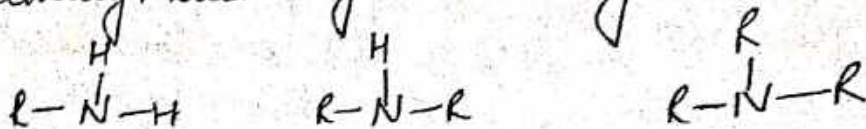
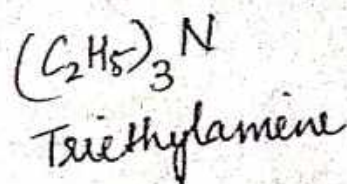
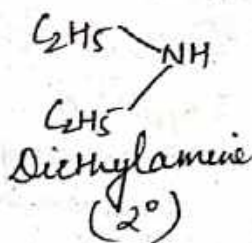
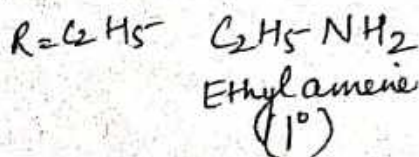


Amines

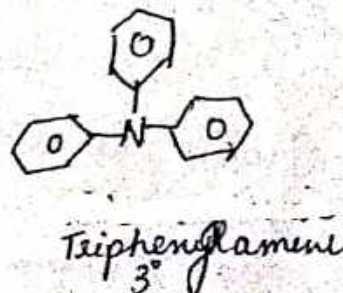
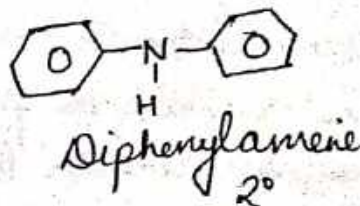
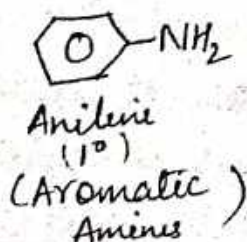
Amines may be regarded as amino derivatives of hydrocarbons. Depending upon whether one, two or all the three H-atoms of NH_3 have been replaced by alkyl groups or aryl, amines are classified as primary, secondary and tertiary amines



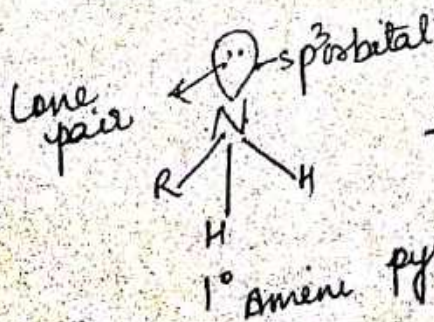
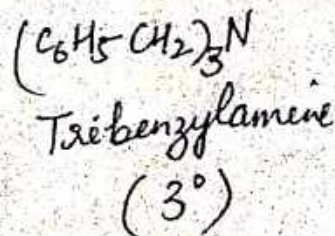
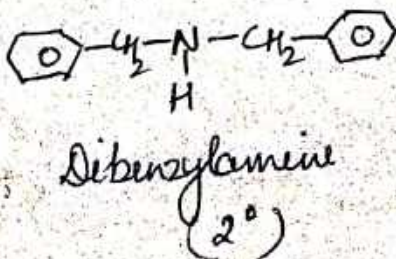
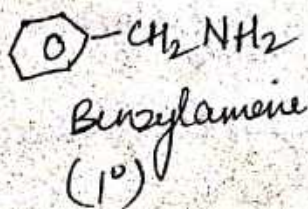
R = alkyl or aryl)



R = C_6H_5



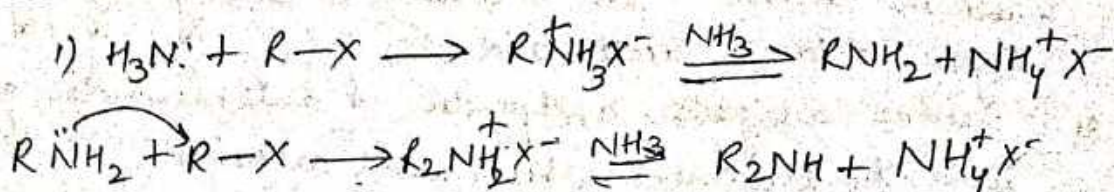
Aralkylamines or side chain substituted amines - Amines in which the nitrogen atom is attached to the side chain/s of one two or three (same or different) aromatic rings are called aralkylamines



