Chapter-13

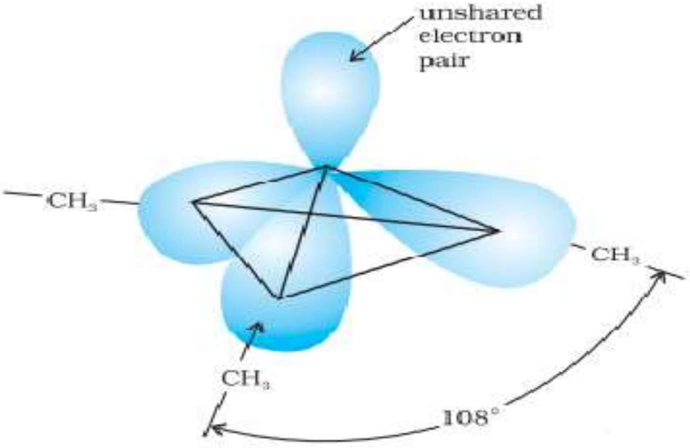
Amines

LECTURE 01

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two, or all the three hydrogen atoms by alkyl and/or aryl groups.

$$\underset{\text{Aryl amine}}{C_6H_5\text{-}NH_2} \xleftarrow[+C_6H_5]{-H} NH_3 \xrightarrow[+R]{-H} \underset{\text{Alkyl amine}}{R\text{-}NH_2}$$

Structure of Amines: Nitrogen atom in amine is sp^3 hybridized and the geometry of amines is pyramidal.



Pyramidal shape of trimethylamine

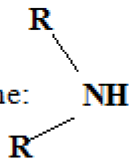
Classification:

(i) Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.

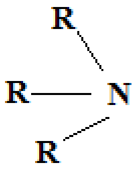
(ii) If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH_2 or $ArNH_2$, a primary amine (1°). Primary amine: $R\text{-}NH_2$

(iii) If two hydrogen atoms of ammonia or one hydrogen atom of $R\text{-}NH_2$ are replaced by another alkyl/aryl(R') group, R-NHR'(secondary amine) is obtained. The second alkyl/aryl group may be the same or different.

Secondary amine:



Tertiary amine:



(iv)Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of the tertiary amine.

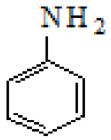
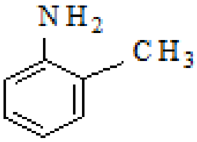
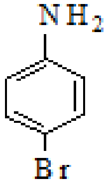
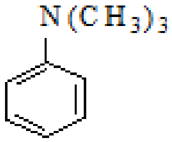
(v)Amines are said to be ‘simple’ when all the alkyl or aryl groups are the same, and ‘mixed’ when they are different.

Nomenclature:

Functional group: $-NH_2$, Suffix: amine,

IUPAC name: Alkanamine, Common name: Alkylamine.

Amine	**Common name**	**IUPAC name**
$CH_3\text{-–}CH_2\text{–}NH_2$	Ethylamine	Ethanamine
$CH_3\text{–}CH_2\text{–}CH_2\text{–}NH_2$	*n-Propylamine*	*Propan-1-amine*
$CH_3\text{-}CH(NH_2)\text{-}CH_3$	Isopropyl amine	Propan-2-amine
$CH_3\text{-}NH\text{-}CH_2\text{-}CH_3$	Ethyl methylamine	N-Methylethanamine.
$(CH_3)_3N$	Trimethylamine	N,N-Dimethylmethanamine.
$(C_2H_5)_2N\text{-}(CH_2)_3\text{-}CH_3$	N,N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2\text{-}CH_2\text{-}CH{=}CH_2$	Allylamine	Prop-2-en-1-amine
$NH_2\text{-}(CH_2)_6\text{-}NH_2$	Hexamethylenediamine	Hexane-1,6-diamine

	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Methylaniline
	p-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

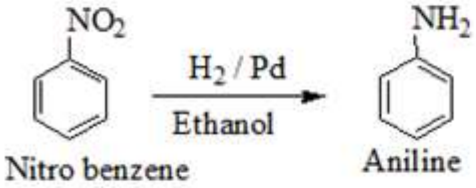
Preparation of amines:

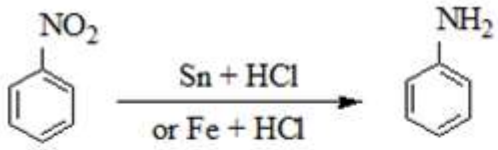
1. Reduction of nitro compounds
2. Ammonolysis of alkyl halides
3. Reduction of nitriles
4. Reduction of amides
5. Gabriel phthalimide synthesis
6. Hoffmann bromamide degradation reaction

1. Reduction of nitro compounds:

(a) Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium, or platinum.

(b) Nitro compounds are also reduced to amines by reduction with metals in an acidic medium.





