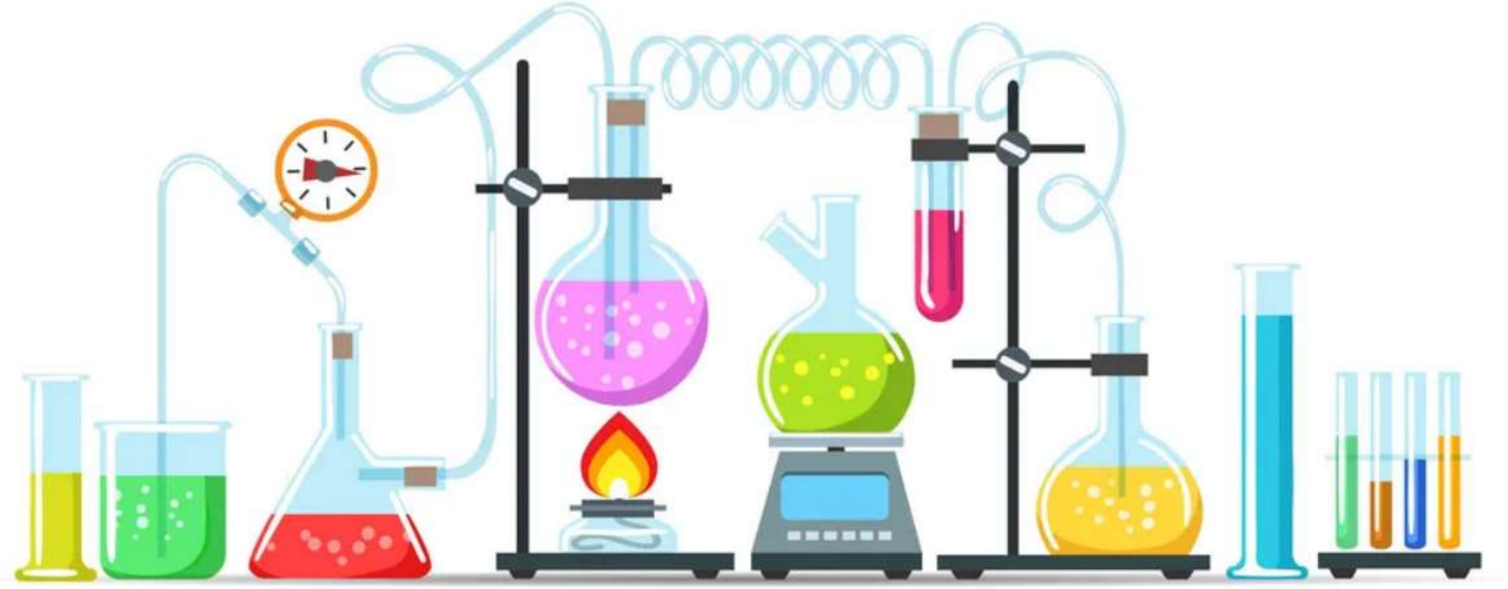
CHEMISTRY



AMINES

Introduction

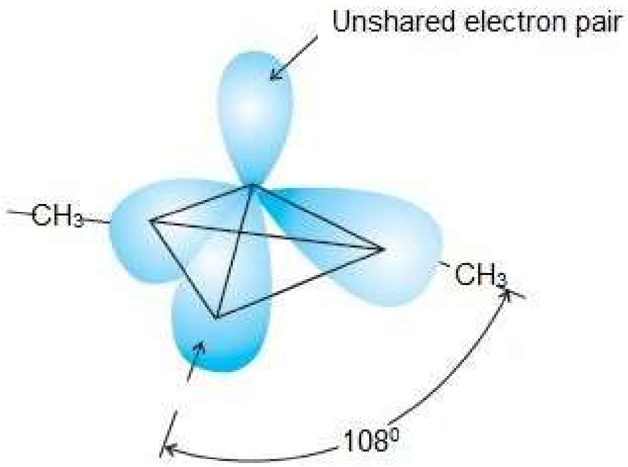
Amines are the derivatives of ammonia prepared by the replacement of one, two or all the three hydrogenatoms by alkyl and/or aryl groups.

Examples:
(i) CH_3-NH_2

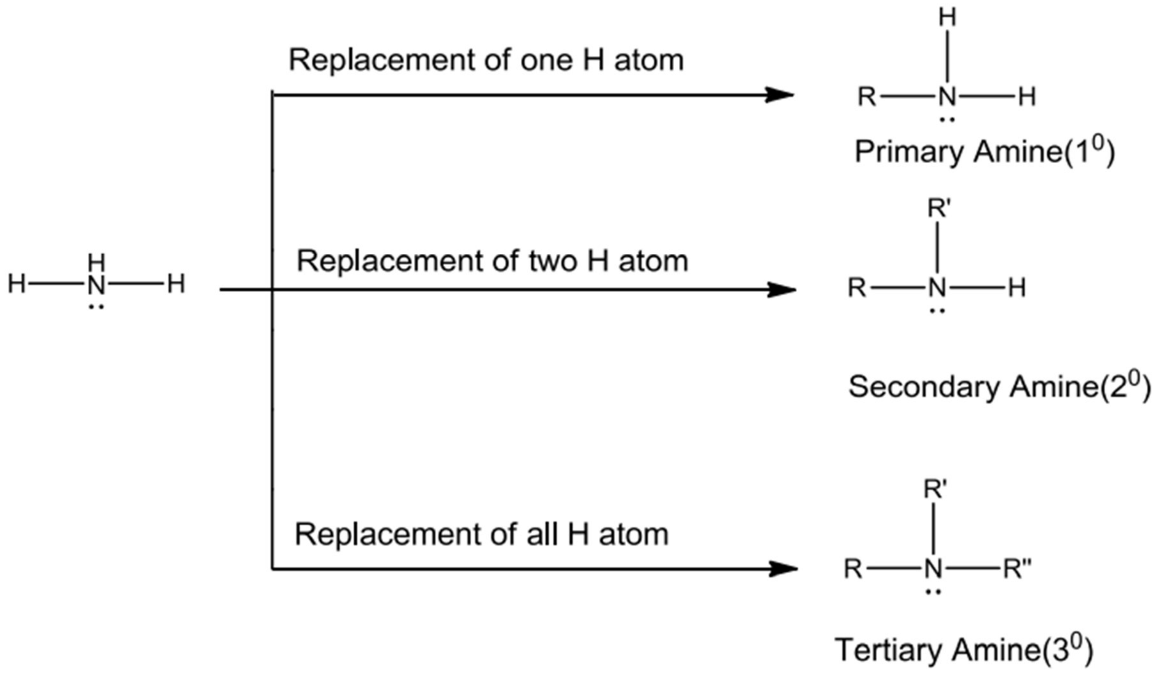
Structure of Amines

- In amines, the nitrogen atom is trivalent and has an unshared pair of electrons. Hence the nitrogenorbitals are sp^3 hybridised with pyramidal geometry.
- The three sp^3 hybrid orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending on thenature of the amines.
- The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. It is due to thepresence of unshared pair of electrons, the angle C-N-E is less than 109.5°.

  For example: The bond angle for trimethyl amine is 108°.