\rightarrow sp^3 hybridised, In All three amines fourth sp^3 orbital contains lone pair of electron shown

4 Preparation

Ammonolysis:- usually gives a mixture of primary secondary & tertiary amines along with some quaternary ammonium salts



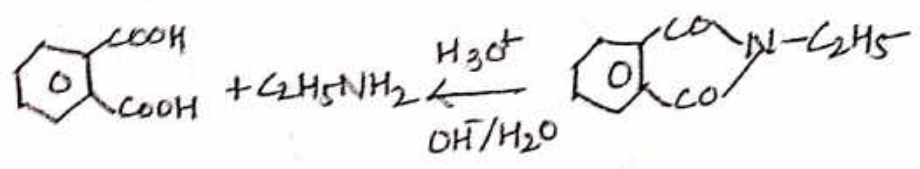
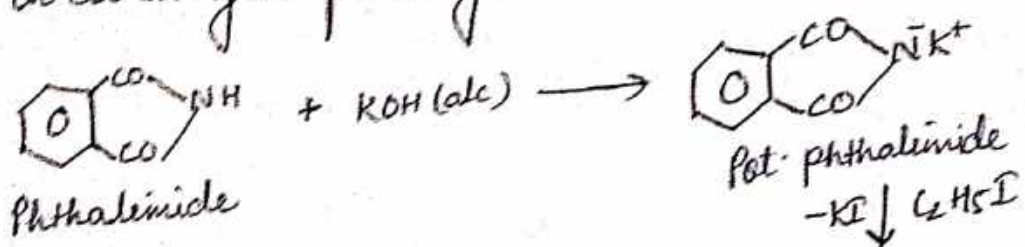
Typical example of a nucleophilic substitution reaction
ammonia act as nucleophile due to lone pair of electrons on nitrogen.

The actual composition of the reaction mix depends upon the ratio of the alkyl halide & ammonia used. if NH_3 used in excess primary amine is the major product if excess of alkyl halide is used quaternary ammonium salt is the main product. (complex mixture is obtained) Therefore this method is used in industry but not in lab.

This method cannot be used for the preparation of arylamines since aryl halides are much less reactive than alkyl halides towards nucleophilic substitution reaction.

Gabriel phthalimide reaction.

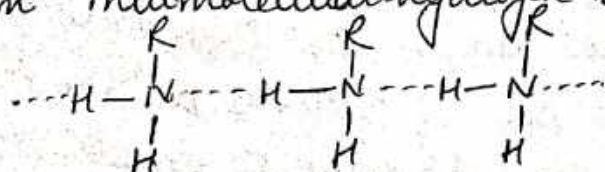
It is a convenient method for preparation of pure aliphatic and aralkyl primary amines. Potassium phthalimide on treatment with a suitable alkyl or aralkyl halide gives N-substituted phthalimides. These upon subsequent hydrolysis with dil HCl or alkali give primary amines.



Physical Properties

① Color and odour - Pure amines are almost colourless but develop colour on keeping in air for long time (amines especially aromatic amines are readily oxidised in air to form coloured oxidation products). Lower aliphatic amines are gases and smell like NH_3 but higher amines are liquids with fishy odours. Lower aromatic amines have characteristic ~~pp~~ unpleasant odours but higher ones are almost odourless.

② Boiling Points - Amines have higher boiling points than hydrocarbons of comparable molecular masses. This is due to the reason that amines being polar form intermolecular hydrogen bonds (except 3° amines) (no hydrogens)



associated molecules

The degree of association however depends upon the extent of hydrogen bonding.

