

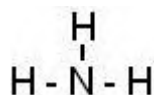
# Amines

## AMINES

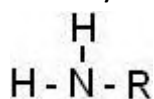
Amine may be regarded as derivative of ammonia formed by replacement of one or more hydrogen atoms by corresponding number of alkyl or aryl group

### CLASSIFICATION

1. Ammonia

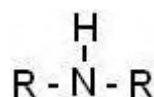


2. Primary amine

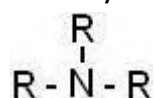


3. Secondary

When two hydrogen atoms are replaced by two alkyl or aryl groups.



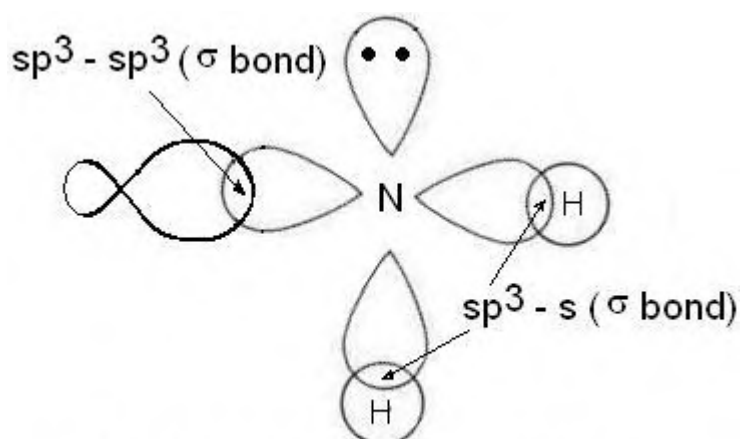
4. Tertiary amine



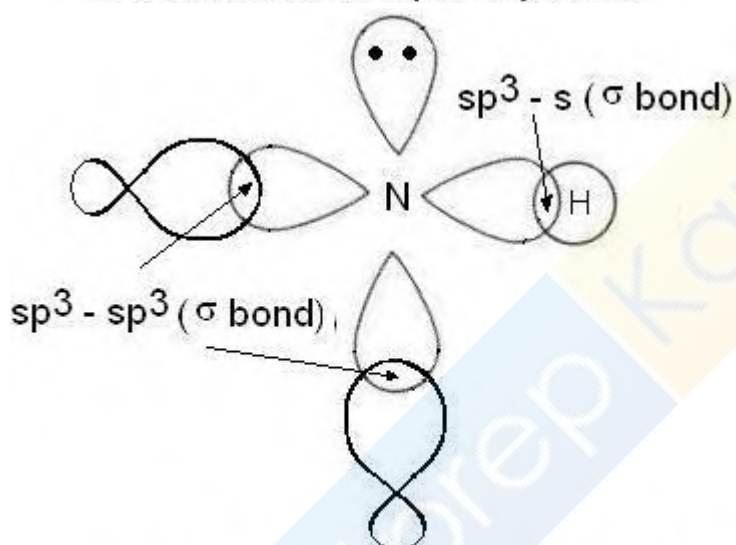
### STRUCTURE OF AMINO GROUP

- Nitrogen atom of amino group is  $sp^3$  hybridised. Three of these orbitals get involved in sigma bond formation with other atoms whereas the fourth orbital contains lone pair of electrons
- Due to presence of unshared pair of electron, the angle is less than  $109.5^\circ$
- The angle around N atom in amines is not fixed and depends upon the number and size of alkyl group bonded to N atom. Therefore, in  $1^\circ$  and  $2^\circ$  amines, the bond angle between any two H atoms (in  $1^\circ$ ) or alkyl group (in  $2^\circ$ ) decreases from the tetrahedral angle of  $109^\circ 28'$  to  $107^\circ$
- In case of  $3^\circ$  amines, the three bulky alkyl groups around N atom due to steric hindrance, the bond angle increases from  $107^\circ$  to  $108^\circ$  in trimethylamine

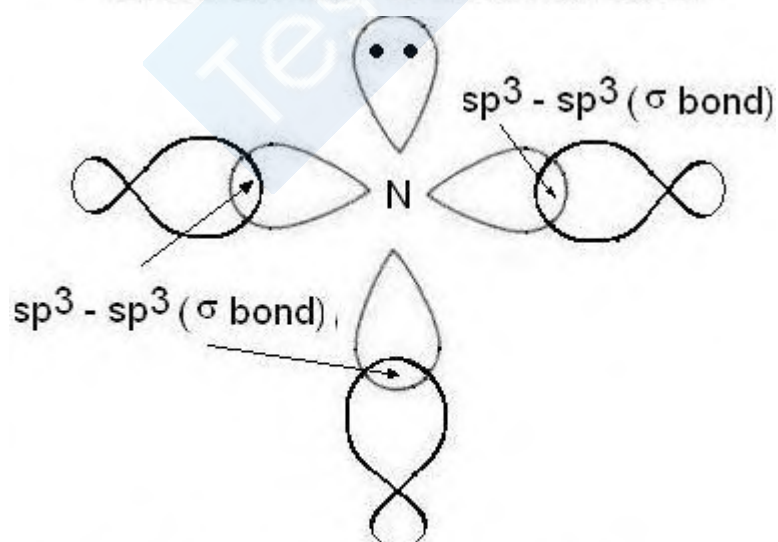
## Amines



Orbital structure of primary amine



Orbital structure of secondary amine



Orbital structure of tertiary amine

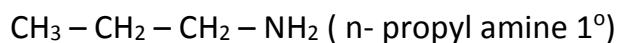
# Amines

## ISOMERISM

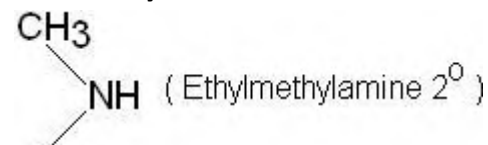
1. Functional Isomerism: This is due to presence of different functional groups

- Molecular formula  $C_3H_9N$  represent three functional isomers

### Primary



### Secondary

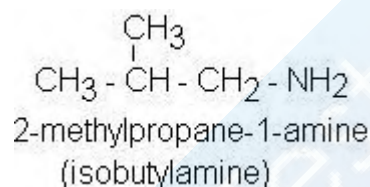
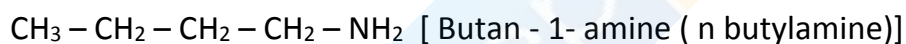


### Tertiary



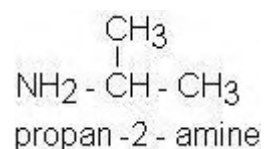
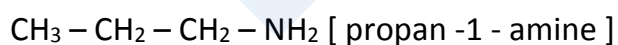
2. Chain isomerism : This is due to difference in the carbon skeleton of the alkyl group attached to amino group

- $C_4H_{11}N$



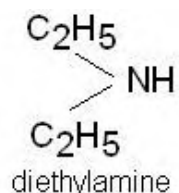
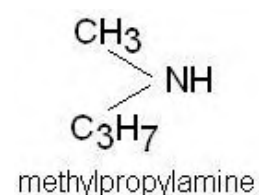
3. Position isomerism : This is due to difference in chain of amino group

- $C_3H_9N$



4. Metamerism : This is due to different alkyl groups attached to same functional group.

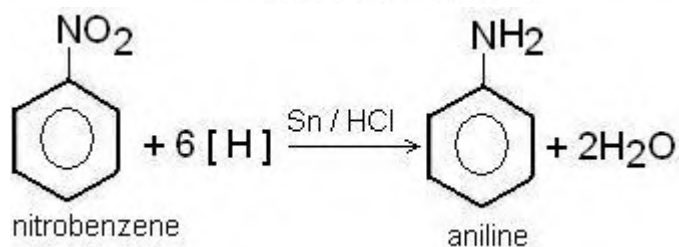
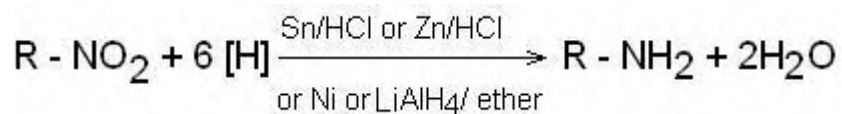
- $C_4H_{11}N$



