2$  is obtained (primary amine, 1°).
- (ii) If two H-atoms of  $\text{NH}_3$  or one H-atom of  $\text{RNH}_2$  are replaced by alkyl or aryl group ( $\text{R}'$ ),  $\text{R}_2\text{NH}$  is obtained (secondary amine, 2°).
- (iii) On the replacement of another hydrogen atom by alkyl or aryl group,  $\text{R}_3\text{N}$  is obtained (tertiary amine, 3°).



### Nomenclature

### Common System

Aliphatic amine: Named by prefixing alkyl group to amine, i.e., alkylamine. Example:  
Methylamine ( $\text{CH}_3\text{NH}_2$ )

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:  $\text{CH}_3\text{NH}_2$  – Methanamine

When more than one amino group is present –

- (i) Suitable prefix such as di-, tri-, etc., is attached to amine.
- (ii) 'e' of the suffix of hydrocarbon is retained.
- (iii) Positions of  $-\text{NH}_2$  group are specified by giving numbers to the parent chain.

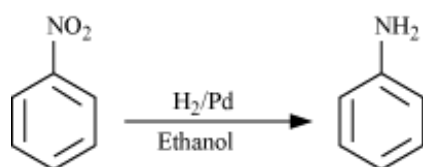
Example:  $\text{H}_2\text{N}-\overset{2}{\text{CH}_2}-\overset{1}{\text{CH}_2}-\text{NH}_2$  Ethane-1, 2-diamine

(iv) or aryl amines  $-\text{NH}_2$  group is directly attached to the benzene ring

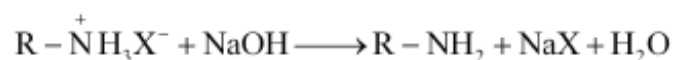
While naming arylbenzenes by IUPAC system, the suffix 'e' of arene is replaced by 'amine'.

### Preparation:

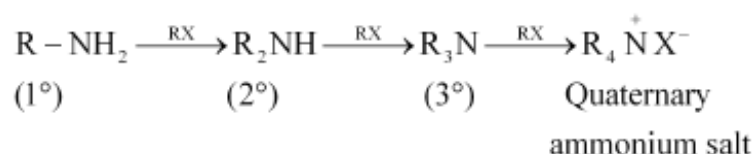
(i) **By reduction of nitro compounds –**



(ii) **By ammonolysis of alkyl halides –** Ammonolysis is the process of cleavage of the C–X bond by ammonia molecule.

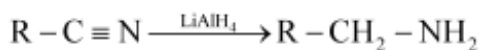


Primary amine obtained behaves as a nucleophile and further reacts as



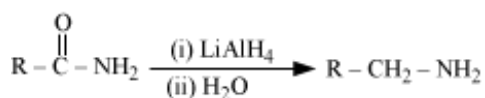
Order of reactivity of halides with amines –  $\text{RI} > \text{RBr} > \text{RCI}$

(iii) **Reduction of Nitrites**



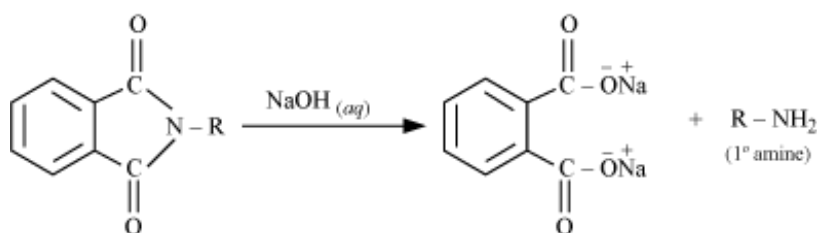
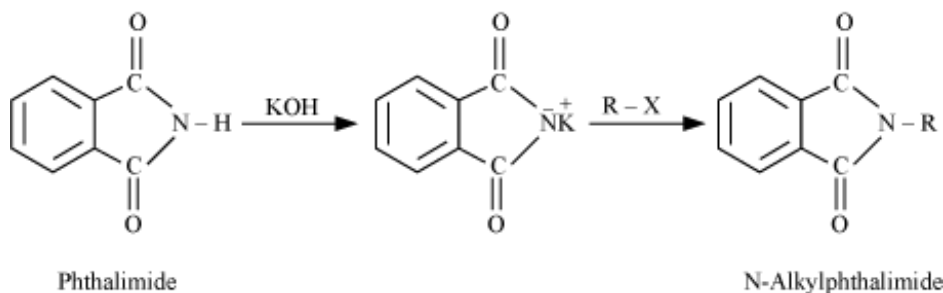
Nitrile

#### (iv) Reduction of Amides

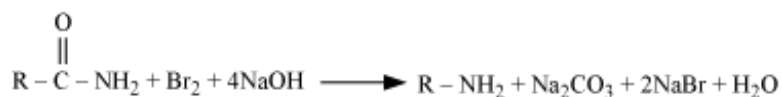


Amide

**(v) Gabriel Phthalimide Synthesis:** Used for the preparation of primary amine.



**(vi) Hoffmann Bromamide Degradation Reaction:**



#### Physical properties:

##### Solubility –

(i) Lower aliphatic amines are soluble in water, but higher amines are insoluble in water. This is because lower amines can form H-bonds with water, but higher amines cannot.