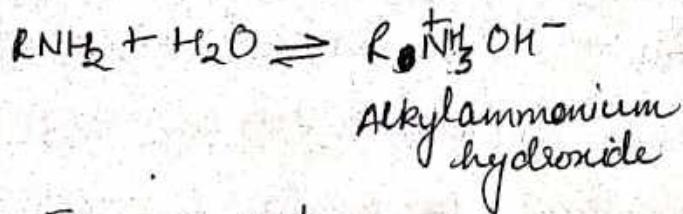
③ Solubility - All three classes of aliphatic amines i.e. primary secondary tertiary form hydrogen bonds with water. As a result lower aliphatic amines are soluble in water. However as the size of alkyl group increases, the solubility decreases due to a corresponding increase in the hydrocarbon part (hydrophobic part) of the molecule. The borderline solubility is reached with amines of about six carbon atoms in the molecule.

Aromatic amines on the other hand are insoluble in water. This is due to the larger hydrocarbon part which tends to retard formation of H-bond. Thus aniline is almost insoluble in water. However quite soluble in benzene, ether etc.

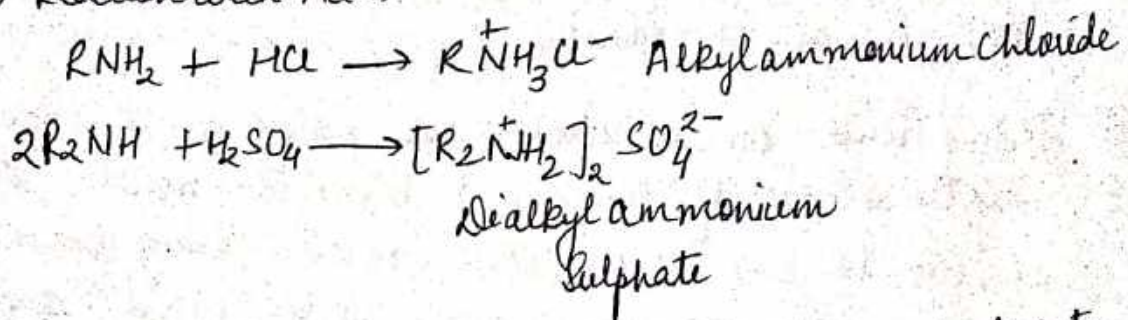
④ Basic character of Amines -

All three classes of amines (1° , 2° and 3°) because of the presence of a lone pair of electrons on the Nitrogen atom behave as bases.

① Reaction with H_2O

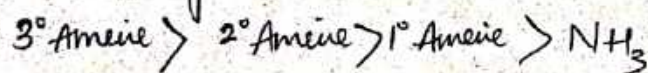


② Reaction with Acids



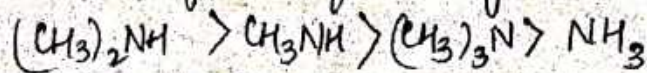
⑤ Basicity of aliphatic amines - All three classes of aliphatic amines contain lone pair of electrons on the Nitrogen. Therefore they have a strong tendency to donate this lone pair of electrons to electron acceptors. As a result all the amines behave as bases.

Aliphatic amines are stronger bases than NH_3 . This is due to reason that alkyl groups are electron donating groups. As a result e^- density on the nitrogen atom increases and they can donate lone pair of electron more easily than NH_3 . Thus basicity order decrease.



* However it has been found that in aq. solution 2° Amine is invariably more basic than 3° Amine.

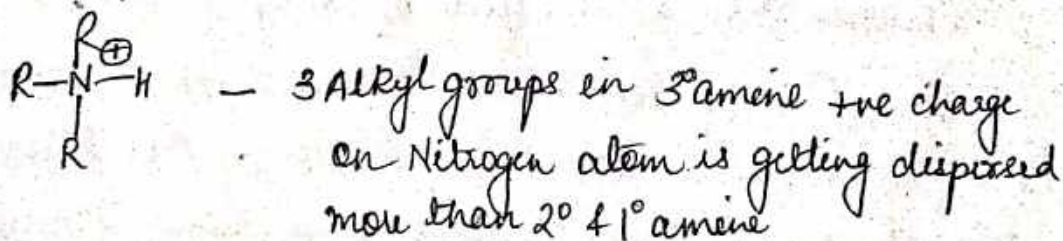
So actual basicity order for methylamines