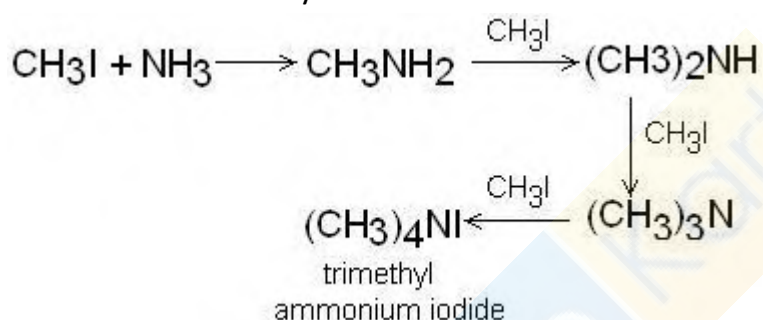
# Amines

## GENERAL METHODS OF PREPARATION OF AMINES

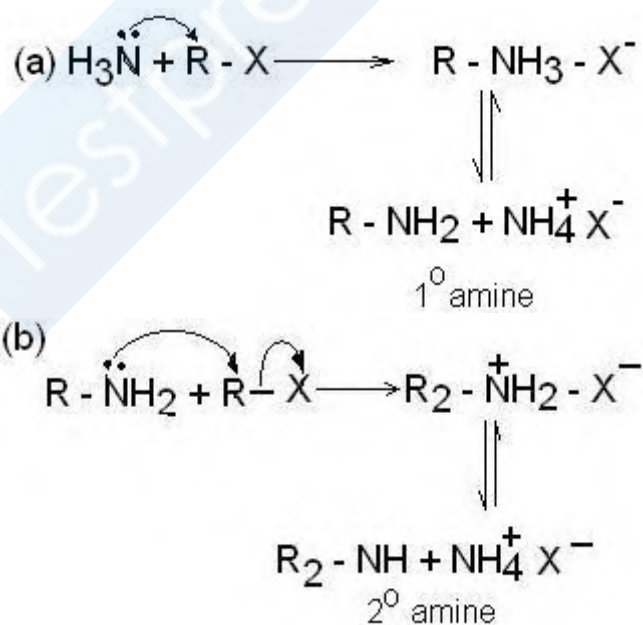
### 1. Reduction of nitro compounds



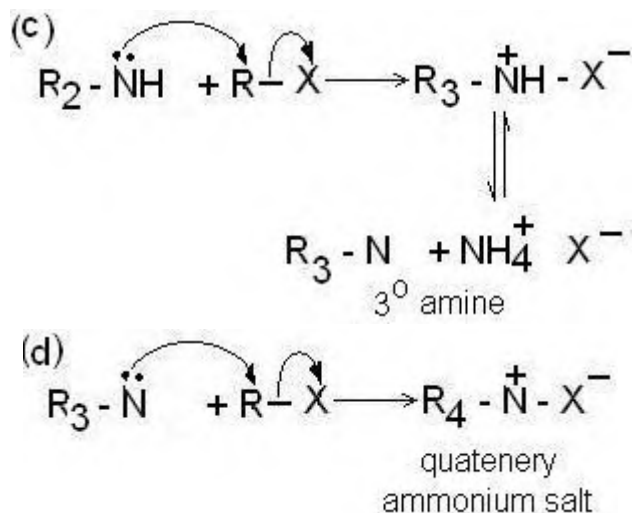
### 2. Hofmann's ammonolysis method



### Mechanism



## Amines



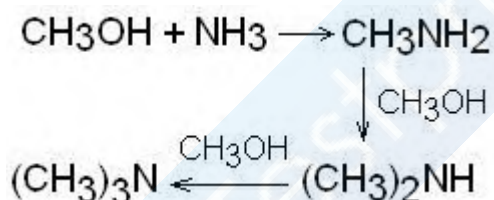
Order of reactivity for this reaction

$R - I > R - Br > R - Cl$  and  $1^\circ > 2^\circ > 3^\circ >$  alkyl halide

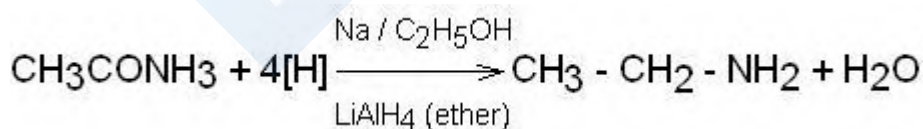
This reaction is not suitable for aryl amines

- If excess of ammonia is used in the above reaction, primary amine is obtained as main product.
- If excess of alkyl halide is used, tertiary amine is obtained as main product.

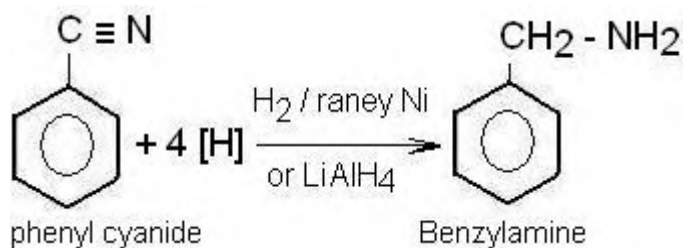
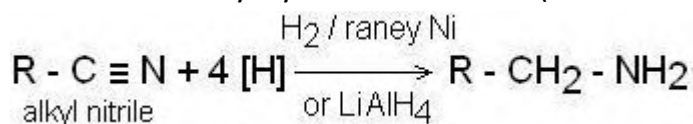
### 3. Ammonolysis of alcohol



### 4. Reduction of primary acid amides

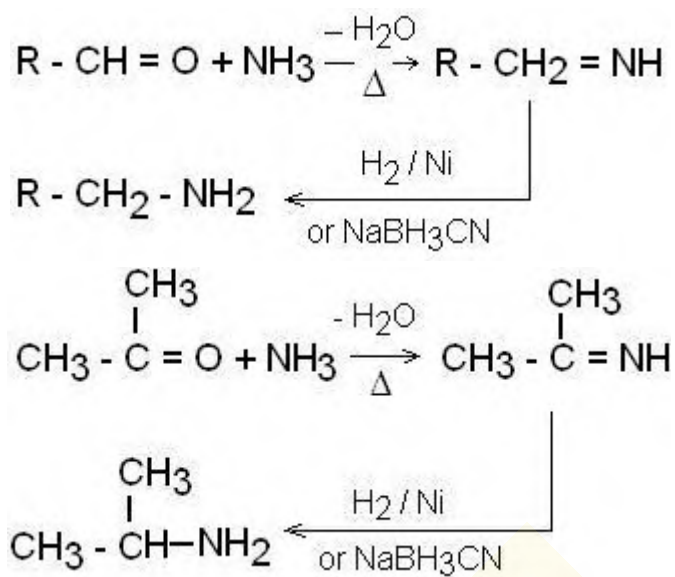


### 5. Reduction of alkyl cyanides or nitriles ( Mendius reaction)

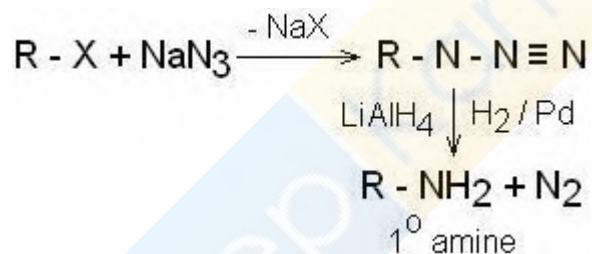


## Amines

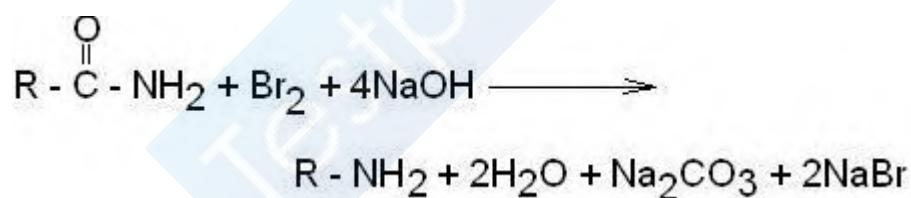
### 6. Reductive amination of aldehydes and ketones