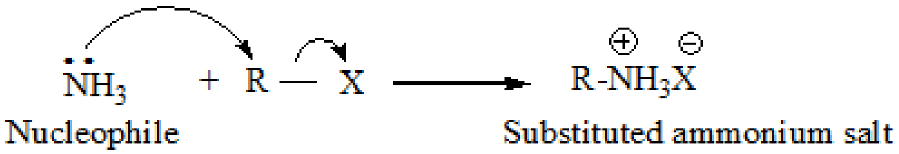
(iii) Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolyzed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

2. Ammonolysis of alkyl halides:

(a) This process of cleavage of the C–X bond by ammonia molecule is known as **ammonolysis.**

(b) An alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes a nucleophilic substitution reaction in which the halogen atom is replaced by an amino (NH_2) group. The reaction is carried out in a sealed tube at 373 K.

(c) The primary amine thus obtained behaves as a nucleophile and can further react with an alkyl halide to form secondary and tertiary amines and finally quaternary ammonium salt.



$$\underset{(1^0)}{RNH_2} \xrightarrow{RX} \underset{(2^0)}{R_2NH} \xrightarrow{RX} \underset{(3^0)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4N^+X^-}$$

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

$$R-NH_3X + NaOH \rightarrow R-NH_2 + H_2O + NaX$$

(e) 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 a large excess of ammonia.

(f) The order of reactivity of halides with amines is RI > RBr >RCl.

3. Reduction of nitriles:

Nitriles on reduction with lithium aluminum hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. This reaction is used for the ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.

$$R\text{-}C\equiv N \xrightarrow[Na(Hg)\ /\ C_2H_5OH]{H_2\ /\ Ni} R\text{-}CH_2\text{-}NH_2$$

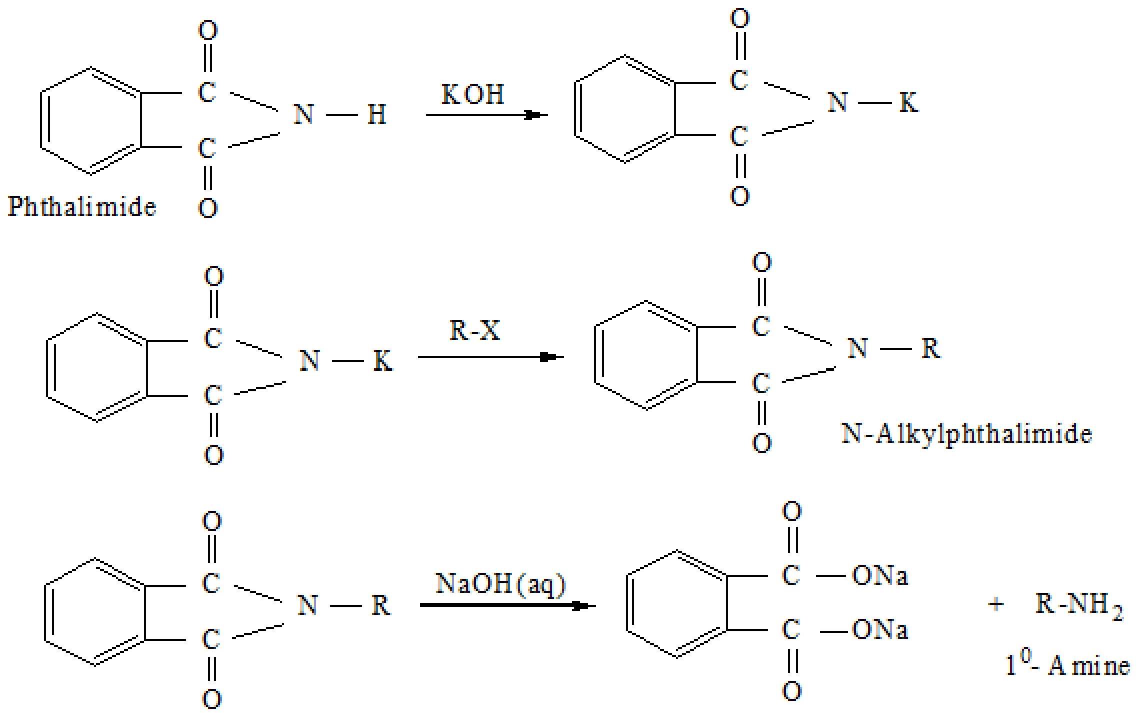
4. Reduction of amides:

The amides on reduction with lithium aluminum hydride yield amines.