(ii) Solubility of amines in water decreases with increase in molar mass of amines as the size of the hydrophobic alkyl part increases.

(iii) The order of increasing boiling points of isomeric amines is

3° amine < 2° amine < 1° amine. This because of intermolecular association of 1 amines due to H-bonding.

## Chemical reactions:

### (i) Basic character of amines –

The order of increasing basicity is

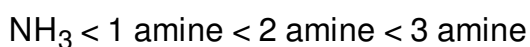
(a) Aromatic amines < Ammonia < Aliphatic amines

Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups.

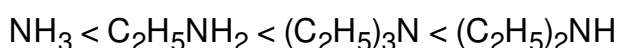
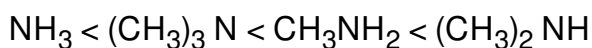
Aromatic amines are weaker bases than ammonia due to electron-withdrawing nature of the aryl group.

### Structure–basicity relationship of amines

The increasing order of basicity of amines in the gaseous phase is



The increasing order of basic strength in the case of methyl-substituted amines and ethyl-substituted amines in aqueous solution.



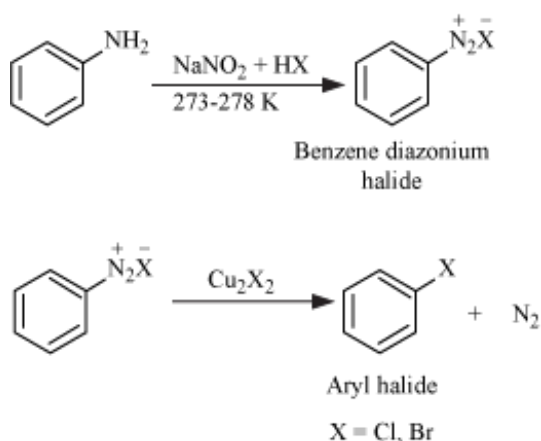
The above order is due to the combined effect of steric hindrance of the alkyl group, inductive effect and solvation effect.

In the case of substituted aniline, electron-withdrawing groups ( $-\text{NO}_2$ ,  $-\text{SO}_3$ ,  $-\text{COOH}$ ,  $-\text{X}$ ) decrease the basicity while electron-donating groups ( $-\text{OCH}_3$ ,  $-\text{CH}_3$ ) increase the basicity.

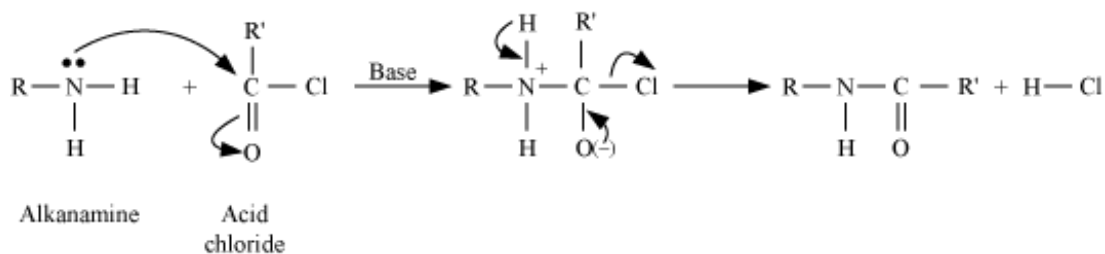
### (ii) Alkylation

Amines undergo alkylation on reaction with alkyl halides.