### 7. Reduction of azides

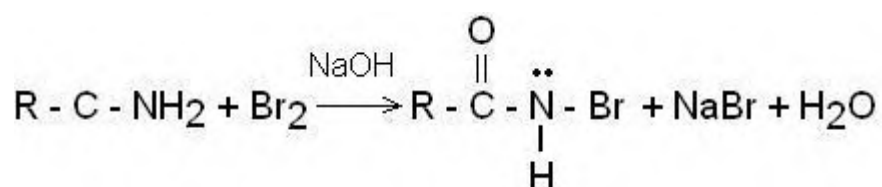


### 8. Hoffmann bromamide degradation reaction



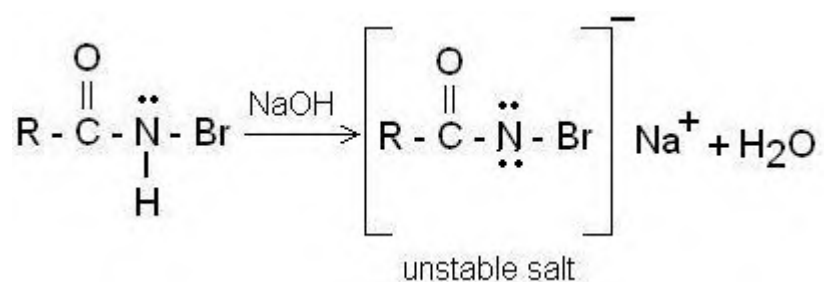
#### Mechanism

##### Step I

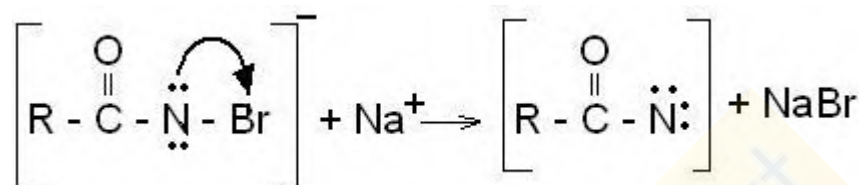


## Amines

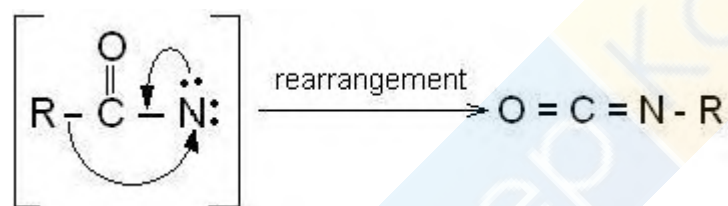
Step II



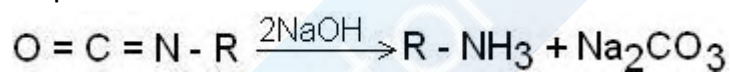
Step III



Step IV



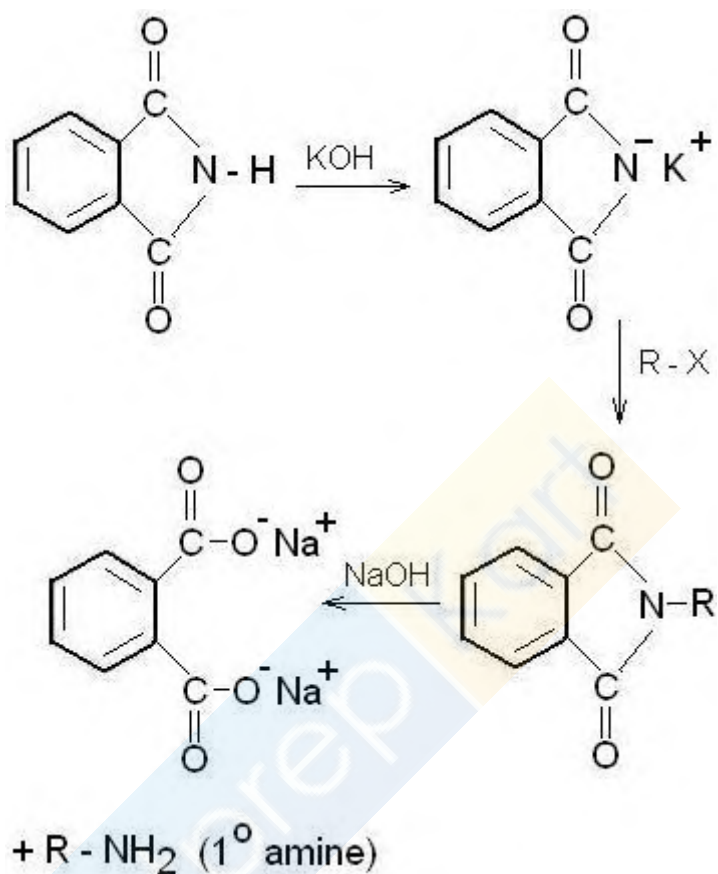
Step V



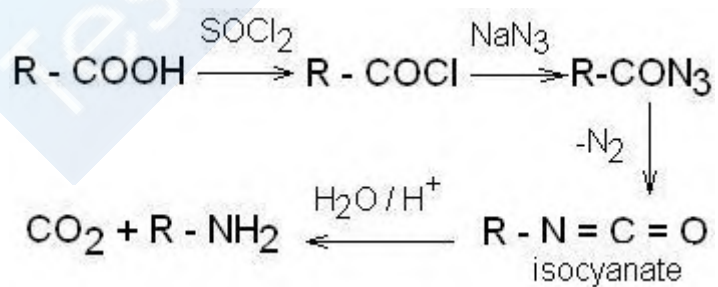


# Amines

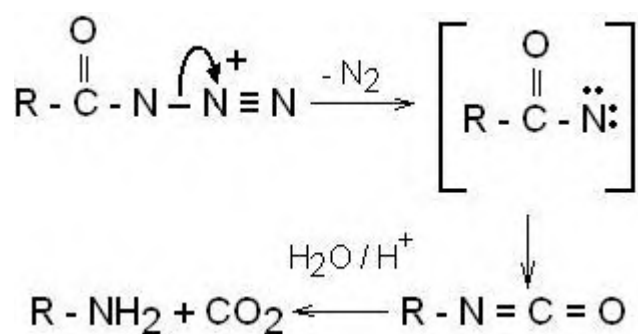
## 9. Gabriel phthalimide synthesis



## 10. Curtius degradation or Curtius rearrangement



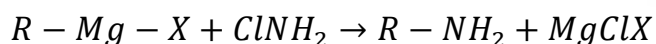
Mechanism



## 11. Using Grignard reagent

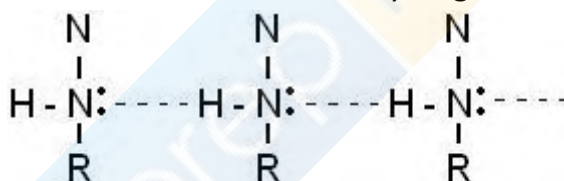


# Amines



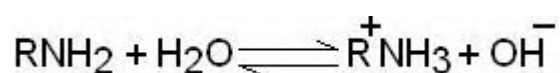
## PHYSICAL PROPERTIES OF AMINE

1. Physical state and smell
  - Lower members are gases, higher amines (C<sub>4</sub> to C<sub>11</sub>) are volatile liquids while still higher members are solids.
  - Lower members have fishy ammoniacal odour.
  - Pure amines are almost colourless but develop colour on keeping in air for long time because amines are readily oxidized in air to form coloured oxidation product.
2. Solubility
  - Lower members are soluble in water, but solubility decreases with increase in molecular weight. Aromatic amines are insoluble in water. Both aliphatic and aromatic amines are fairly soluble in organic solvents.
3. Boiling point
  - Amines have higher boiling points than hydrocarbons of comparable molecular masses because of intermolecular hydrogen bonding