Classification of Amines



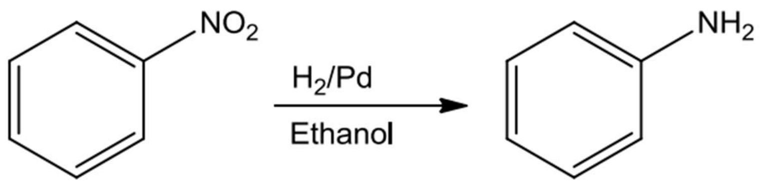
R, R' and R'' can be alkyl or aryl

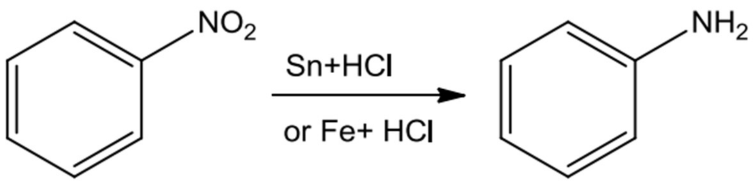
Preparation of Amines

Reduction of Nitro Compounds

Nitro compounds on reduction with hydrogen gas in the presence of finely divided nickel, palladium orplatinum and also on reduction with metals in acidic medium give amines.

$$CH_3NO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} CH_3NH_2$$





Ammonolysis

Alkyl halides or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen atom is replaced by an amino (-NH_2) group. The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis.

$$\underset{\text{Nucleophile}}{\ddot{N}H_3} + R-X \longrightarrow \underset{\text{Substituted ammonium salt}}{R\overset{+}{N}H_3\overset{-}{X}}$$

The primary amine prepared behaves as a nucleophile and reacts with further alkyl halide to formsecondary, tertiary amines, and finally quaternary ammonium salt.

$$\underset{(1^0)}{R-NH_2} \xrightarrow{RX} \underset{(2^0)}{R_2NH} \xrightarrow{RX} \underset{(3^0)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

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

$$R\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R-NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

In this method, a mixture of primary, secondary and tertiary and also a quaternary ammonium salt.However a primary amine is prepared by taking large excess of ammonia. The order of reactivity of halides with amines is RI > RBr > RCl

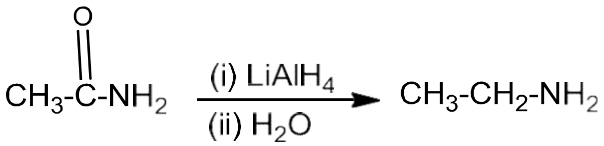
Reduction of Nitriles

Nitriles on reducing with $LiAlH_4$ or catalytic hydrogenation produce primary amines.

$$CH_3C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} CH_3-CH_2-NH_2$$

Reduction of Amides

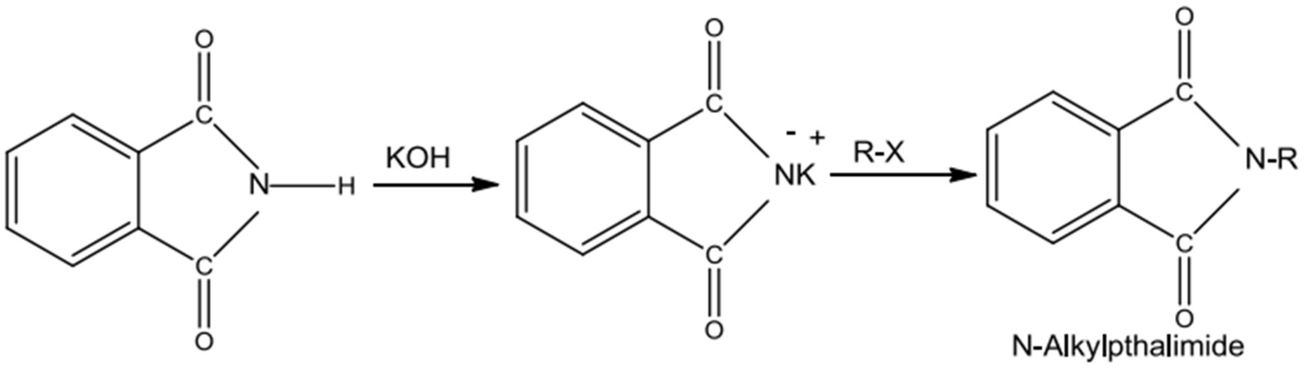
Amides on reducing with $LiAlH_4$ yield amines.

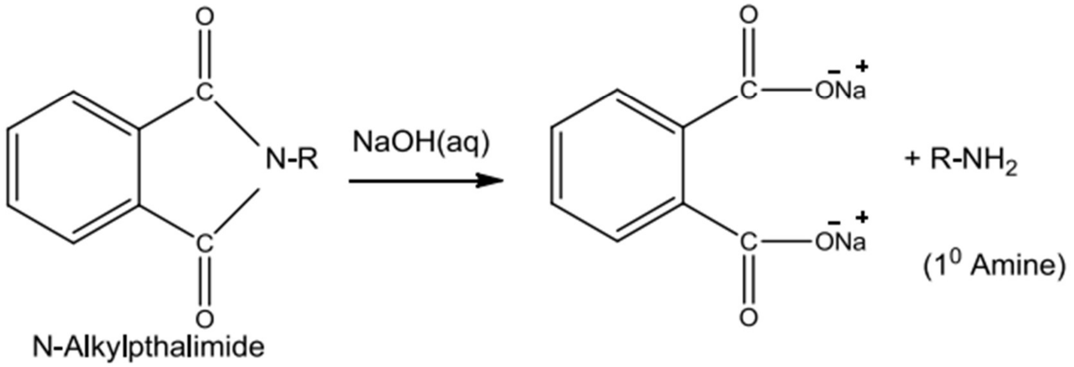


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} CH_3-CH_2-NH_2$$

Gabriel pthalimide synthesis

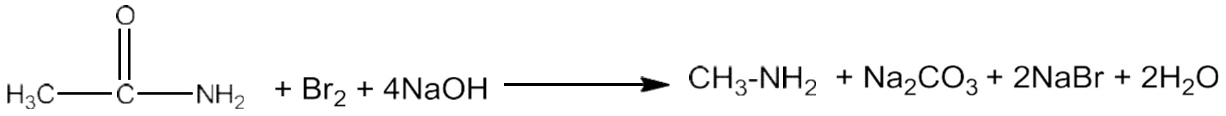
Pthalimide on reacting with ethanolic solution of KOH forms potassium salt of pthalimide which on heating with alkyl halide followed by alkaline hydrolysis yields the corresponding primary amine.





Hoffmann bromamide degradation reaction

In this method, primary amines are prepared by treating an amide with bromine in an aqueous orethanolic solution of NaOH.
The amine formed has one carbon atom less than the starting amide.



$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3\text{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Physical Properties of Amines

- **Solubility**
  Lower aliphatic amines are soluble in water because they can form a hydrogen bond with water. Solubility decreases with increase in molar mass of amines due to an increase in the size of thehydrophobic group.

- **Boiling points**
  Among the isomeric amines, primary and secondary amines have a high boiling point because theycan form hydrogen bonds.
  Tertiary amines cannot form hydrogen bonds due to the absence of a hydrogen atom for hydrogenbond formation.
  Hence, the order of boiling points of isomeric amines isPrimary > Secondary > Tertiary

Chemical Properties of Amines

a) Basic character of amines

- Amines have an unshared pair of electrons on the nitrogen atom due to which they act as a Lewisbase.
- The basic character of amines can be better understood in terms of their K_b and pK_b values.