$$R-CONH_2 \xrightarrow{(i)\ LiAlH_4,\ (ii)\ H_2O} R-CH_2-NH_2$$

5. Gabriel phthalimide synthesis:

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



6. Hoffmann bromamide degradation reaction:

Hoffmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

$$R-CONH_2 + Br_2 + 4\,NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$$

LECTURE 02

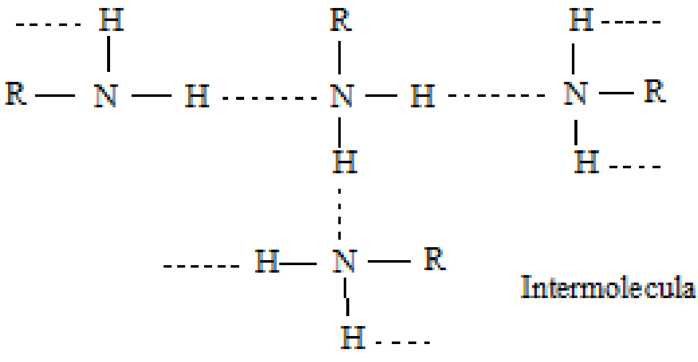
Physical Properties:

Physical state, odour, and color: The lower aliphatic amines are gases with a fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colorless but get colored on storage due to atmospheric oxidation.

Solubility: Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with an increase in the molar mass of amines due to an increase in the 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, the solubility of amines and alcohols in water can predict. 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. Alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.

Boiling point: Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between the 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 associations 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



Intermolecular hydrogen bonding in primary amines

Chemical Reactions:

(a) The difference in electronegativity between nitrogen and hydrogen atoms and the presence of an unshared pair of electrons over the nitrogen atom makes amines reactive.

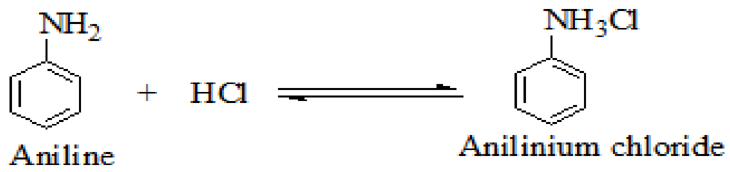
(b) The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary ($-NH_2$), secondary (-NH-), and tertiary amines (R_3N) differ in many reactions.

(c) Moreover, amines behave as nucleophiles due to the presence of unshared electron pair.

1. The basic character of amines:

(a) Amines, being basic, react with acids to form salts.

$$R - \ddot{N}H_2 \quad + \quad H\text{-}X \rightleftharpoons R\text{-}NH_3X \quad \text{(Salt)}$$



(b) Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R-NH_3X + OH^- \rightarrow R-NH_2 + H_2O + X^-$$

(c) Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non-basic organic compounds insoluble in water.

(d) The reaction of amines with mineral acids to form ammonium salts shows that these are basic. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. The basic character of amines can be better understood in terms of their K_b and pK_b *values.*

$$R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}\overset{+}{N}H_3 + \overset{-}{O}H$$

$$K = \frac{[R\text{-}\overset{+}{N}H_3]\,[\overset{-}{O}H]}{[R\text{-}NH_2]\,[H_2O]} \quad \text{or} \quad K\,[H_2O] = \frac{[R\text{-}\overset{+}{N}H_3]\,[\overset{-}{O}H]}{[R\text{-}NH_2]} \quad \text{or} \quad K_b = \frac{[R\text{-}\overset{+}{N}H_3]\,[\overset{-}{O}H]}{[R\text{-}NH_2]}$$

$$\boxed{pK_b = -\log K_b}$$

(e) The larger the value of K_b or the smaller the value of pK_b, the stronger is the base. pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to the +I effect of alkyl groups leading to high electron density on the nitrogen atom. Their pK_b 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.

(f) Besides the inductive effect, there are other effects like the solvation effect, steric hindrance, etc., which affect the basic strength of amines.

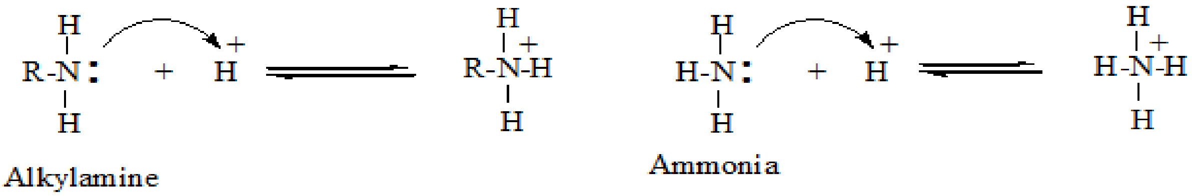
LECTURE 03

Structure-basicity relationship of amines:

The basicity of amines is related to their structure. The 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 the amine, the more basic is the amine.

(a) Alkanamines versus ammonia:

Considering the reaction of an alkanamine and ammonia with a proton to compare their basicity.