- But amines have lower boiling points than those of alcohols or carboxylic acid since intermolecular H-bonding in amines is not as strong as in case of alcohols or acid
- Among the isomeric amines, the boiling point are in order  
Primary > Secondary > Tertiary

## BASIC CHARACTER OF AMINES



$$K_b = \frac{[R^+NH_3][OH^-]}{[RNH_2]}$$

Greater the value of  $K_b$ , stronger is the base

$$pK_b = -\log K_b = \log \frac{1}{K_b}$$

Smaller the value of  $pK_b$ , stronger is the base

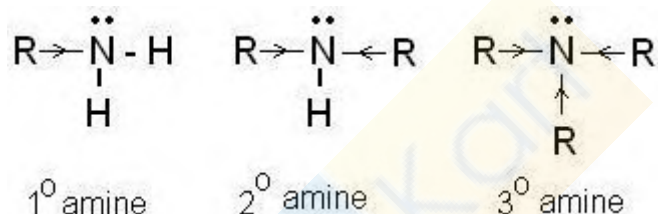
# Amines

## FACTORS INFLUENCING BASIC STRENGTH OF AMINE

1. Ability of nitrogen atom to donate lone pair of electrons
2. Stability of cation formed after accepting a proton

### Basic strength of ammonia and aliphatic amines

- Aliphatic amines are stronger than ammonia
- Since alkyl group exert electron donating inductive effect (+I effect) on nitrogen, electron density on nitrogen atom increases and thus aliphatic amines can donate pair of electrons more easily. Whereas ammonia has no such electron density groups.



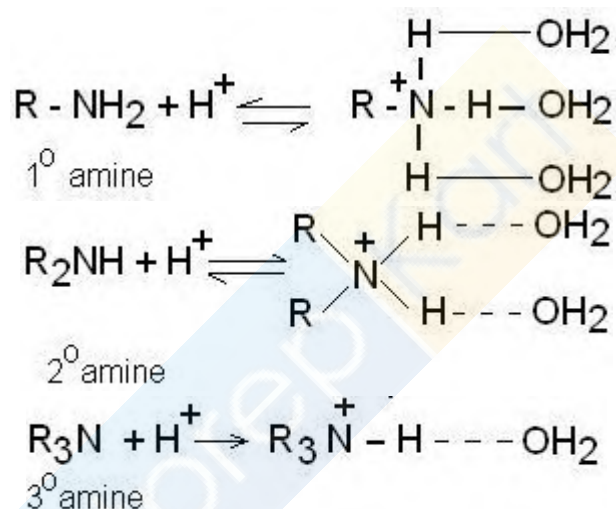
- Cation formed after accepting a proton from acid is stabilized by +I effect in aliphatic amines, whereas there is no stabilization in case of ammonia
- Basic strength of amines follows ( in gas phase)  
 $3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine} > \text{NH}_3$
- Actual order of basic strength in aqueous solution in case of lower members is found to be as  
 $2^\circ \text{ amine} > 1^\circ \text{ amine} > 3^\circ \text{ amine} > \text{NH}_3$   
i.e.  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$   
However, if the alkyl group is bigger than  $\text{CH}_3$  group i.e. ethyl, propyl etc, there will be some steric hindrance to H-bonding. As a result the overall decreasing strength of ethylamine is  $2^\circ \text{ amine} > 3^\circ \text{ amine} > 1^\circ \text{ amine} > \text{NH}_3$   
 $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
- Basic strength of different alkyl amines depends on following factors
  - (I) +I effect  

+ I effect of alkyl groups tend to increase the electron density on nitrogen atom and hence the basic strength. Greater the number of alkyl groups attached to nitrogen more is the basic strength

It follows the following order  $3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine} > \text{NH}_3$
  - (II) Steric effect

## Amines

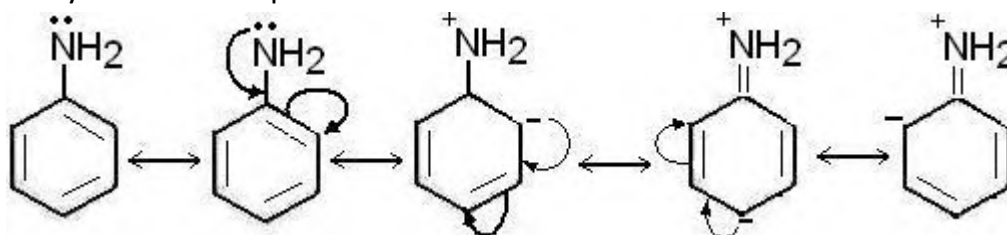
- Presence of alkyl group hinders the attack of acid on amine, thus reduces the basic strength
- Greater the number of bulky alkyl groups attached to nitrogen, less will be the basic strength
- It follows the following order  $1^\circ$  amine  $>$   $2^\circ$  amine  $>$   $3^\circ$  amine  
(III) Solvation effect
- Amines get protonated by accepting a  $H^+$  ion from aqueous solution and thus ammonium cation. These ammonium cations are stabilized by intermolecular H – bonding
- Greater the number of H-atoms on N-atom, greater will be the extent of hydrogen bond and thus higher will be stability of ammonium cation.



Hence the order of basic strength of different alkyl amines in their aqueous solution is given by the combined effect of the above factors.

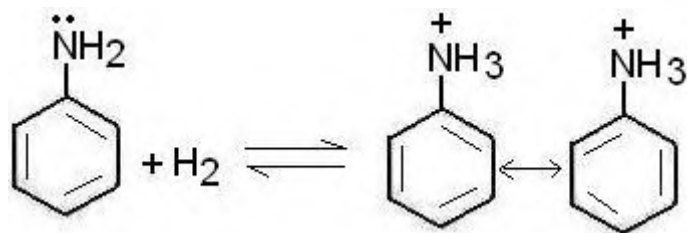
### Basic strength of aromatic amines

- Aromatic amines are far less basic than ammonia
- Aromatic amines are resonance stabilized as a result of which lone pair of electrons on nitrogen atom gets delocalized over benzene and hence less easily available for protonation.



- Cation formed from aromatic amines after protonation is less stable than original amine since it is resonance hybrid of only two structures

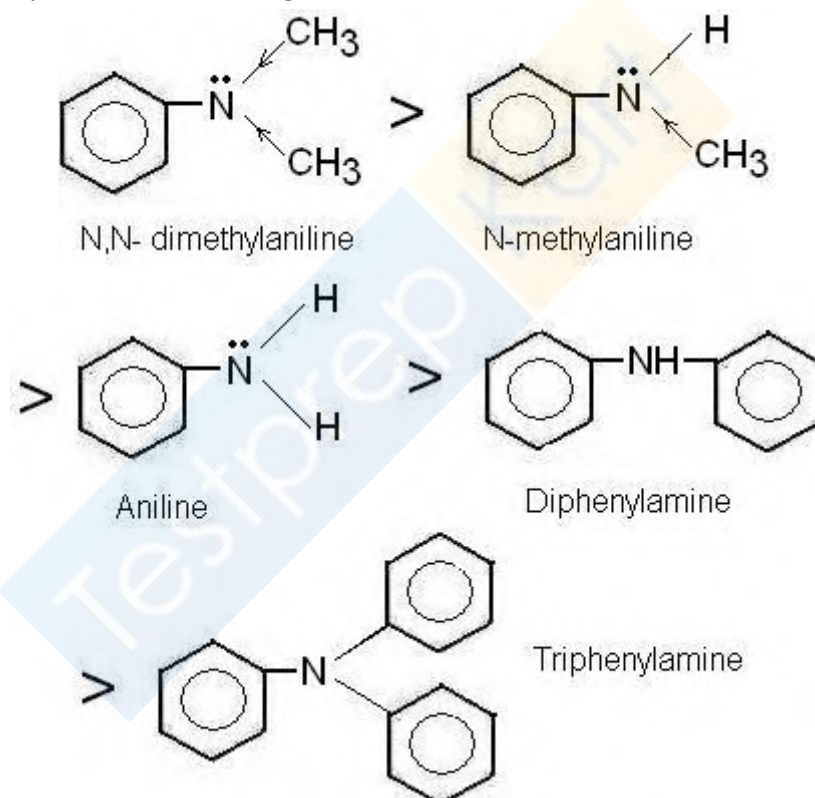
## Amines



- As a result, aromatic amines have less tendency towards protonation.