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + OH^-$$

$$K = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

$$K[H_2O] = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

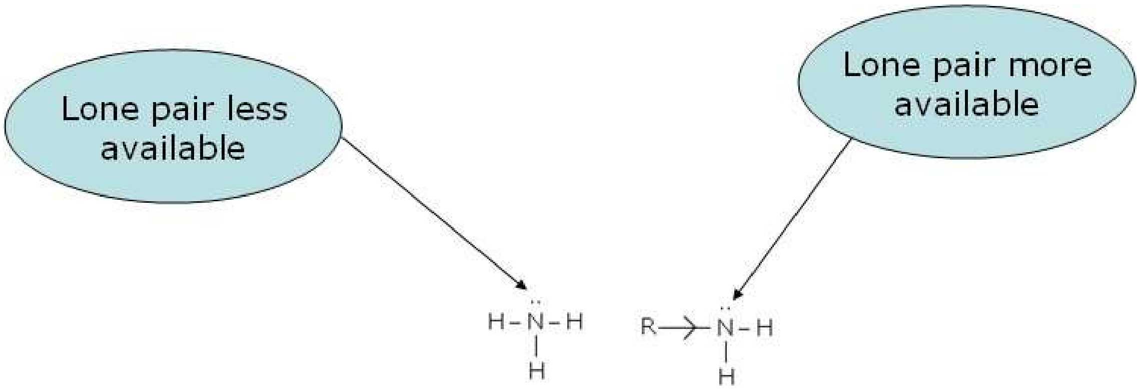
$$K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

- Greater K_b value or smaller pK_b indicates that a base is strong.

b) Comparison of basic strength of aliphatic amines and ammonia

Aliphatic amines are stronger bases than ammonia due to the +I effect of alkyl groups, leading to highelectron density on the nitrogen atom.



c) Comparison of basic strength of primary, secondary and tertiary amines

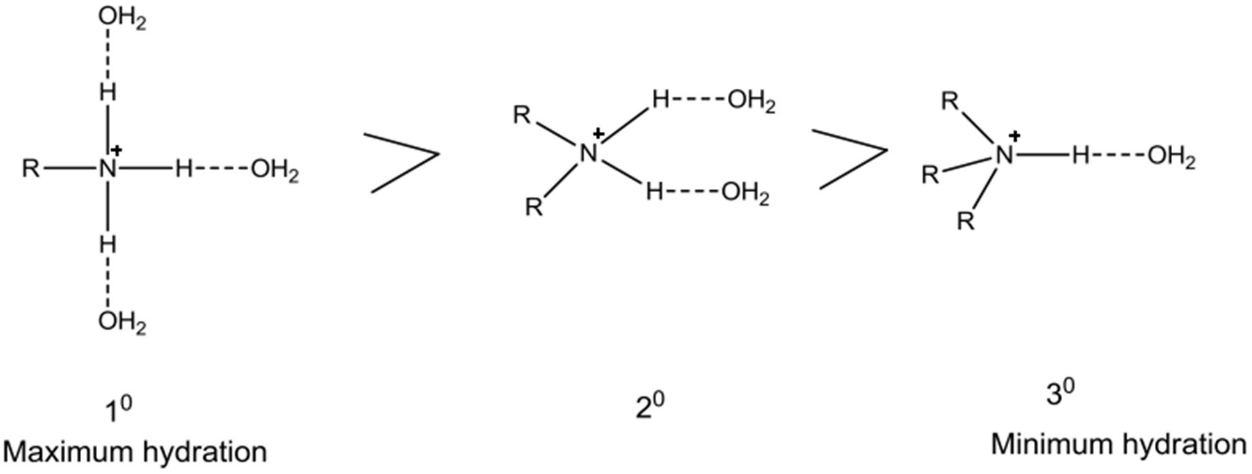
- The order of basicity of amines in the gaseous phase follows the expected order on the basis ofthe +I effect:

- In aqueous solution, tertiary amines are less basic than either primary or secondary amines. Thiscan be explained on the basis of the following factors:

  Tertiary amine > Secondary amine > Primary amine > NH_3

➢ Solvation effect

- ✓ Greater the stability of the substituted ammonium cation formed, stronger is the correspondingamine as a base.
- ✓ The tertiary ammonium ion is less hydrated than the secondary ammonium ion, which is less hydrated than the primary amine. Thus, tertiary amines have less tendency to form ammoniumion and consequently are least basic.



- ✓ On the basis of the solvation effect, the order of basicity of aliphatic amines should be:Primary amine > Secondary amine > Tertiary amine NH_3

➢ Steric factor

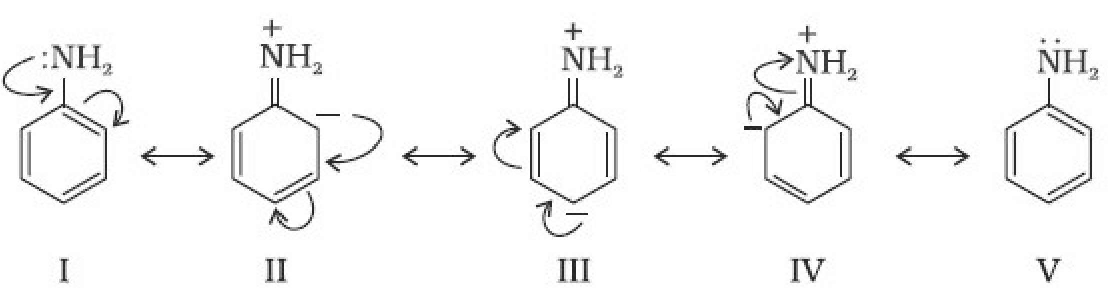
- ✓ As the crowding of the alkyl group increases from primary to tertiary, amine hindrance to hydrogen bonding increases which eventually decreases the basic strength. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.

- ✓ When the alkyl group is small like CH_3, there is no steric hindrance to hydrogen bonding. In this case, the order of basicity in aqueous medium is:
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

- ✓ When the alkyl group is the ethyl group, the group order of basicity in the aqueous medium is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

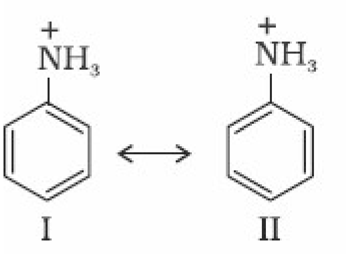
➢ Comparison of basic strength of aryl amines and alkanamines

- ✓ Generally, aryl amines are considerably less basic than alkyl amines.
  Example: Ethyl amine is more basic than aniline.
- ✓ In aniline, the $-NH_2$ group is directly attached to the benzene ring. Hence, the unshared pair of electrons on nitrogen is less available for protonation because of resonance.



- ✓ In the above resonating structures, there is a positive charge on the nitrogen atom making the lone pair less available for protonation. Hence, aniline is less basic than ethyl amine which hasno resonating structures.
- ✓ Less basicity of aniline can also be explained by comparing the relative stability of aniline andanilinium ion obtained by accepting a proton.
- ✓ Greater the number of resonating structures, greater is the stability of that species.
- ✓ Aniline is a resonance hybrid of five resonating structures, whereas anilinium ion

has only tworesonating structures.