Sandmeyer's reaction



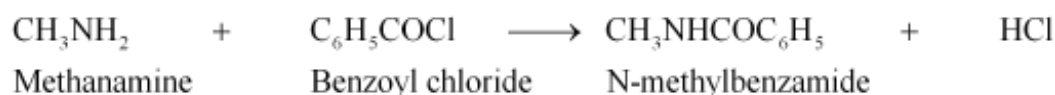
### (iii) Acylation



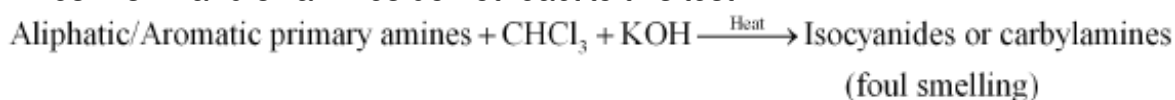
For example:



**(iv) Benzoylation** – Reaction of amines with benzoyl chloride ( $\text{C}_6\text{H}_5\text{COCl}$ )

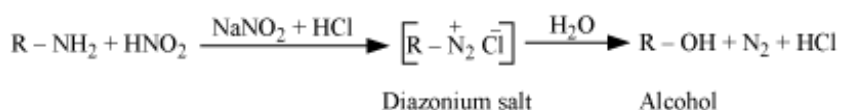


**Carbylamines reaction (or isocyanide test)** – Used as test to distinguish  $1^\circ$ ,  $2^\circ$ , and  $3^\circ$  amines. As  $2^\circ$  and  $3^\circ$  amines do not react to this test.

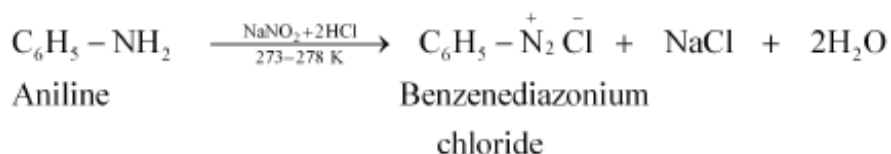


**Reaction with nitrous acid** – Nitrous acid is prepared in situ from a mineral acid and sodium nitrate.

**Primary aliphatic amines:**

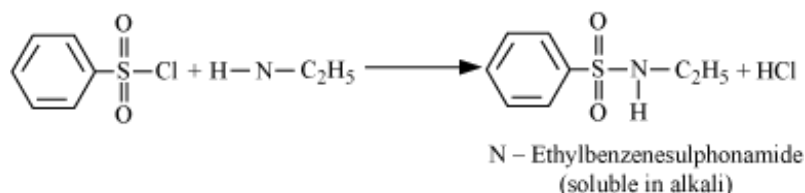


**Aromatic amines:**

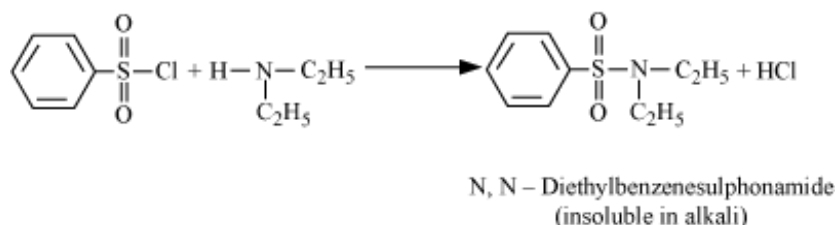


**Reaction with arylsulphonyl chloride** – Hinsberg's reagent Benzenesulphonyl chloride ( $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ ). This reaction can be used for distinguishing and separating  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines

(i) Primary amine: The amide formed is soluble in alkali because the hydrogen attached to nitrogen is strongly acidic due to the presence of a strong electron-withdrawing sulphonyl group.



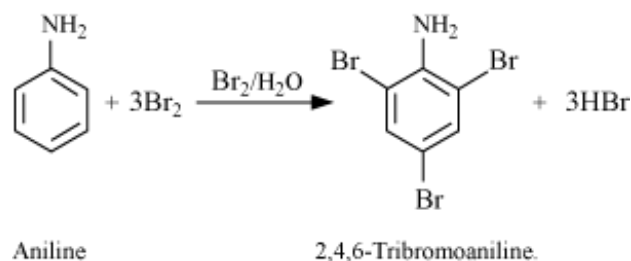
(ii) Secondary amine: The amide formed is insoluble in alkali. As it does not contain any hydrogen atom attached to nitrogen atom, it is not acidic.