### Aniline and N-substituted anilines

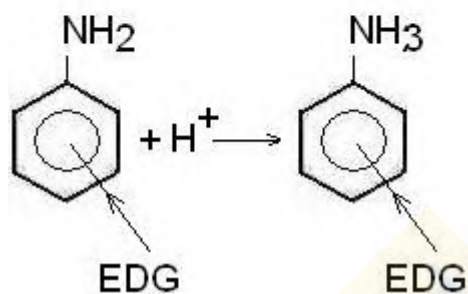
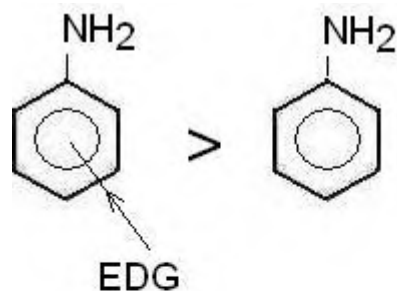
- Substitution of hydrogen atom of aniline with some electron donating group (like alkyl) increases the basic strength
- Whereas if substitution is made by an electron – withdrawing group (like phenyl group), the basic strength of amine decreases



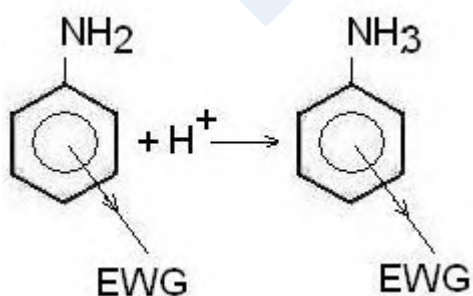
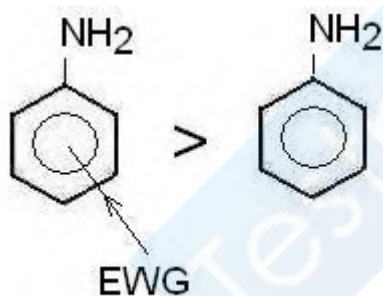
### Effect of substitution on basic strength of aromatic amines

- Electron donating group (like  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{NH}_2$ , etc) increases the electron density of amino group so that electron releasing tendency of amine and thus its basic strength increases.
- In addition to it an electron donation group stabilizes the cation formed after protonation by dispersing its positive charge.

## Amines

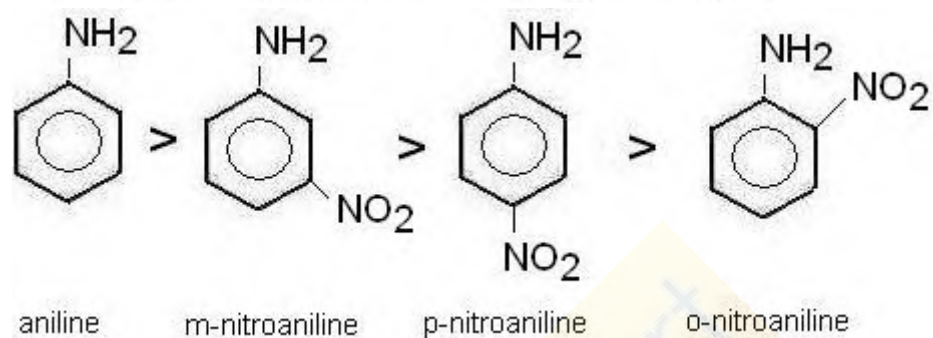
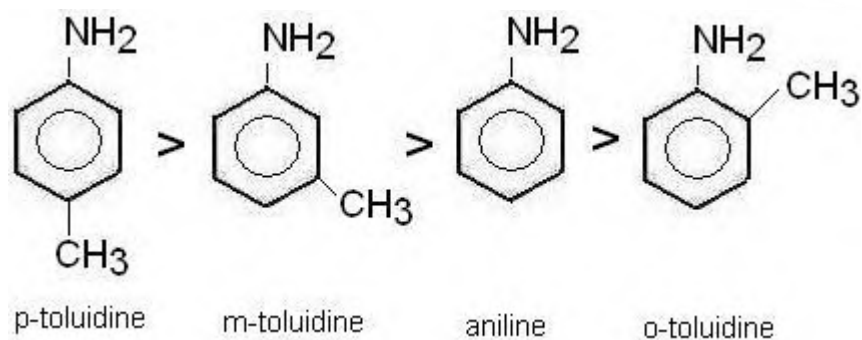


- Electron withdrawing group ( like  $-NO_2$ ,  $-CN$ ,  $-X$  etc) decreases the electron density of amino group. So that electron releasing tendency of amine and thus its basic strength decreases.
- In addition to its an electron withdrawing group destabilizes the cation formed after protonation by intensifying its positive charge.

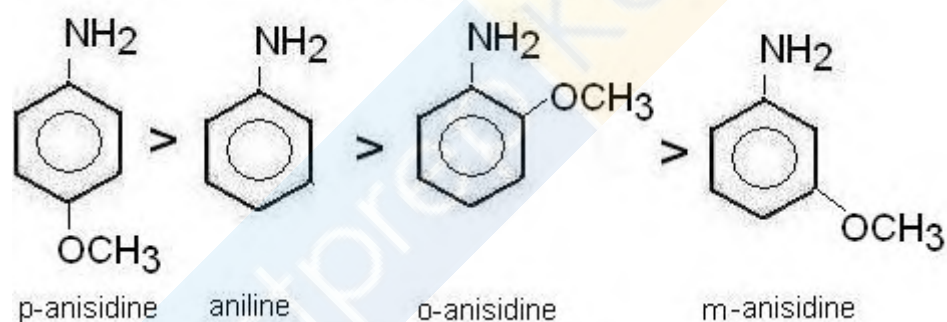


- Effect of any substituent ( whether electron donating or electron withdrawing) is more pronounced at para-position than meta-position
- Ortho substituted anilines are weaker bases than anilines.