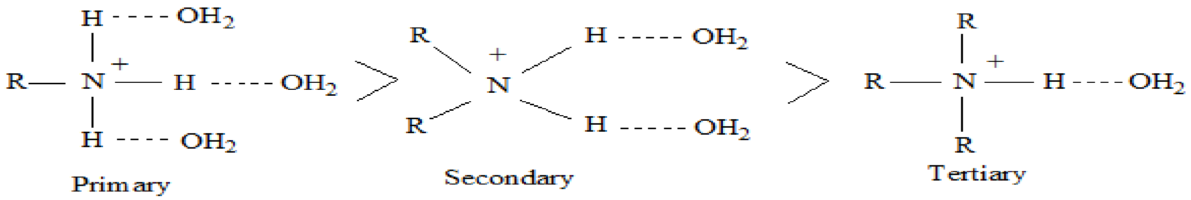
(i) Due to the electron releasing nature of the alkyl group, it pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid.

(ii) Moreover, the substituted ammonium ion formed from the amine gets stabilized due to the dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with an increase in the number of alkyl groups. This trend is followed in the gaseous phase.

(iii) The order of the basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3.

(iv) The trend is not regular in the aqueous state as evident by their pK_b *values.*

(v) In the aqueous phase, the substituted ammonium cations get stabilized not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, the lesser will be the solvation and the less stabilized is the ion. The order of stability of ions is given as:



(vi) Greater is the stability of the substituted ammonium cation, stronger is the basicity of the corresponding amine. Thus, the order of the basicity of aliphatic amines should be primary > secondary > tertiary, which is opposite to the order suggested by the inductive effect.

(vii) When the alkyl group is small, like $-CH_3$ group, there is no steric hindrance to H-bonding.

(viii) If the alkyl group is bigger than the CH_3 group, there will be a steric hindrance to H-bonding.

(ix) Therefore, the change of nature of the alkyl group, e.g., from $-CH_3$ to $-C_2H_5$ results in a change of the order of basic strength.

(x) Thus, on account of the interplay of the inductive effect, solvation effect, and steric hindrance of the alkyl group the basic strength of alkylamines in the aqueous state is decided as. For ethyl substituted amine:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ $[2^0 > 3^0 > 1^0]$

For methyl substituted amine:

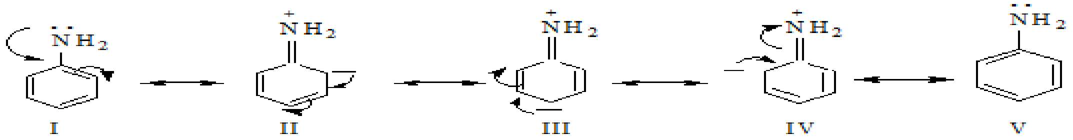
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ $[2^0 > 1^0 > 3^0]$

(b) Arylamines versus ammonia:

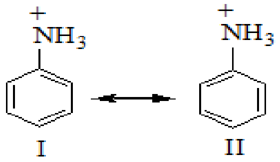
(i) pK_b *value of aniline is quite high. It is because, in aniline or other arylamines, the* $-NH_2$ *group is attached directly to the benzene ring.*

(ii) Thus the unshared electron pair on the nitrogen atom is in conjugation with the benzene ring and thus making it less available for protonation.

(iii) This can be understood from resonating structures of aniline. Aniline is the resonance hybrid of the following structures:



(iv) On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures.



(v) The greater the number of resonating structures, the 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.

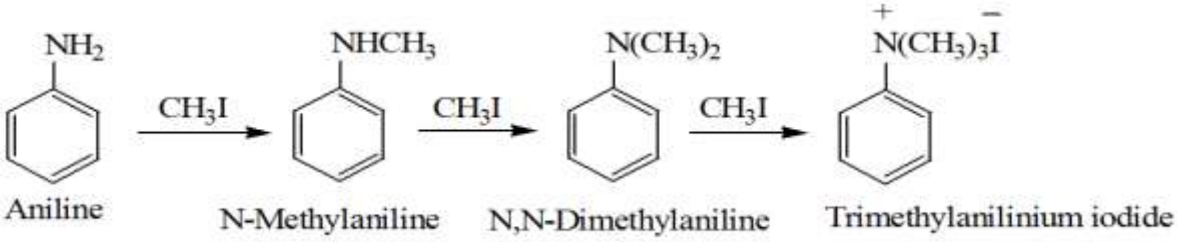
(vi) In the case of substituted aniline, it is observed that electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength whereas electron-withdrawing groups like $-NO_2$, $-SO_3H$, $-COOH$, $-X$ decreases it.