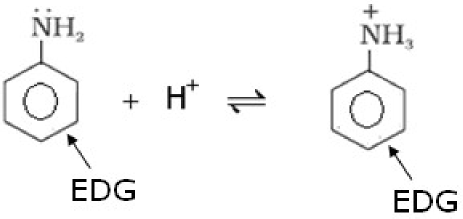
- ✓ Thus, aniline has less tendency to accept a proton to form the anilinium ion.

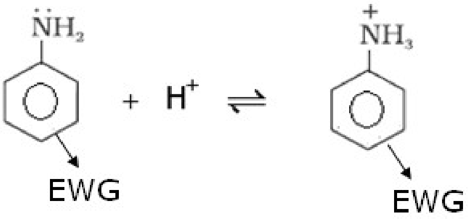
➢ Effect of substituent on the basic character of amines

- ✓ An electron-donating or electron-releasing group (EDG) increases basic strength.
- ✓ An electron-withdrawing group (EWG) decreases basic strength.

EDG: releases electrons, stabilizes the cation and increases basic strength

EWG: withdraws electrons, destabilizes the cation and decreases basic strength





EDG = $-CH_3, -OCH_3, -NH_2$

EWG = $-NO_2, -CN, -X$ (Halogen)

Reaction of Amines

Acylation reaction

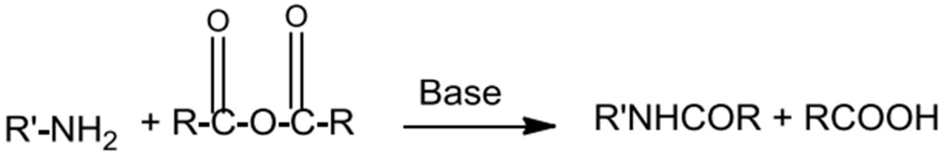
- ➢ Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogen atoms) react with acid chlorides, anhydrides and esters to form substituted amide.
- ➢ The process of introducing an acyl group (R–CO–) into the molecule is called acylation.
- ➢ The reaction is carried out in the presence of a stronger base than the amine, such

as pyridine, which removes HCl formed and shifts the equilibrium to the product side.

$$R\text{-}NH_2 + RCOCl \xrightarrow{Base} RNHCOR + HCl$$

Acid chloride

Substitutd amide



$$R'\text{-}NH_2 + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{Base} R'NHCOR + RCOOH$$

Acid anhydride

Substituted amide

$$R_2NH + RCOCl \xrightarrow{Base} R_2NCOR + HCl$$

Important Note: Because tertiary amines do not contain a replaceable hydrogen atom, they do notundergo acylation.

Carbylamine reaction

- On heating aliphatic and aromatic primary amines with chloroform and ethanolic KOH they formisocyanides or carbylamines which have foul odour.
- Secondary and tertiary amines do not show this reaction.
- This reaction is used as a test for primary amines.

$$CH_3 - NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} CH_3 - NC + 3KCl + 3H_2O$$

Reaction with Nitrous acid

- Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts. Being unstable diazonium salts liberate nitrogen gas quantitatively which is used in the estimation of amino acidsand proteins.

$$CH_3 - NH_2 + HNO_3 \xrightarrow{NaNO_2 + HCl} [CH_3 - \overset{+}{N}_2 Cl^-] \xrightarrow{H_2O} CH_3OH + N_2 + HCl$$

- Aromatic amines on treating with nitrous acid at low temperatures to form diazonium salts whichare used in the synthesis of a variety of aromatic compounds.

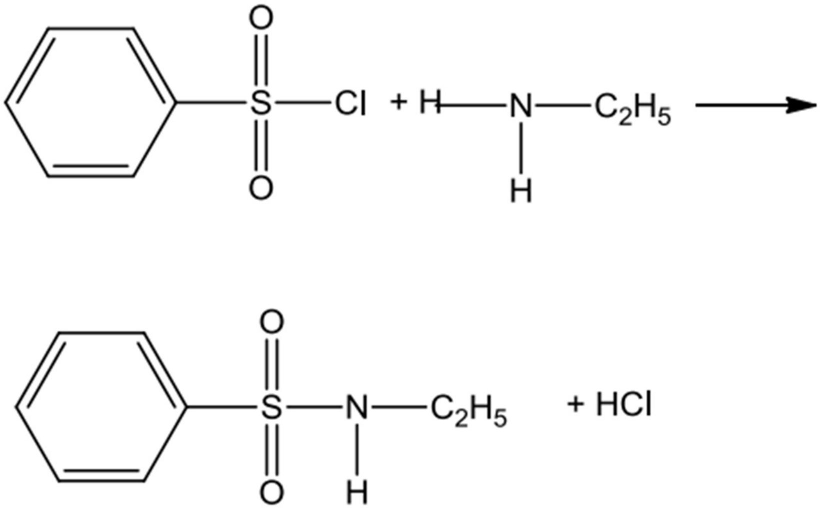
$$C_6H_5 - NH_2 \xrightarrow[273-278K]{NaNO_2 + HCl} C_6H_5 - \overset{+}{N}_2 Cl^- + NaCl + 2H_2O$$

- Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with arylsulphonyl chloride

Hinsberg’s reagent or benzenesulphonyl chloride ($C_6H_5SO_2Cl$) reacts with primary amines and secondary amines to form sulphonamides.

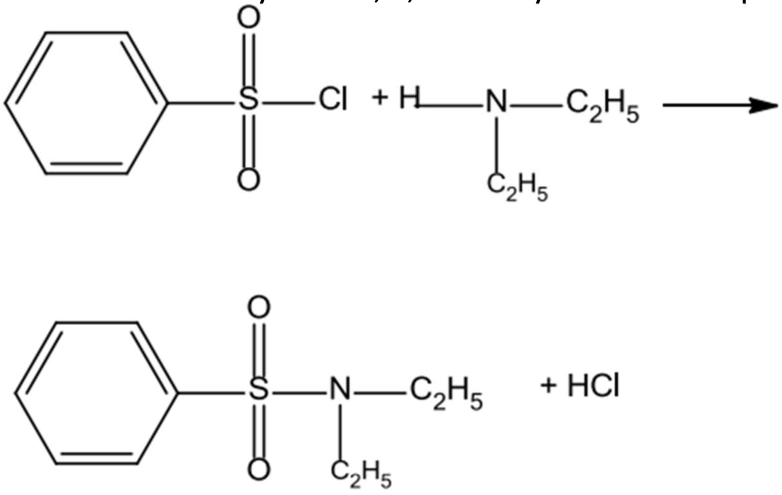
- Primary amine reacts with benzenesulphonyl chloride to form N-ethylbenzenesulphonyl amide.



N-ethylbenzenesulphonamide

The hydrogen bonded to nitrogen is strongly acidic due to the presence of strong electron withdrawing sulphonyl group and is hence soluble in alkali.

- With secondary amine,N,N-diethyl-benzenesulphonamide is formed.



N,N-diethylbenzenesulphonamide

N, N-diethylbenzene sulphonamide does not contain any H atom attached to nitrogen atom so it is not acidic and is therefore insoluble in alkali.