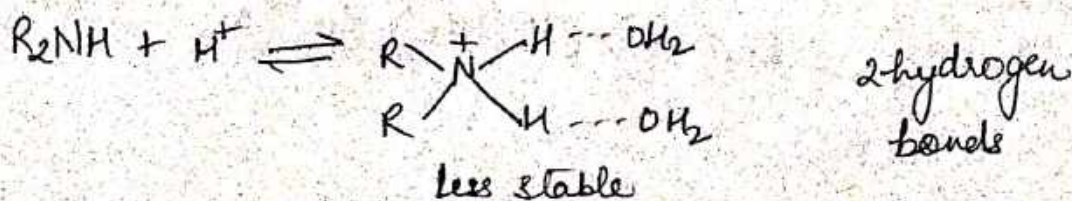
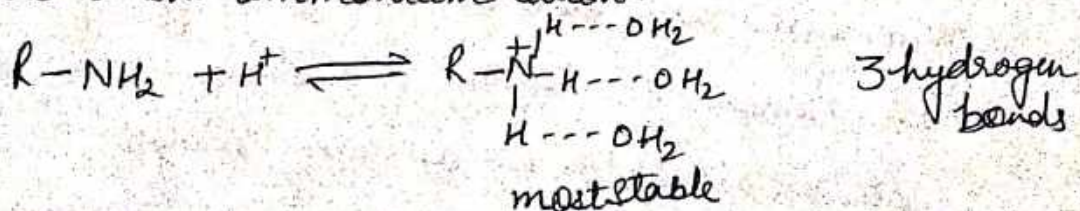
The basicity of an amine in aq. solution primarily depends upon the stability of ammonium cation formed by accepting proton from water. The stability of ammonium cation in depends upon combination of three factors

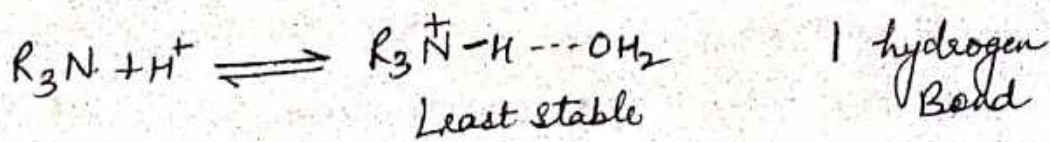
- 1) +I effect of alkyl groups
- 2) Extent of H-bonding with H₂O molecules
- 3) Steric effect of alkyl group

* As number of alkyl group increases the dispersal of +ve charge on NH₄⁺ cation by +I effect of alkyl groups increases. Thus on basis of +I effect alone basicity order

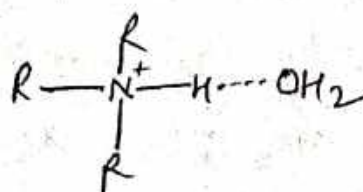
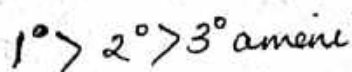


The stability of ammonium cation due to H-bonding depends upon the number of H-atoms present on N-atom. Greater the number of H-atoms on N-atom more stable is the ammonium cation.





However in case of ammonium cation derived from tertiary amines there is some steric repulsion to H-bonding and hence stability further decreases. Thus on the basis of hydrogen bonding and steric factors basicity of amines should decrease in order



steric repulsion to hydrogen bonding (three alkyl groups)

From the above discussion we may conclude that it is combination of +I effect of alkyl groups, H-bonding and steric factors which determine the stability of ammonium cations in solution. All these three factors are favourable for 2° amines and hence 2° amines are strongest bases. If the alkyl group is small (CH₃), then there is no steric hindrance to H-bonding. In other words the stability due to H-bonding predominates over stability due to +I effect of the CH₃ group hence 1° amine i.e. CH₃NH₂ is a stronger base than (CH₃)₃N. So overall order in decreasing strength