2. Alkylation:

Amines undergo alkylation on reaction with alkyl halides.

$$CH_3NH_2 \xrightarrow{CH_3I} (CH_3)_2NH \xrightarrow{CH_3I} (CH_3)_3N \xrightarrow{CH_3I} (CH_3)_4N^+I^-$$

Methyl amine Dimethyl amine Trimethyl amine Tetramethyl ammonium iodide



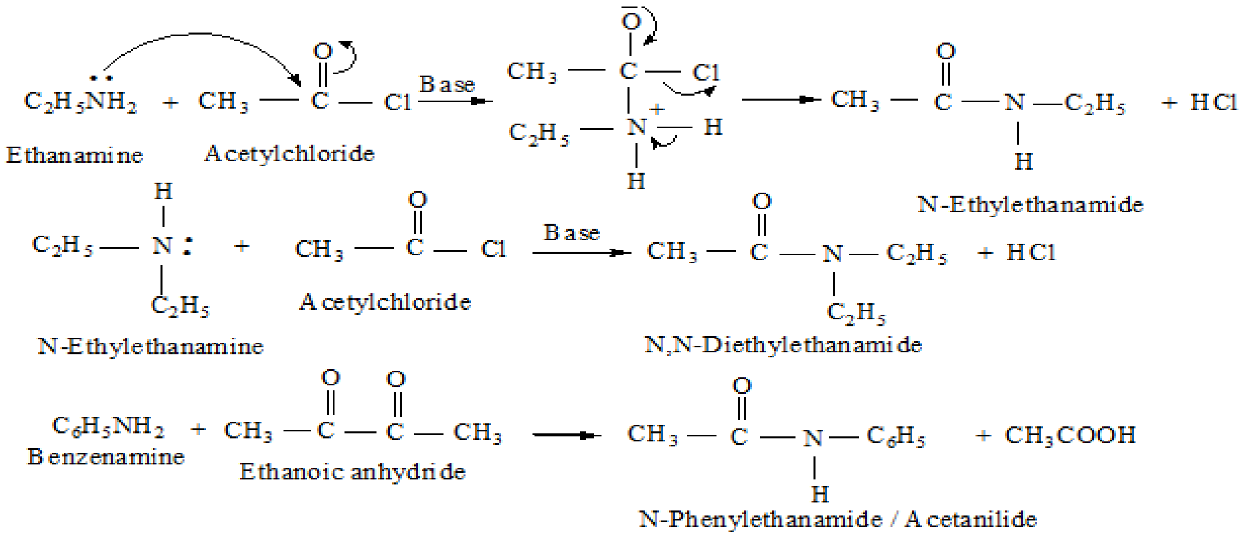
Aniline N-Methylaniline N,N-Dimethylaniline Trimethylanilinium iodide

3. Acylation:

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

(ii) This reaction involves the replacement of hydrogen atom of $–NH_2$ or >N–H group by the acyl group. The products obtained by acylation reactions are known as **amides.**

(iii) The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right-hand side.



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

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{N-Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

LECTURE-4

4. Carbylamine reaction:

(i) Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul-smelling substances.

(ii)Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2+CHCl_3+3KOH\xrightarrow{Heat}R-NC+3KCl+3H_2O$$

$$\underset{\text{Ethyl amine}}{C_2H_5-NH_2}+CHCl_3+3KOH\xrightarrow{Heat}\underset{\text{Ethyl isocyanide}}{C_2H_5-NC}+3KCl+3H_2O$$

$$\underset{\text{Aniline}}{C_6H_5-NH_2}+CHCl_3+3KOH\xrightarrow{Heat}\underset{\text{Phenyl isocyanide}}{C_6H_5-NC}+3KCl+3H_2O$$

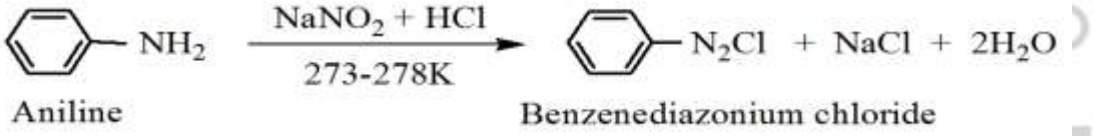
5. Reaction with nitrous acid:

Three classes of amines react differently with nitrous acid which is prepared in *situ from a mineral acid and sodium nitrite.*

(a))Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively, and alcohol. The quantitative evolution of nitrogen is used in the estimation of amino acids and proteins.

$$R\text{-}NH_2 + HNO_2 \xrightarrow{NaNO_2+2HCl}\left[R\text{-}\overset{+}{N_2}\overset{-}{Cl}\right]\xrightarrow{H_2O} R\text{-}OH + N_2 + HCl$$

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



Secondary and tertiary amines react with nitrous acid differently.

(b) Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosamines.

$$\underset{\text{Dimethyl amine}}{(CH_3)_2NH}+HNO_2\xrightarrow{NaNO_2+HCl}\underset{\text{N}-\text{Nitrosodimethylamine}}{(CH_3)_2N-N=O}+H_2O$$

Nitrosamines are water-insoluble yellow oils and when warmed with crystals of phenol and few drops of conc.H_2SO_4 produce a green solution that turns blue on adding alkali. This reaction is known as Libermann’s nitroso reaction and is used for the test of secondary amines.