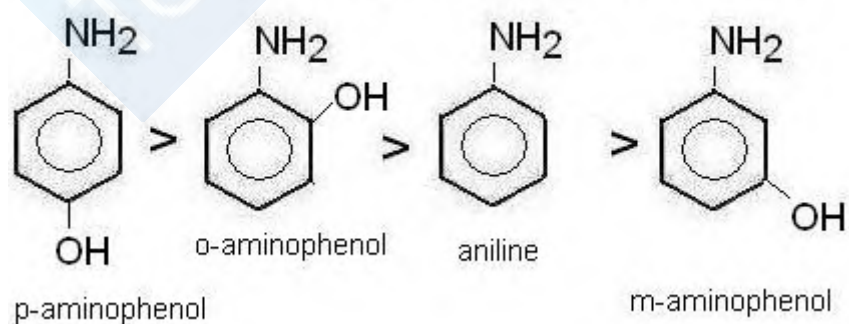
## Amines



- OCH<sub>3</sub> → strong +R effect, weak -I effect



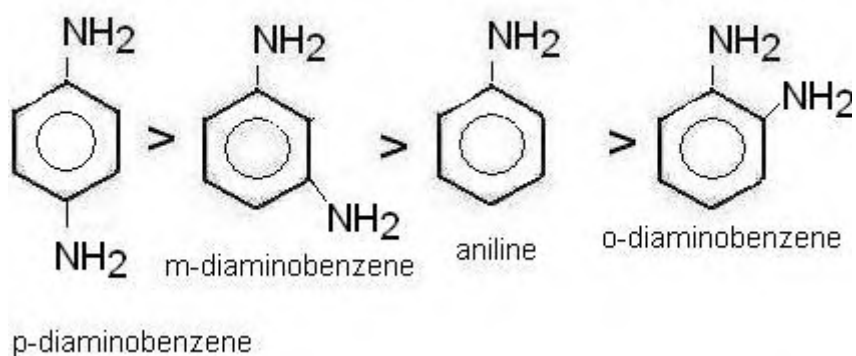
- OH → strong +R effect, weak -I effect



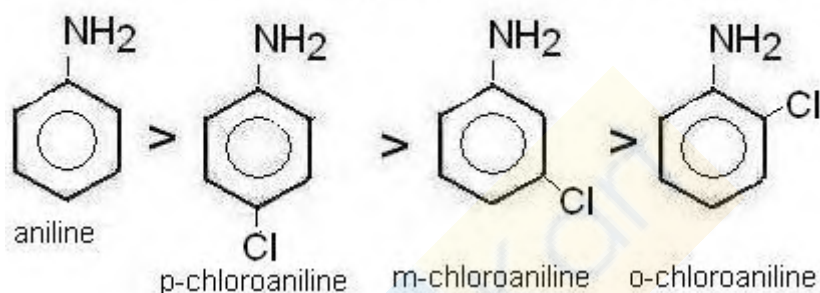


## Amines

- NH<sub>2</sub> → strong +R effect, strong +I effect

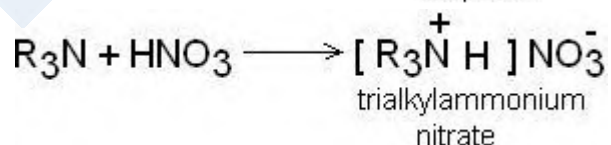
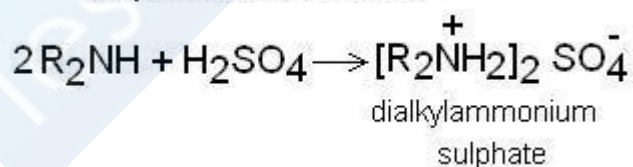
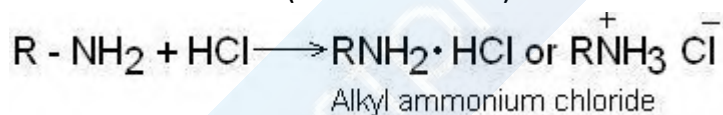


- Cl → strong +R effect, strong -I effect

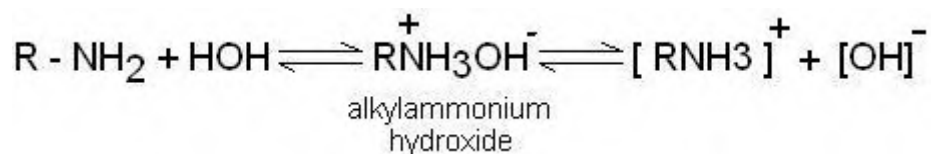


### CHEMICAL PROPERTIES OF AMINES

#### 1. Reaction with acids ( salt formation)



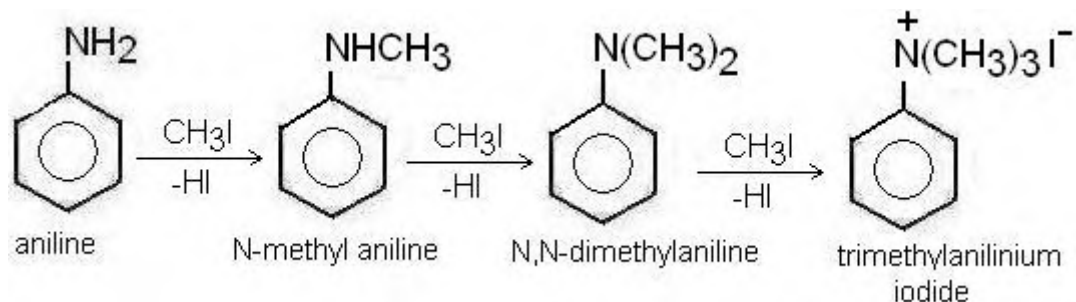
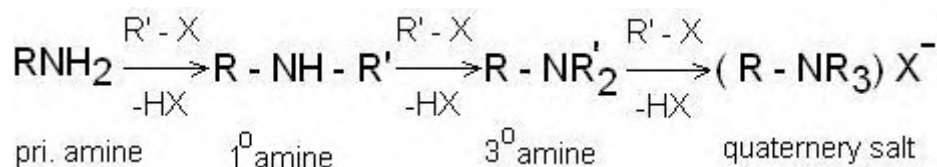
#### 2. Reaction with water



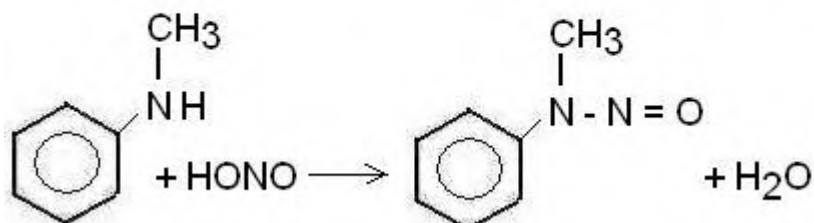
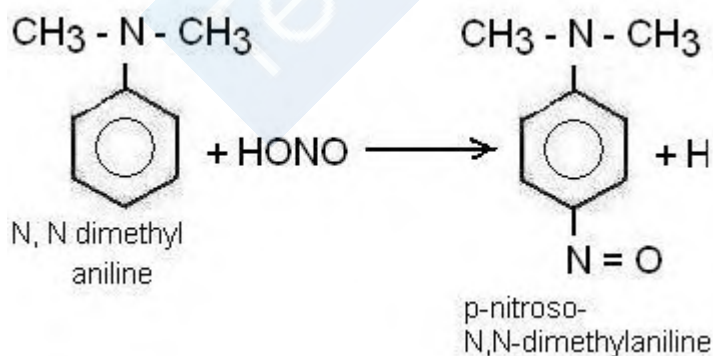
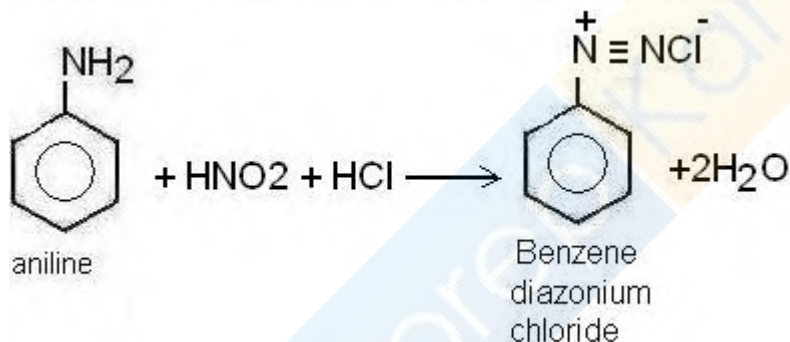
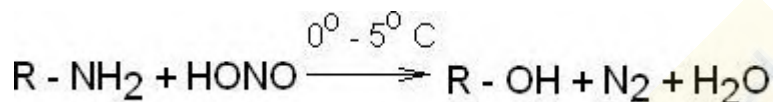
#### 3. Reaction with alkyl halides ( Alkylation)



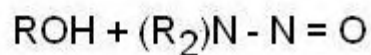
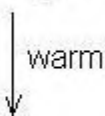
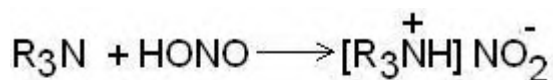
## Amines