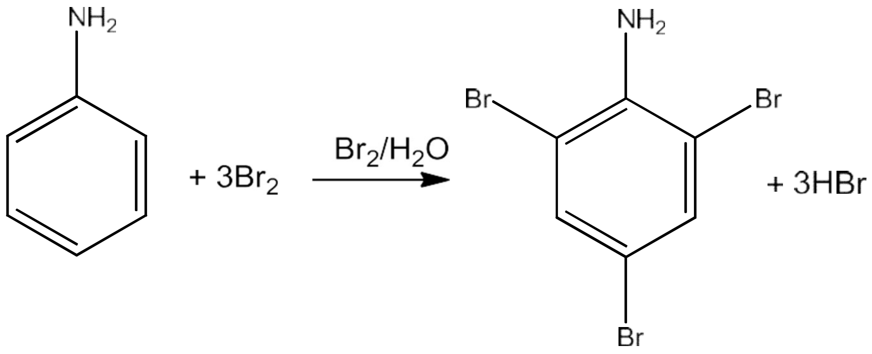
- Tertiary amines do not react with benzenesulphonyl chloride.

Electrophilic substitution

Ortho- and para-positions to the $-NH_2$ group become centres of high electron density. So $-NH_2$ group is ortho and para directing and a powerful activating group.

(a)Bromination

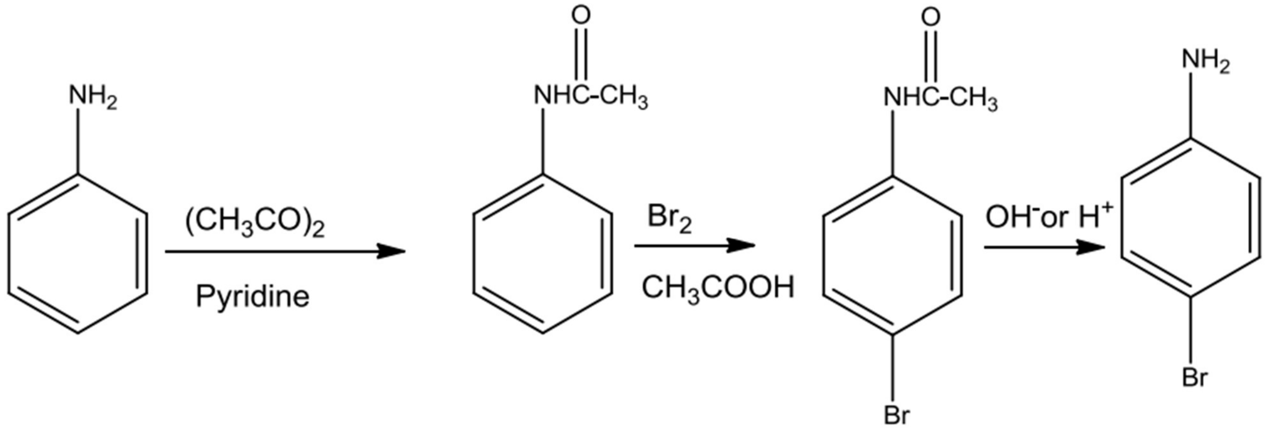
- Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4,6-tribromoaniline.



2,4,6-tribromoaniline

Due to the high reactivity of aromatic amines, electrophilic substitution takes place at ortho- and para-positions.

For preparing monosubstituted aniline derivative, the $-NH_2$ group is protected by acetylation with acetic anhydride then carrying out the desired substitution followed by the hydrolysis of the substituted amide to the substituted amine.

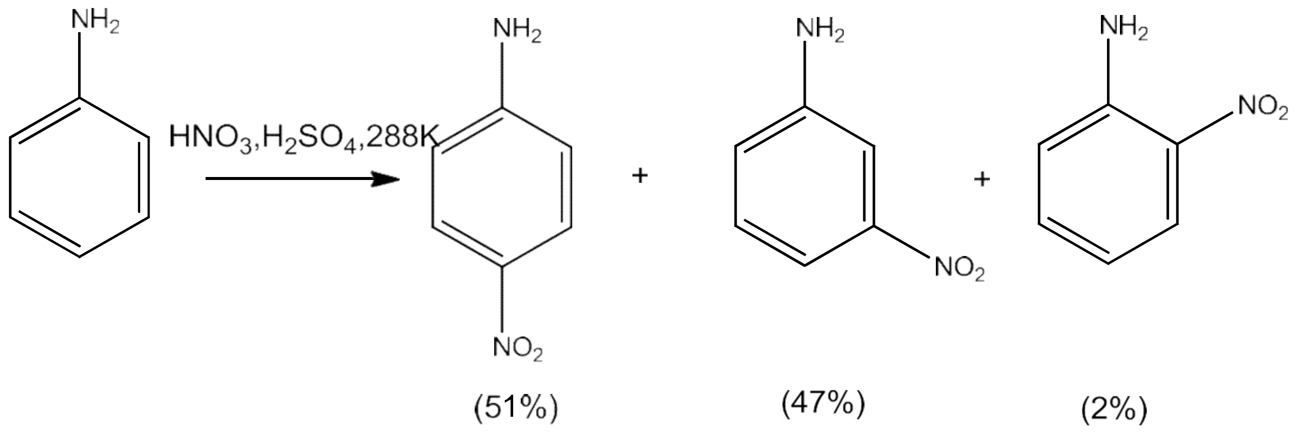


4-Bromoaniline

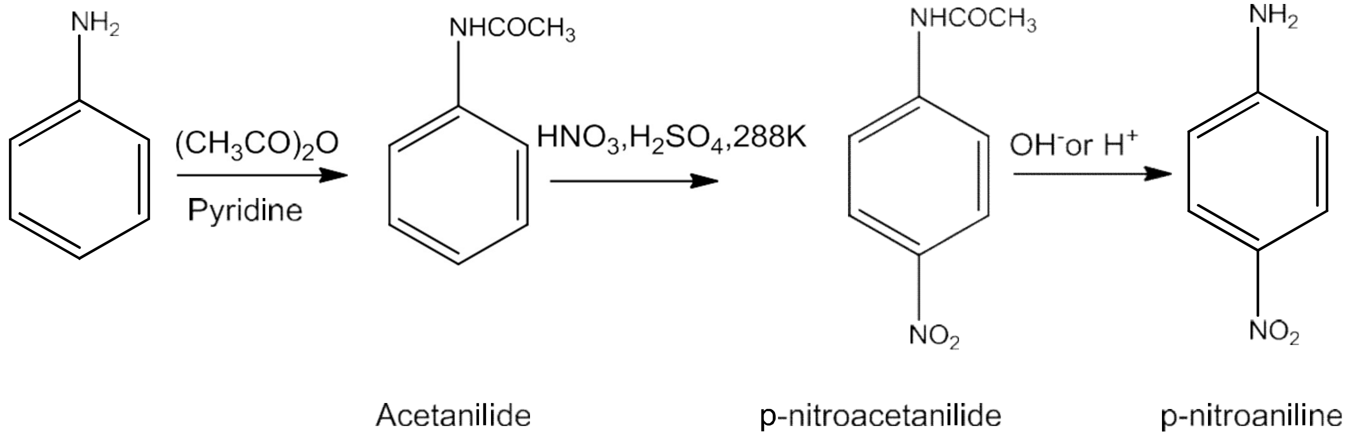
(b) Nitration

- Nitric acid is a nitrating agent plus a good oxidising agent. So direct oxidation of aromatic amines is not useful since it gives tarry oxidation products along with some nitro derivatives.
- In strong acidic medium, aniline is protonated to form the anilinium ion which is meta

directing. Hence besides the ortho and para derivatives, significant amount of meta derivative is also formed.