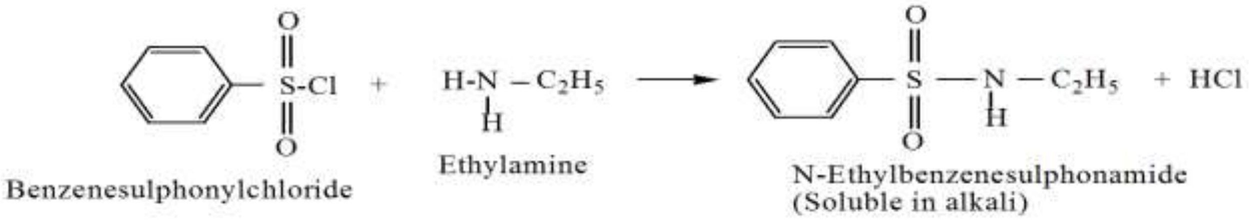
(c) Aliphatic tertiary amines react with nitrous acid to form unstable nitrites which decompose on warming to give nitrosamines and alcohol.

$$(CH_3)_3N + HNO_2 \rightarrow (CH_3)_3NHNO_2 \xrightarrow{Heat} (CH_3)_2NNO + CH_3OH$$

6. Reaction with aryl sulphonyl chloride:

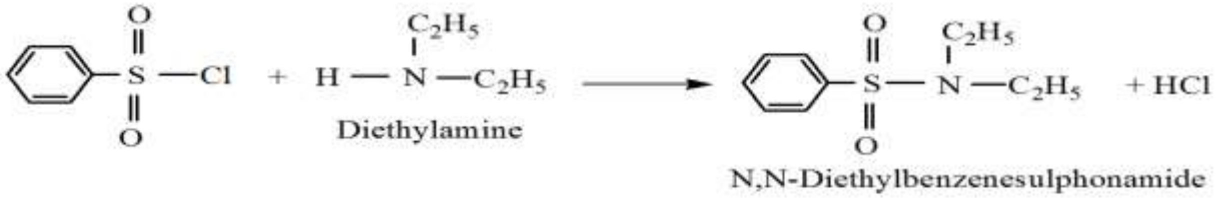
Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

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



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of a strong electron-withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with a secondary amine, N, N-diethyl benzene sulphonamide is formed. Since N, N-diethyl benzene sulphonamide does not contain any hydrogen atom attached to the nitrogen atom, it is not acidic and hence insoluble in alkali.



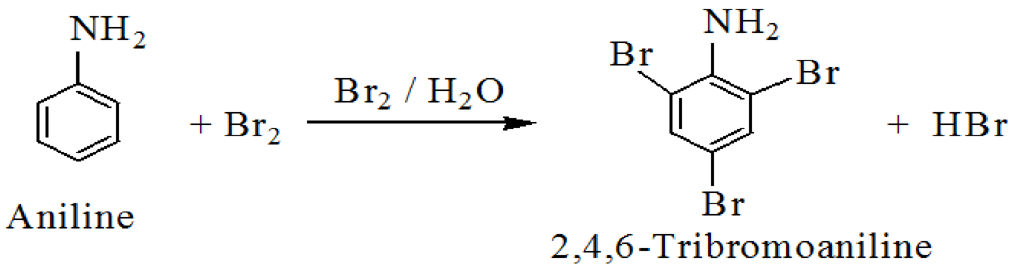
c) Tertiary amines do not react with benzene sulphonyl chloride. This property of amines reacting with benzene sulphonyl chloride differently is used for the distinction of primary, secondary, and tertiary amines and also for the separation of a mixture of amines. However, these days benzene sulphonyl chloride is replaced by p-toluenesulphonyl chloride.

7. Electrophilic substitution:

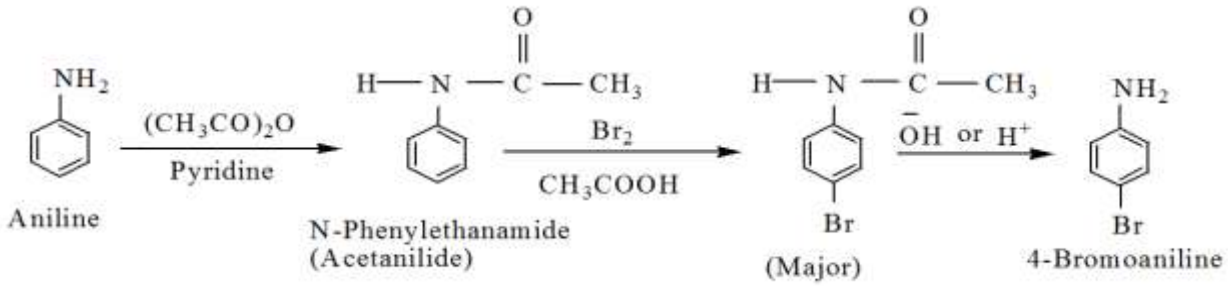
In aniline, Ortho- and para-positions to the –NH_2 group are electron-rich. Thus –the NH_2 group is ortho and para directing and a powerful activating group.

