Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen

atoms of ammonia molecule by alkyl/aryl group(s).

I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all t he three

hydrogen atoms by alkyl and/or aryl groups.

Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is C or H) is less than 109.5°; for instance, it is 108° in case of trimethylamine.

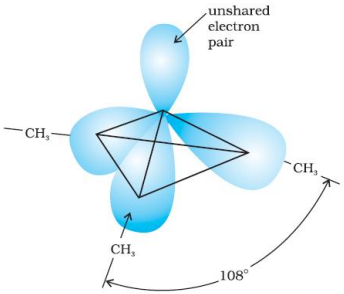


Fig. 13.1 Pyramidal shape of trimethylamine

Amines are classified as primary, secondary and tertiary depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.

Preparation of amines

1. Reduction of nitro compounds:

2. Ammonolysis of alkyl halides:

The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.

The free amine can be obtained from the ammonium salt by treatment with a strong base:

Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia. The order of reactivity of halides with amines is RI > RBr>RCl.

3. Reduction of nitriles:

4. Reduction of amides:

5. Gabriel phthalimide synthesis:

6. Hoffmann bromamide degradation reaction:

Physical Properties

The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Considering the electronegativity of nitrogen of amine and oxygen of

alcohol as 3.0 and 3.5 respectively, you can predict the pattern of solubility of amines and alcohols in water. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why? Amines

are soluble in organic solvents like alcohol, ether and benzene. You may remember that alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines. Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and

hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary.

Chemical Reactions

Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the

course of reaction of amines; that is why primary, secondary and tertiary amines differ in many reactions. Moreover, amines behave as nucleophiles due to the presence of unshared electron pair.

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.

Larger the value of Kb or smaller the value of pKb, stronger is the base. p*Kb* value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron

density on the nitrogen atom. Their p*Kb* values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Structure-basicity relationship of amines

Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to theamine, more basic is the amine.

(a) Alkanamines versus ammonia

The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH3. The trend is not regular in the aqueous state as evident by their p*Kb* values given in Table 13.3. In the aqueous phase, the substituted ammonium cations get stabilisednot only by electron releasing effect of the alkyl

group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. Theorder of stability of ions are as follows:

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effec t based order. Secondly, when the alkyl group is small, like –CH3 group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH3 group, there willbe steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from –CH3 to –C2H5 results in change of the order of basic strength. Thus, there is a subtle interplay of the inductiveeffect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethylsubstituted amines in aqueous solution is as follows:

(b) Arylamines versus ammonia

p*Kb* value of aniline is quite high because in aniline or other arylamines, the -NH2 group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. Aniline is a resonance hybrid of the following five structures.

anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).

We know that greater the number of resonating structures, greater is the stability. Thus aniline (five resonating structures) is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines

would be less than that of ammonia. In case of substituted aniline, itis observed that electron releasing groups like –OCH3, –CH3 increase basic strength whereas electron withdrawing groups like –NO2, –SO3, –COOH, –X decrease it.

2. Alkylation

Amines undergo alkylation on reaction with alkyl halides

3. Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation.

Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

4. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines

do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test for primary amines.

5. Reaction with nitrous acid

(a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols.

(b) Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts

6. Reaction with arylsulphonyl chloride

(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide is formed.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl

chloride is replaced by *p*-toluenesulphonyl chloride.

7. Electrophilic substitution

The –NH2 group is *ortho* and *para* directing and a powerful activating group.

(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.

The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their very high reactivity. Substitution tends to occur at *ortho*- and *para*-positions. To prepare monosubstituted aniline derivative, the activating effect of –NH2 group can be controlled by protecting the -NH2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance.

Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of –NHCOCH3 group is less than that of amino group.

(b) Nitration:

by protecting the –NH2 group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.

(c) Sulphonation*:*

Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts

DIAZONIUM SALTS

The diazonium salts have the general formula $R\overset{+}{N}_2\bar{X}$ where R stands for an aryl group and $\bar{X}$ ion may be Cl^- Br^-, HSO_4^-, BF_4^- etc. They are named by suffixing diazonium to the name of the parent hydrocarbon

from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. $C_6H_5\overset{+}{N}_2\bar{Cl}$ is named as benzenediazonium chloride $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium

hydrogensulphate. The stability of arenediazonium ion is explained on the basis of resonance.

Method of Preparation of Diazoniun Salts

The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2Cl + NaCl + 2H_2O$$

Physical Properties

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

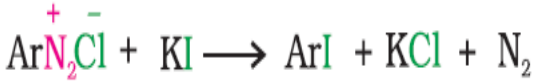
Chemical Reactions

A. Reactions involving displacement of nitrogen

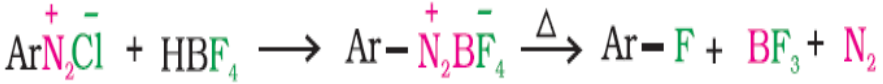
1. *Replacement by halide or cyanide ion*: This reaction is called **Sandmeyer reaction**.

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.

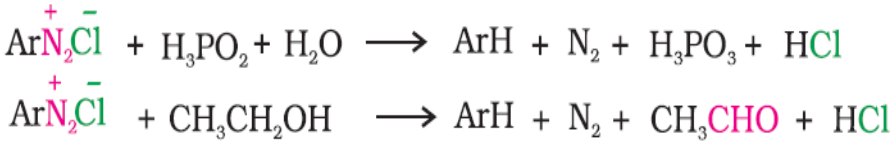
2. *Replacement by iodide ion*:



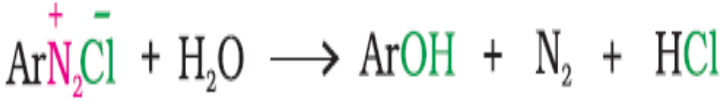
3. *Replacement by fluoride ion*:



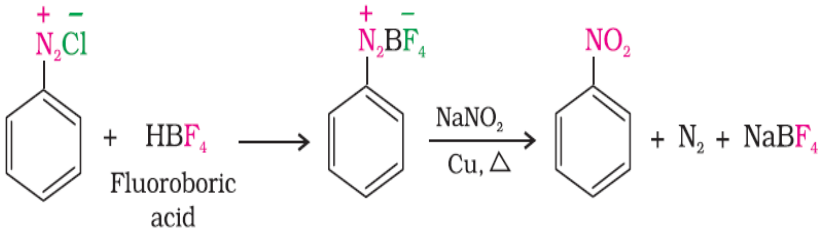
4. *Replacement by H*:



5. *Replacement by hydroxyl group*:



6. *Replacement by –NO2 group*:



B. Reactions involving retention of diazo group coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.

Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, –NO2 groups into the aromatic ring. Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

Thus, the replacement of diazo group by other groups is helpful in preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.