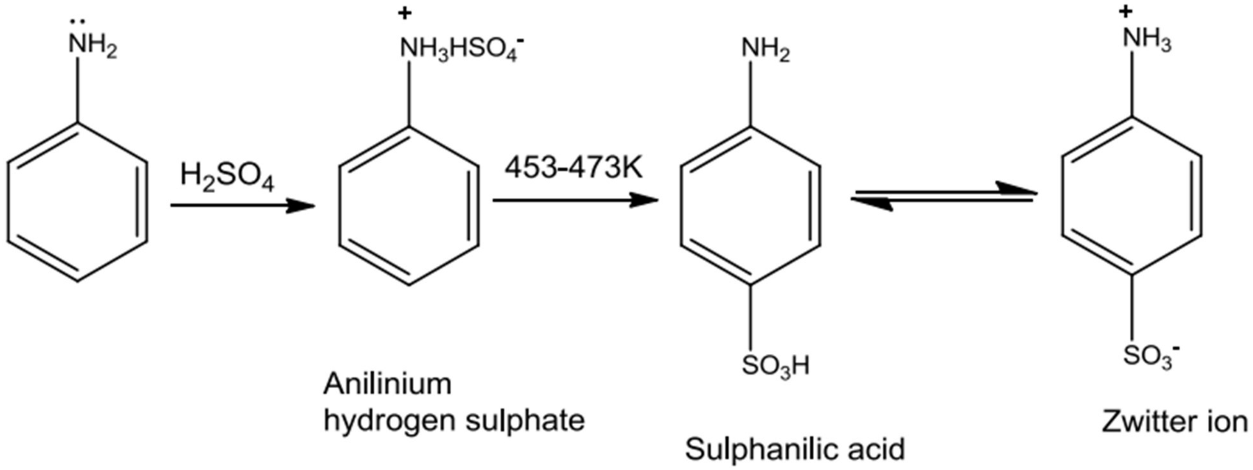


- However if we protect the –NH₂ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative derivative can be prepared as the major product.



(c) Sulphonation

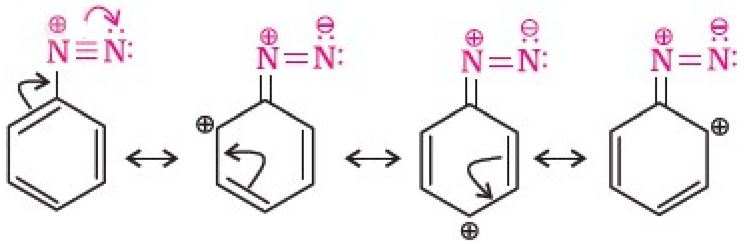
Aniline on reacting with sulphuric acid forms anilinium hydrogen sulphate which on heating with sulphuric acid at 453-473K gives p-aminobenzene sulphonic acid as the major product.



Aniline does not undergo Friedel-Crafts reaction due to salt formation with Lewis acid aluminium chloride which is used as a catalyst. As a result, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Diazonium Salts

- Diazonium salts have the general formula $R\overset{+}{N}_2\overset{-}{X}$.
  - ✓ Where R = Aryl group
  - ✓ X^- ion = Cl^- Br^-, HSO_4^-, BF_4^- etc.
- A suffix diazonium is added to the parent hydrocarbon from which they are formed followed by thename of the anion.
  - ✓ Anion = chloride, hydrogensulphate, etc.
  - ✓ Diazonium group = $N^+{}_2$
- Primary aliphatic amines form highly unstable alkyldiazonium salts whereas primary aromatic aminesform arenediazonium salts which are stable for a short time in a solution at low temperatures.
- The stability of arenediazonium ion is explained on the basis of resonance.



Preparation of Diazonium Salts

- Benzenediazonium chloride is prepared by the action of aniline with nitrous acid at 273-278K.
- The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N}_2Cl^- + NaCl + 2H_2O$$

Physical Properties

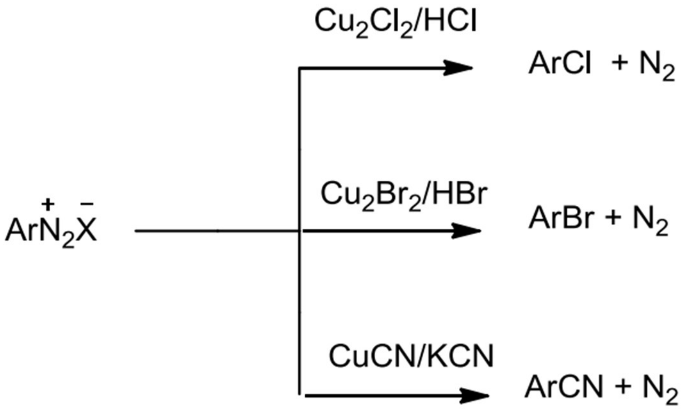
- Benzenediazonium chloride is a colourless crystalline solid.
- It is readily soluble in water and is stable in cold but reacts with warm water.
- It decomposes easily in the dry state.
- Benzenediazonium fluoborate is water insoluble and stable at room temperature.

Chemical Reactions

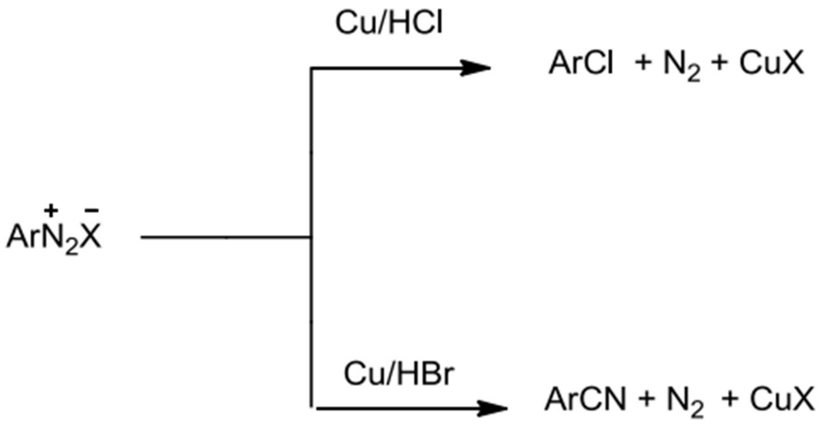
Reactions involving displacement of Nitrogen

- **Replacement by halide or cyanide ion:**

This reaction is called Sandmeyer reaction in which nucleophiles like Cl$^-$,Br$^-$ and CN$^-$ can be easilyintroduced in the benzene ring in the presence of Cu(I) ion.



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 Cu powder. This isreferred as Gatterman reaction.



- **Replacement by iodide ion:**

Iodobenzene is formed on treating diazonium salt solution with potassium iodide.

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{X}} + \mathrm{KI} \longrightarrow \mathrm{ArI} + \mathrm{KCl} + \mathrm{N_2}$$

- **Replacement by fluoride ion:**

Arenediazonium chloride on treating with fluoboric acid gives a precipitate of arene diazoniumfluoroborate which on heating decomposes to give aryl fluoride.

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{HBF_4} \longrightarrow \mathrm{Ar\text{-}}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{BF_4}} \xrightarrow{\triangle} \mathrm{Ar\text{-}\,F} + \mathrm{BF_3} + \mathrm{N_2}$$

- **Replacement by H:**

Hypophosphorus acid or ethanol are mild reducing agents and reduce diazonium salts to arenesand themselves get oxidised to phosphorus acid and ethanal respectively.