(a) Bromination:

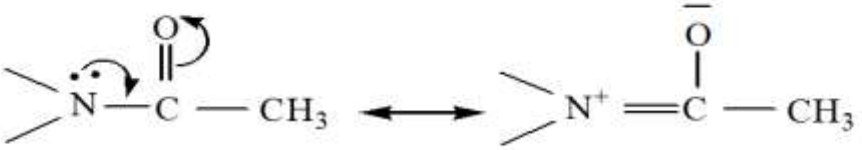
Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



Due to the very high reactivity of aromatic amine, Substitution tends to occur at ortho- and para-positions. To prepare a monosubstituted aniline derivative, the activating effect of $–NH_2$ group is to be controlled first by acetylation with acetic anhydride. Then the reaction carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.



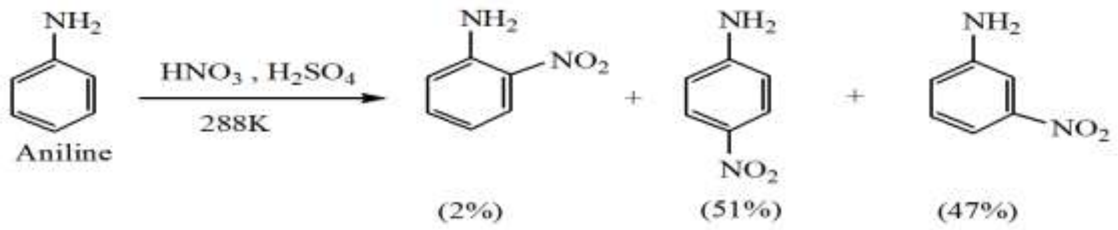
The lone pair of electrons on the nitrogen of acetanilide interacts with oxygen atom due to resonance as:



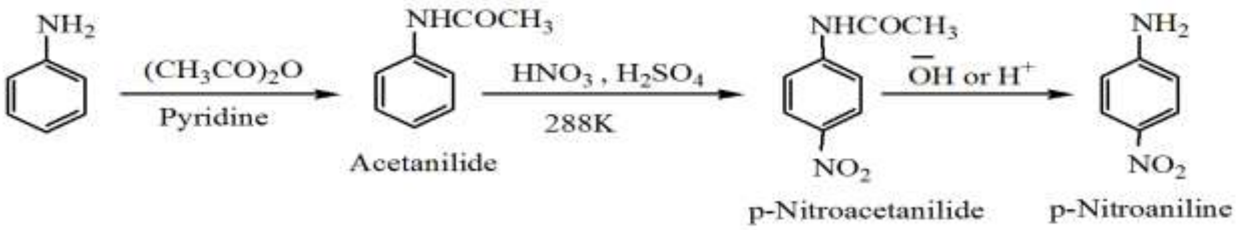
Hence, the lone pair of electrons on nitrogen is less available for donation to the benzene ring by resonance. Therefore, the activating effect of $–NHCOCH_3$ group is less than that of the amino group.

(b) Nitration:

Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, a significant amount of meta derivative is also formed.

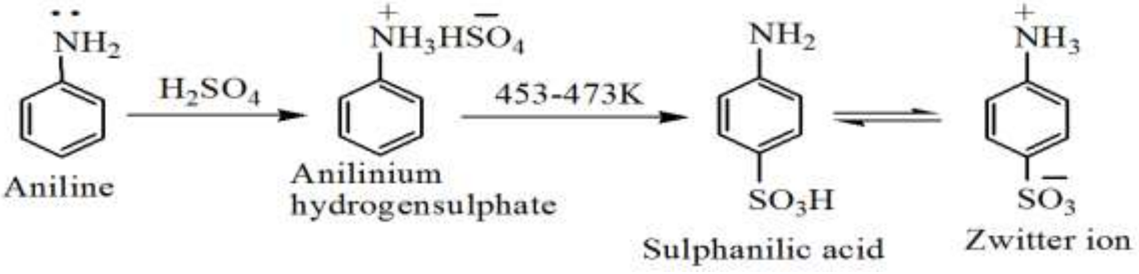


However, by protecting the $–NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative can be obtained as the major product.