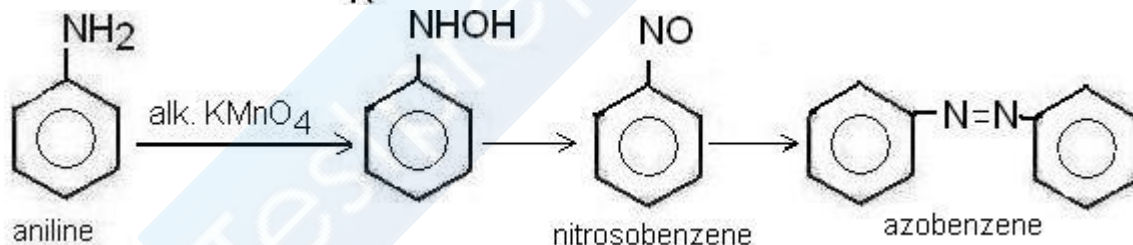
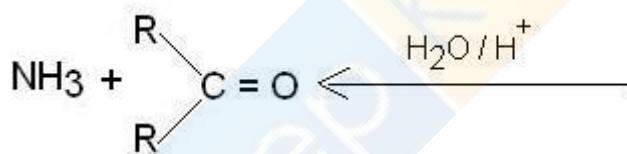
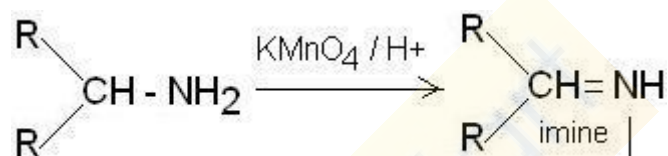
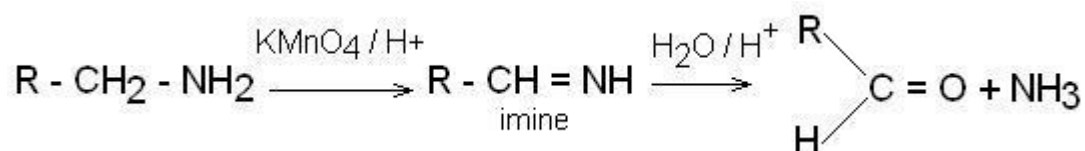
### 4. Reaction with nitrous acid



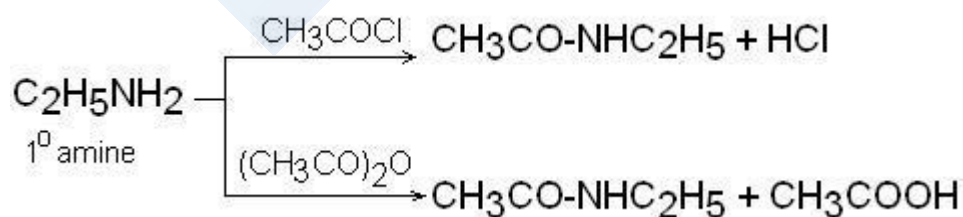
## Amines



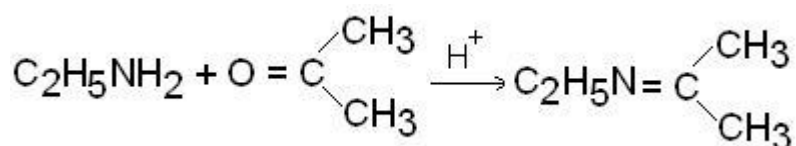
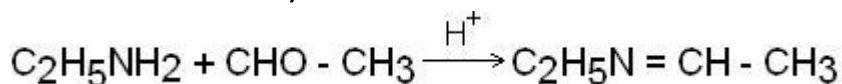
### 5. Oxidation



### 6. Acylation

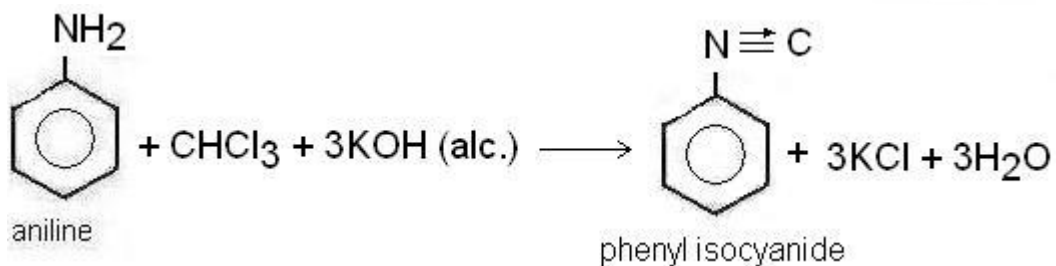


### 7. Reaction with aldehydes and ketones.

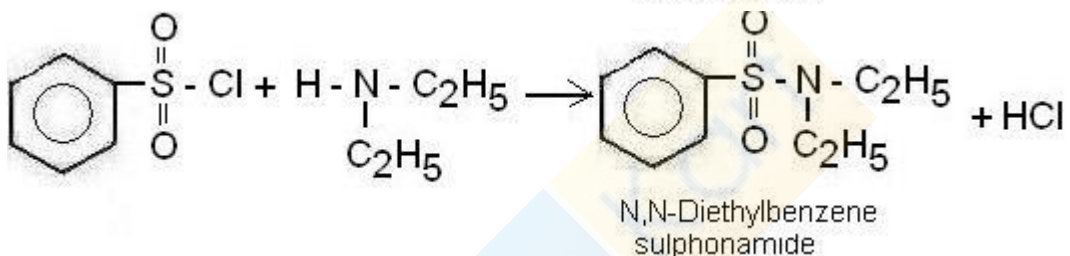
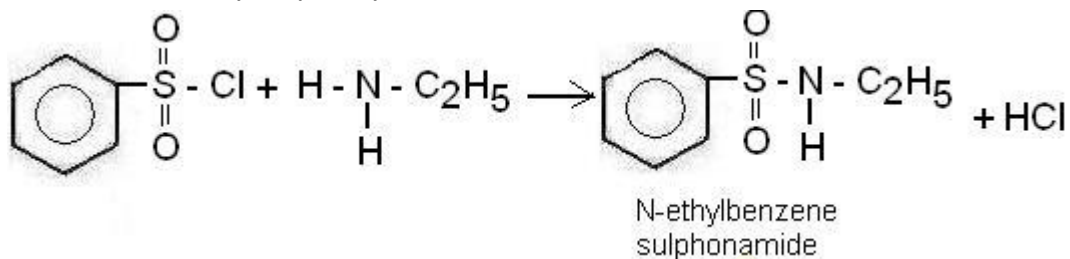