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{H_3PO_3} + \mathrm{H_2O} \longrightarrow \mathrm{Ar\,H} + \mathrm{N_2} + \mathrm{H_3PO_3} + \mathrm{HCl}$$

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{CH_3\,CH_2OH} \longrightarrow \mathrm{Ar\,H} + \mathrm{N_2} + \mathrm{CH_3CHO} + \mathrm{HCl}$$

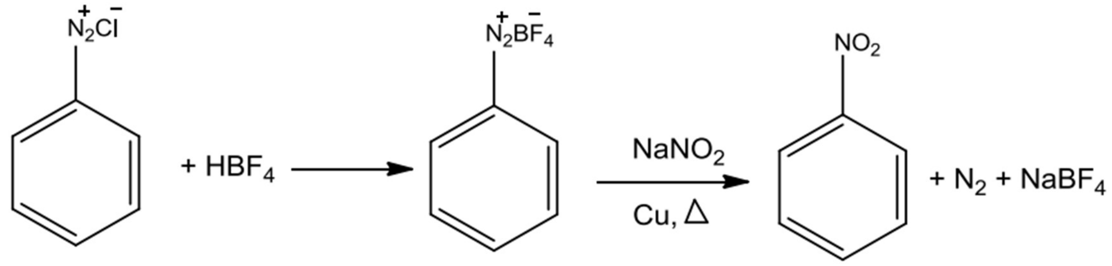
- **Replacement by hydroxyl group:**

Diazonium salt solution gets hydrolysed to phenol when the temperature is allowed to rise up to283K.

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{H_2O} \longrightarrow \mathrm{ArOH} + \mathrm{N_2} + \mathrm{HCl}$$

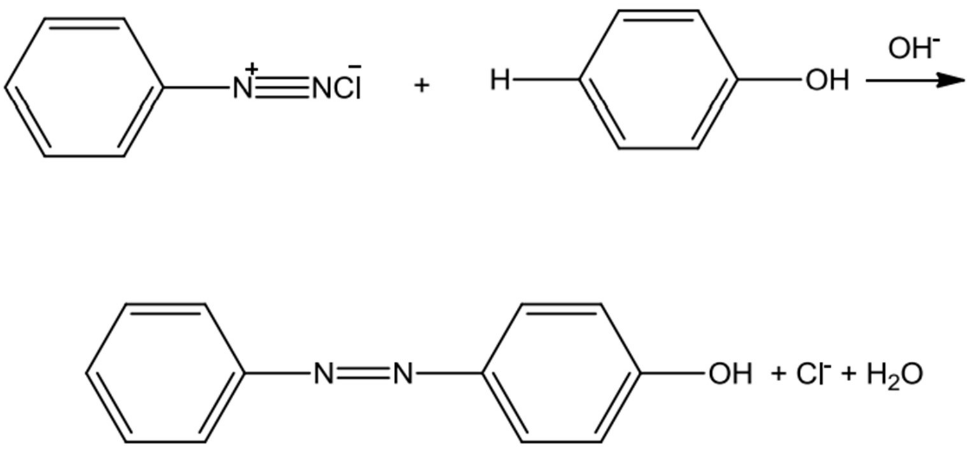
- **Replacement by –NO_2 group:**

On heating diazonium fluoroborate with aqueous sodium nitrite solution in the presence of copper,the diazonium group is replaced by –NO_2 group.

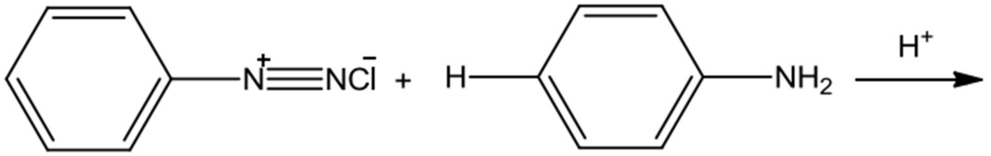


Reactions involving retention of diazo group coupling reactions

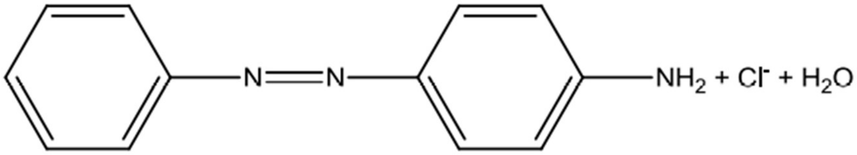
- ✓ Benzene diazonium chloride reacts with phenol in which the phenol at its para position is coupled with the diazonium salt to form orange colour dye called p-hydroxyazobenzene.
- ✓ The reaction of diazonium salt with aniline gives yellow dye p-aminoazobenzene.
- ✓ The reaction is known as coupling reaction and it is an example of electrophilic substitutionreaction.



p-hydroxyazobenzene (orange dye)



p-aminoazobenzene (yellow dye)



p-hydroxyazobenzene (orange dye)

Importance of Diazonium Salts in Synthesis of Organic Compounds

- Diazonium salts are very good intermediates for introducing –F, –Cl, –Br, –I, –CN, –OH,–NO_2 groupsinto the aromatic ring.
- Direct halogenation method cannot be used for preparing aryl fluorides and iodides.
- Cyanobenzene can be easily prepared from diazonium salt.
- Thus the replacement of diazo group by other groups is useful in preparing substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

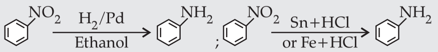
MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 13

Amines

Preparation :

1.Reduction of nitro compounds

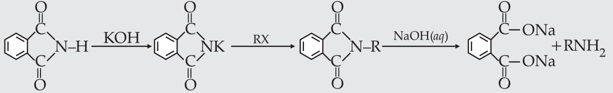


2. Ammonolysis of alkyl halides $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$

3.Reduction of nitriles $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$

4.Reduction of amides $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$

5.Gabriel phthalimide synthesis



6.Hoffmann bromamide degradation reaction

$R-\overset{O}{\overset{\|}{C}}-NH_2+Br_2+4NaOH \longrightarrow R-NH_2 + Na_2CO_3+2NaBr+2H_2O$

Physical properties

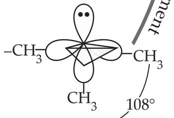
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association
- Boiling point : primary > secondary > tertiary

Importance of diazonium salts in synthesis of aromatic compounds :

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Derivatives of ammonia, obtained by replacement of one, two or all the three Hatoms by alkyl and/or aryl groups

Structure



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Classification

$NH_3 \rightarrow RNH_2 \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>N-H \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>N-R''$

Nomenclature:

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group. IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Chemical reactions

(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5-\underset{C_2H_5}{\underset{|}{N}}H+CH_3-\underset{O}{\underset{\|}{C}}-Cl \xrightarrow[Base]{} C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-CH_3+HCl$

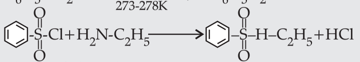
(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

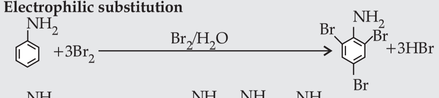
$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

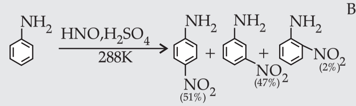
$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

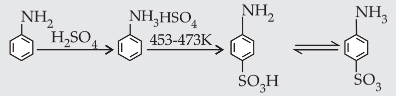
(v)