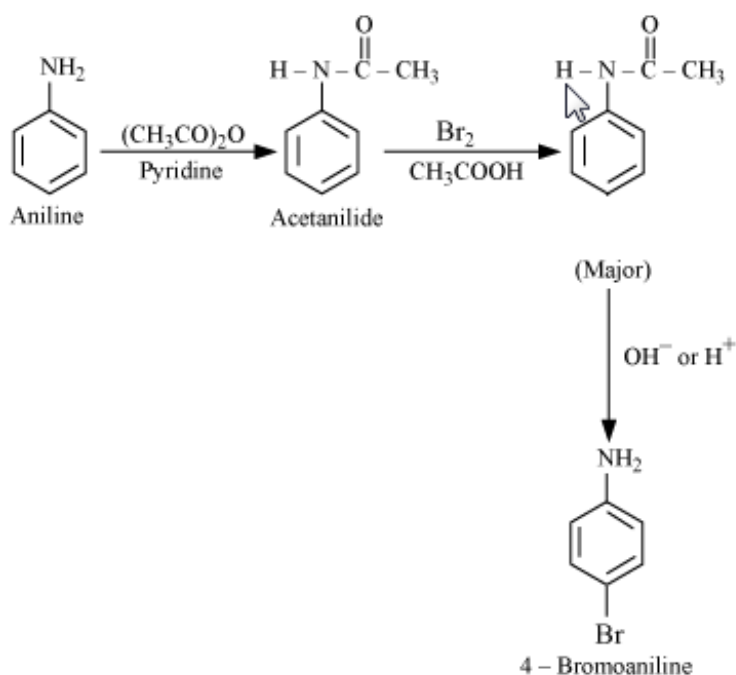
(iii) Tertiary amines do not react with Hinsberg's reagent.

### Electrophilic substitution –

**(i) Bromination:** Electrophilic substitution reaction of aromatic amines is of very high reactivity – tends to occur both at *ortho* and *para* positions.

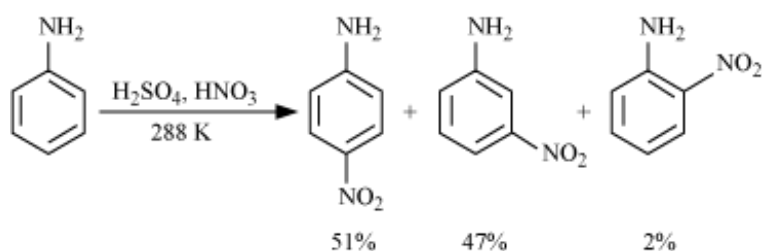


To prepare monosubstituted aniline,  $-\text{NH}_2$  group is protected by acetylation with acetic anhydride; then the desired substitution is carried out, followed by hydrolysis.