(c) Sulphonation:

Aniline reacts with concentrated sulphuric acid to form anilinium hydrogen sulfate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



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

LECTURE 05

DIAZONIUM SALTS

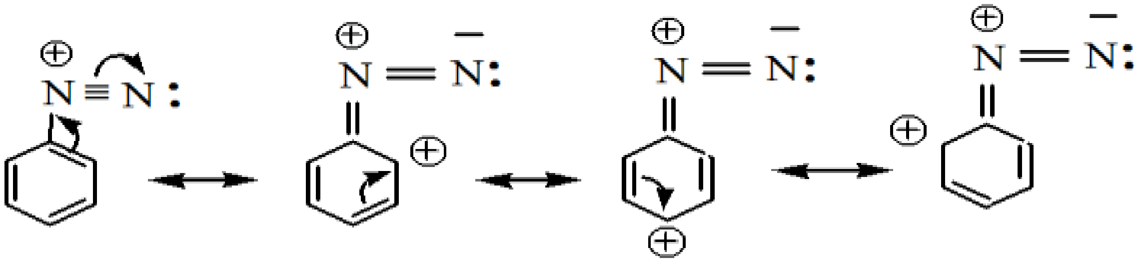
The naming of Diazonium salts:

The diazonium salts have the general formula RN_2X where R stands for an aryl group and 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, hydrogen sulfate, etc. The N_2^+ group is called the diazonium group.

For example, $C_6H_5N_2^+Cl^-$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate. $C_6H_5N_2Br$: Benzenediazoniumbromide, $C_6H_5N_2BF_4$: Benzenediazoniumfluoroborate.

Stability:

Primary aliphatic amines from highly unstable alkyl diazonium salts. Primary aromatic amines form arene diazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of the arene diazonium ion is explained based on resonance.



Method of Preparation of Diazonium Salts:

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as diazotization. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow{273-278\text{K}} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Physical Properties:

(i) Benzenediazonium chloride is a colorless crystalline solid.
(ii) It is readily soluble in water and is stable in cold but reacts with water when warmed.
(iii) It decomposes easily in the dry state.

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

LECTURE 06

Chemical Reactions:

The reactions of diazonium salts can be broadly divided into two categories, namely

(A) reactions involving the displacement of nitrogen.

(B) reactions involving the retention of the diazo group.

Reactions involving the displacement of nitrogen:

The Diazonium group being a very good leaving group is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. Replacement by halide or cyanide ion:

a) The nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called the **Sandmeyer reaction.**

$$ArN_2{}^+X^- \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$

$$ArN_2{}^+X^- \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$

$$ArN_2{}^+X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

b) 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 known as the **Gatterman reaction.**

$$ArN_2{}^+X^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$

$$ArN_2{}^+X^- \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

2. Replacement by iodide ion:

Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$$ArN_2{}^+Cl^- + KI \rightarrow ArI + KCl + N_2$$

3. Replacement by fluoride ion:

When arene diazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$$ArN_2^+Cl^- + HBF_4 \rightarrow Ar-N_2^+BF_4^- \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

4. Replacement by H:

Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidized to phosphorous acid and ethanal, respectively.

$$ArN_2^+Cl^- + H_3PO_2 + H_2O \rightarrow Ar-H + N_2 + H_3PO_3 + HCl$$

$$ArN_2^+Cl^- + CH_3CH_2OH \rightarrow Ar-H + N_2 + CH_3CHO + HCl$$

5. Replacement by hydroxyl group:

If the temperature of the diazonium salt solution is allowed to rise to 283 K, the salt gets hydrolyzed to phenol.

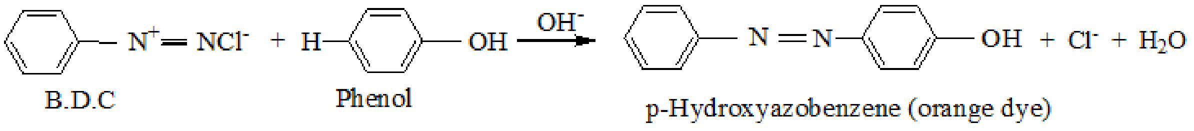
$$ArN_2^+Cl^- + H_2O \rightarrow ArOH + N_2 + HCl$$

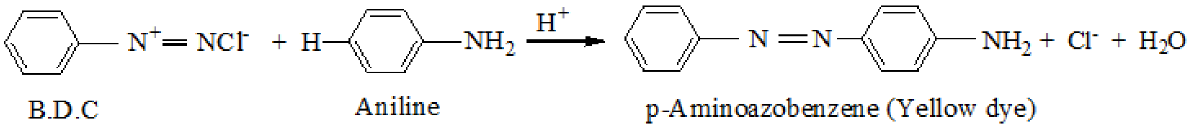
6. Replacement by –NO_2 group:

When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by –NO_2 group

Reactions involving retention of the 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 colored 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 a coupling reaction. Similarly the reaction of the diazonium salt with aniline yields p-aminoazobenzene. This is an example of an electrophilic substitution reaction.





Importance of Diazonium Salts in Synthesis of Aromatic Compounds:

(i) 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.

(ii) 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.

(iii) Thus, the replacement of the diazo group by other groups helps to prepare those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.