## Amines

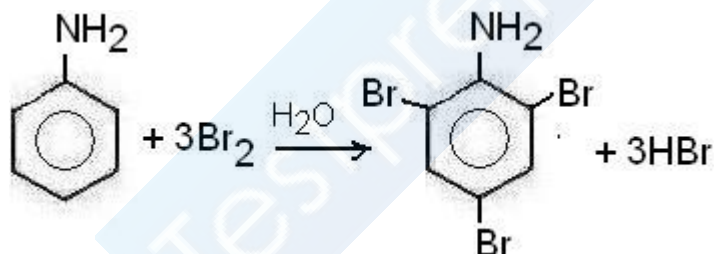


### 10. Reaction with arylsulphonyl chloride



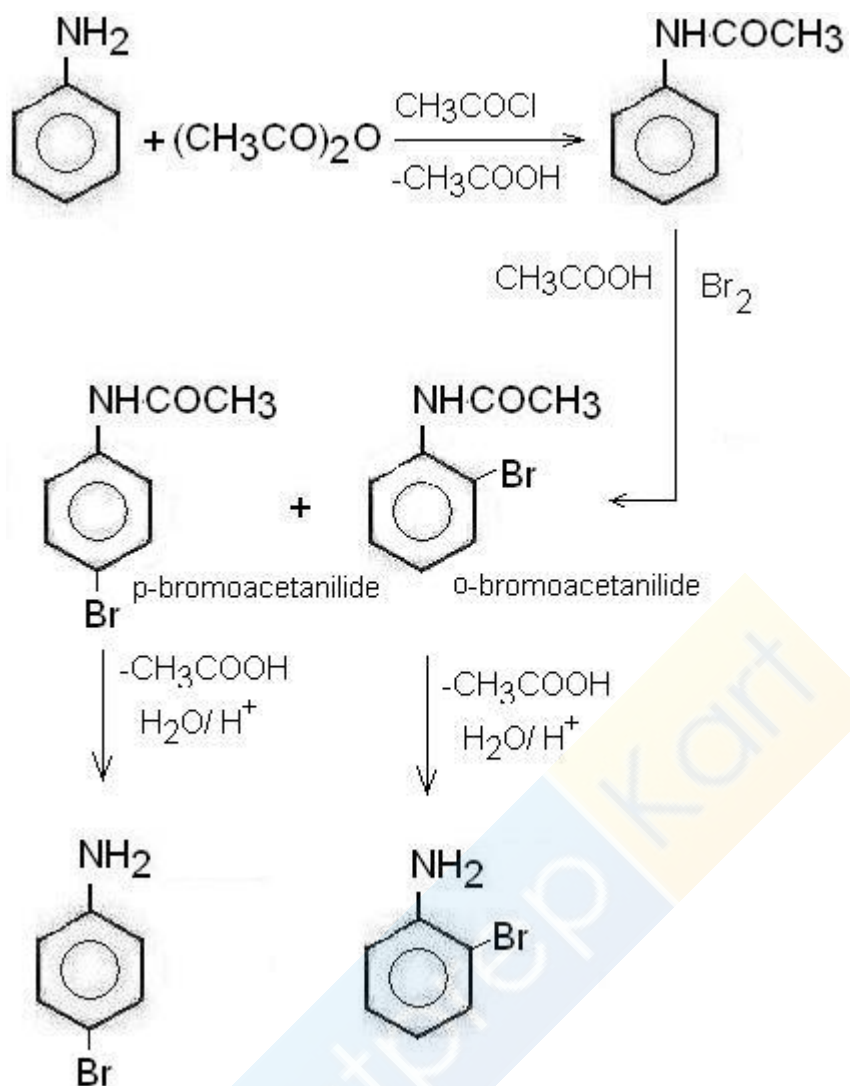
### 11. Electrophilic substitution

#### (1) Bromination

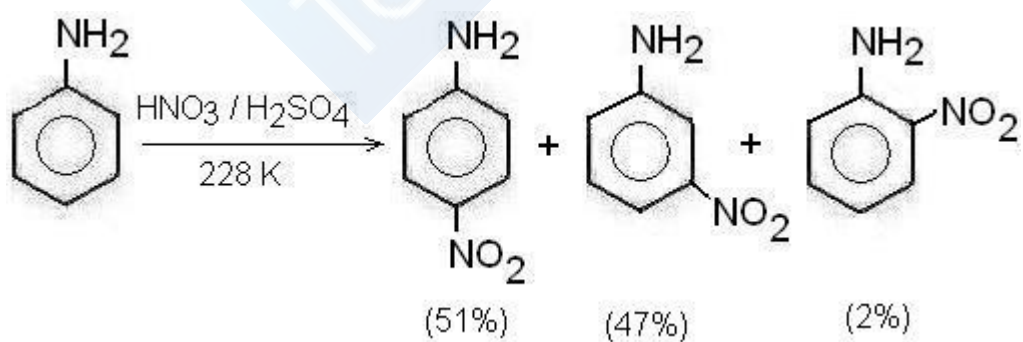


- If a monohalogenated derivatives is required, then activation of benzene ring has to be lowered down which can be done by acylating the amino group. Thus Bromination takes place only at one position, either ortho or para.

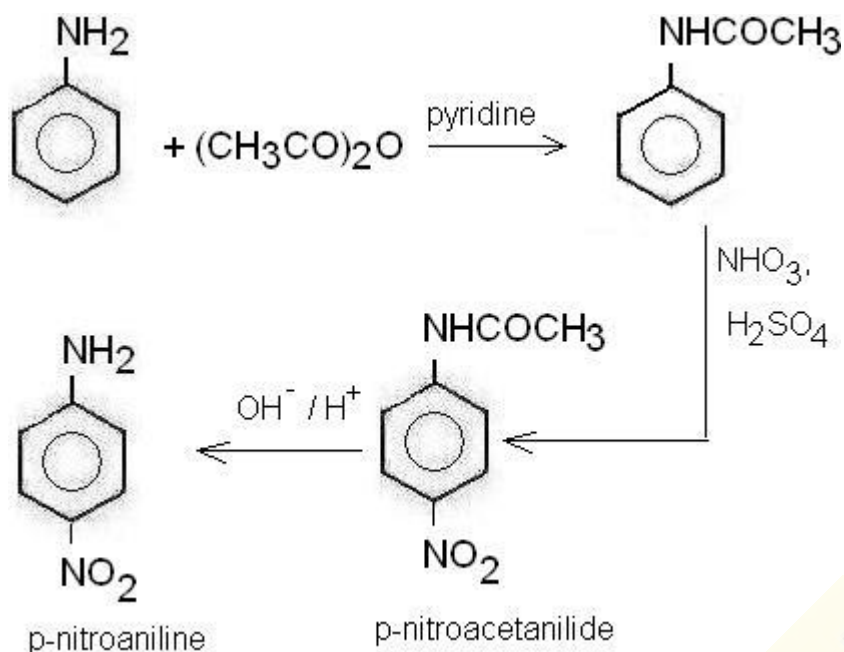
## Amines



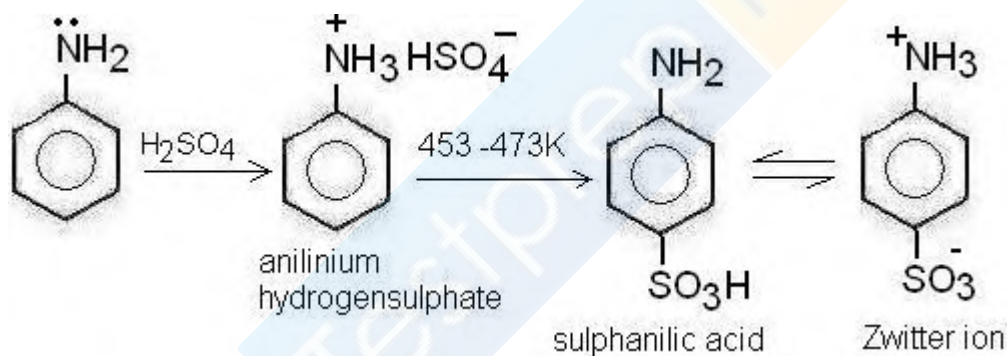
### (ii) Nitration



## Amines



### (iii) Sulphonation



### DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

1. Action of  $\text{CHCl}_3$  and alcoholic  $\text{KOH}$  (Carbylamine test)  
Primary amines : Bad smelling carbylamines ( Isocyanide) is formed  
Secondary amines: No reaction  
Tertiary amines : No action.
2. Action of  $\text{CS}_2$  and  $\text{HgCl}_2$   
Primary amines : Alkyl isothiocyanate is formed which has pungent smell like mustard oil.  
Secondary amines: No action  
Tertiary amines : No action
3. Action of nitrous acid  
Primary amines : Alcohol is formed with evolution of nitrogen gas.



## Amines

Secondary amines: Forms nitrosoamine which gives green colour with phenol and conc.  $\text{H}_2\text{SO}_4$  ( Liebermann's test)

Tertiary amines : Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.

### 4. Action of acetyl chloride

Primary amines : Acetyl derivative is formed

Secondary amines: Acetyl derivatives is formed

Tertiary amines : No action

### 5. Action of Benzene sulphonyl chloride ( Hinsberg's reagent) in excess of potassium hydroxide solution

Primary amines : Monoalkyl sulphonamide is formed which is soluble in KOH

Secondary amines: Dialkyl sulphonamide which is insoluble in KOH

Tertiary amines : No action

### 6. Action of methyl iodide

Primary amines : 3 molecules ( moles) of  $\text{CH}_3\text{I}$  to form quaternary salt with one mole of secondary amine.

Secondary amines: 2 molecules ( moles) of  $\text{CH}_3\text{I}$  to form quaternary salt with one mole of secondary amine.

Tertiary amines : 1 mole of  $\text{CH}_3\text{I}$  to form quaternary salt with one mole of tertiary amine

## USES

### 1. Lower aliphatic amines are used:

- (i) As solvent in laboratory and industry
- (ii) As stabilizers for rubber latex
- (iii) In petroleum refining and manufacture of detergents
- (iv) As reagents in organic synthesis

### 2. Aromatic amines ( Such as aniline) are used:

- (i) For the preparation of benzenediazonium salt which is starting material for preparation of many organic compounds
- (ii) For preparing many useful derivatives such as acetanilide, sulphanilic acid, sulpha drugs etc
- (iii) For the preparation of phenyl isocyanide needed for the manufacture of polyurethane plastics.