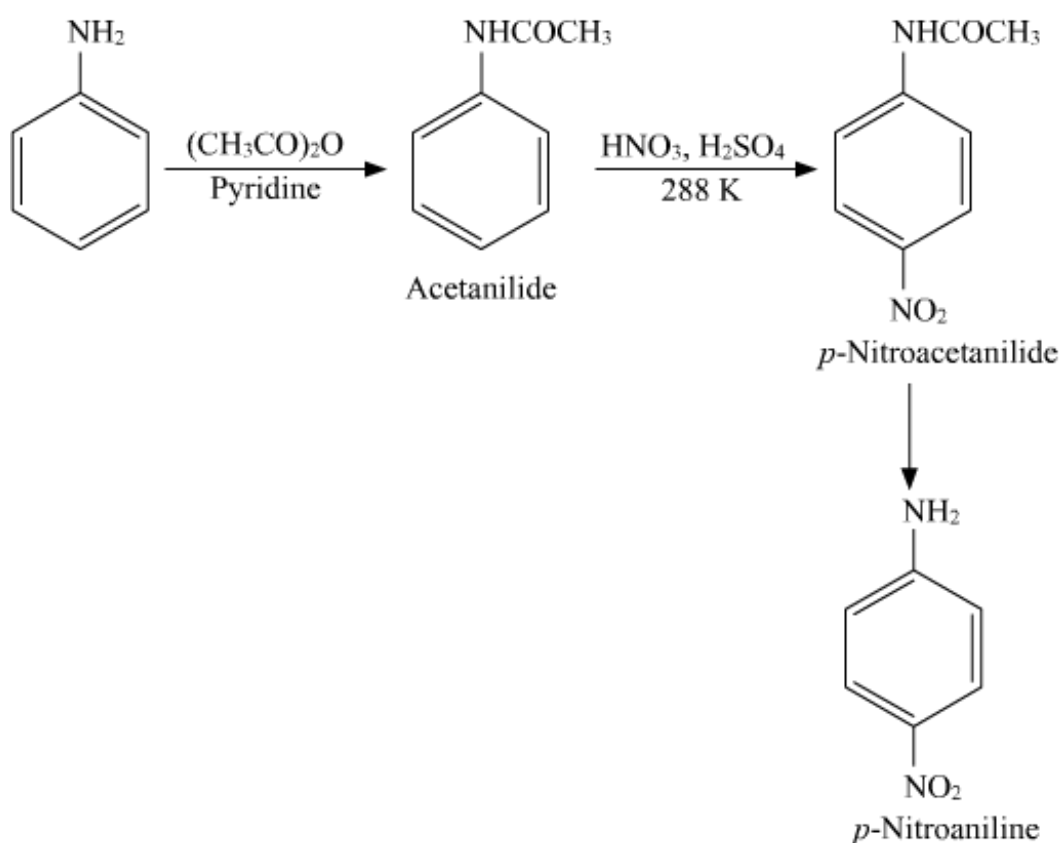


**(ii) Nitration:** In strong acidic medium, anilinium ion is formed, which is *meta* directing. Hence,

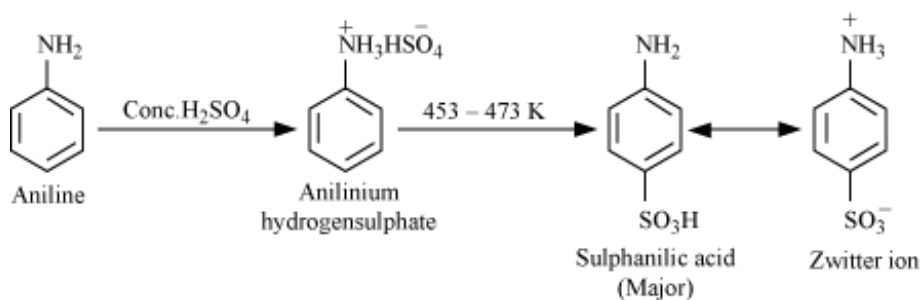
significant amount of *meta* derivative is also formed along with *ortho* and *para* isomers.



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



### (iii) Sulphonation:

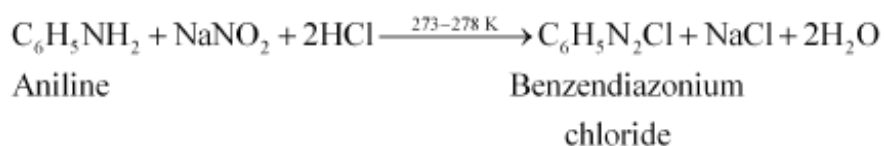


(iv) Aniline does not undergo Friedel–Crafts reaction (alkylation and acylation).

Diazonium salts:  $\text{R-N}_2^+ \text{X}^-$

### Preparation:

**Diazotisation :** The conversion of primary aromatic amines into diazonium salts.

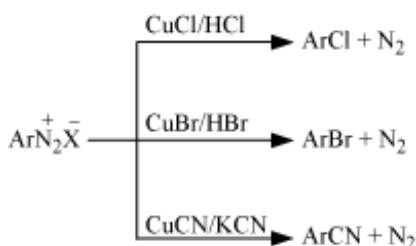


## Chemical reactions:

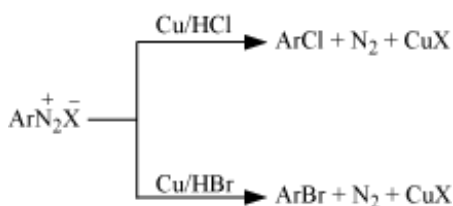
Reactions that involve displacement of nitrogen

### (i) Replacement by halide or cyanide ion

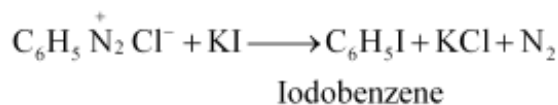
#### Sandmeyer's reaction



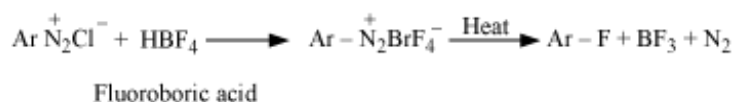
#### Gattermann reaction



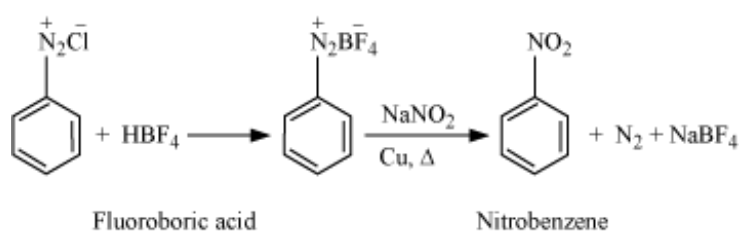
### Replacement by iodide ion



### Replacement by fluoride ion



### (ii) Replacement by NO<sub>2</sub> group



### (iii) Reactions that involve retention of diazo group:



## Coupling reactions (Electrophilic substitution reaction)