(vi) Electrophilic substitution







Diazonium Salts (RN_2X)

Preparation :

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

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction: $ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$; $ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$; $ArN_2X \xrightarrow{CuCN/KCN} ArCN+N_2$

Gattermann reaction :

$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2+CuX$

$ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2+CuX$

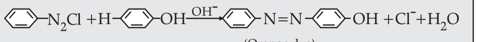
(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

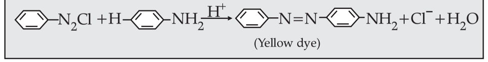
(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**



(Orange dye)



(Yellow dye)

Important Questions

Multiple Choice questions-

Question 1. Which of the following does not react with Hinsberg reagent?
(a) Ethylamine
(b) $(CH_3)_2NH$
(c) $(CH_3)_3N$
(d) Propan-2-amine

Question 2. $C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow{P/Br_2} Y \xrightarrow[(excess)]{NH_3} Z.$
in above sequence, Z is
(a) Cyanoethane
(b) Ethanamide
(c) Methanamine
(d) Ethanamine

Question 3. Oxidation of aniline with $K_2Cr_2O_7/H_2SO_4$ gives
(a) phenylhydroxylamine
(b) p-benzoquinone
(c) nitrosobenzene
(d) nitrobenzene
Question 4. Which of the following amines can exhibit enantiomerism?
(a) Benzeamine
(b) 2-Butanamine
(c) 2-Propanamine
(d) 2-Methyl-propanamine.

Question 5. Which of the following: when heated with a mixture of ethanmine and alcoholic potash gives ethyl isocyanide?
(a) 2-chloropropane
(b) 2,2-dichloropropane
(c) trichloromethane
(d) tetrachloromethane

Question 6. Which of the following pair of species will yield carbylamine?
(a) CH_3CH_2Br and KCN
(b) CH_3CH_2Br and NH_3 (excess)
(c) CH_3CH_2Br and AgCN
(d) $CH_3CH_2NH_2$ and HCHO

Question 7. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Hinsberg method
(b) Hoffmann method
(c) Wurtz reaction
(d) Curticus reaction

Question 8. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by
(a) $NaBH_4$
(b) H_2-Pd/C
(c) $LiAlH_4$
(d) Zn-Hg/HCl
Question 9. $C_6H_5N^+_2 Cl^- + CuCN \rightarrow C_6H_5CN + N_2 + CuCl$. The above chemical reaction is associated with which of the following name:
(a) Balz Schiemen
(b) Gattermann
(c) Shimonini
(d) Sandmeyer.
Question 10. The reaction of aniline with benzoyl chloride gives
(a) Benzoin
(b) Benzanilide
(c) Benzalaniline
(d) Benzamide

Very Short Questions-

1.For an amine RNH_2, write an expression to indicate its basic strength.
2. Give one use of quaternary ammonium salts.
3. Give one example of Hoffmann – Bromamide reaction
4. Distinguish between ethylamine and aniline.
5.The IUPAC name of secondary amine having lowest molecular mass is _________.
6.Give an example of diazotization
7. Write one use of diazonium salt
8.How can the reactivity of aromatic amines be controlled?
9.Give one use of tertiary amines.
10. Name a reagent which can distinguish between primary, secondary and tertiary amine

Short Questions--

1. It is difficult to prepare pure amines by ammonolysis of alkylhalides.
2. Amines have higher boiling points than hydrocarbons of similar molecular mass.
3. Aniline is weaker base than cyclohexylamine.
4. Methylamine is a stronger base than aniline.

5. Before nitration, aniline is converted to acetanilide.
6. It is easier to brominate aniline as compared to benzene.
7. Reduction of nitro compound to aniline using iron scrap and HCl is preferred.
8. Aromatic amines cannot be prepared by Gabriel Phthalimide synthesis.
9. During acylation of amines, pyridine is added.
10. Aniline does not undergo Friedel – Craft's reaction.

Long Questions-

1. (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$
(ii) Write IUPAC names of all the isomers.
(iii) What type of isomerism is exhibited by different pairs of amines?
2. Arrange the following in increasing order of their basic strength:
(i) $C_2H_5NH_2, C_6H_5NH_2, NH_3, C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
(ii) $C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N, C_6H_5NH_2$
(iii) $CH_3NH_2, (CH_3)_2NH, (CH_3)_3N, C_6H_5NH_2, C_6H_5CH_2NH_2$.
3. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

4. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.
(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$
(iii) $CH_3NHCH(CH_3)_2$ (iv) $(CH_3)_3CNH_2$
(v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$ (vii) $m-BrC_6H_4NH_2$

5. Give one chemical test to distinguish between the following pairs of compounds.
(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline
(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

6. Account for the following:
(i) p*Kb* of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not.
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
(iv) Although amino group is *o*, *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.
(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

7. Arrange the following:

(i) In decreasing order of the p*Kb*values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, *p*-nitroaniline and *p*-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, (C2H5)2NH, $(C_2H_5)_3Nz$ and NH_3

(v) In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_6H_5NH_2$.

8. How will you convert:

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Ortho substituted anilines are usually weaker bases than anilines.

Reason: This is due to ortho effect.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Amines are alkyl or aryl derivatives of ammonia formed by replacement of one or more hydrogen atoms. Alkyl derivatives are called aliphatic amines and aryl derivatives are known as aromatic amines. The presence of aromatic amines can be identified by performing dye test. Aniline is the simplest example of aromatic amine. It undergoeselectrophilic substitution reactions in which -NH_2 group strongly activates the aromatic ring through delocalisation of lone pair of electrons of N-atom. Aniline undergoes electrophilic substitution reactions. Ortho and para positions to the -NH_2 group become centres of high electrons density. Thus, -NH_2 group is ortho and para-directing and powerful activating group.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Cyclohexylamine and aniline can be distinguished by:

  a) Hinsberg test.
  b) carbylamine test.
  c) Lassaigne test.
  d) azo dye test.

(ii) Which of the following compounds gives dye test?

a) Aniline.
b) Methyl amine.
c) Diphenyl amine.
d) Ethyl amine.

(iii) Aniline when acetylated, the major product on nitration followed by alkaline hydrolysis gives:

a) Acetanilide.
b) o-nitroacetanitide.
c) p-nitroaniline.
d) m-nitroanitine.

(iv) Oxidation of aniline with manganese dioxide and sulphuric acid produces:

a) Phenylhydroxylamine.
b) Nitrobenzene.
c) p-benzoquinone.
d) Phenol.

(v) Aniline when treated with cone. HNO_3 and H_2S0_4 gives:

a) p-phenylenediamine.
b) m-nitroaniline.
c) p-benzoquinone.
d) Nitrobenzene.

2. Read the passage given below and answer the following questions:

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the -NH_2 group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the +I effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be 3° > 2° > 1°, however the observed order is 2° > 1° > 3°. This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases.

Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as -CH_3, -OCH_3, etc. increase the basicity while electron-withdrawing substitutes such as -NO_2, -CN, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at p than at m-positions.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which one of the following is the strongest base in aqueous solution?

a) Methyl amine.
b) Tri methyl amine.
c) Aniline.
d) Dimethyl amine.

(ii) Which order ofbasicity is correct?

a) Aniline > m-toluidine > o-toluidine
b) Aniline> o-toluidine > m-toluidine
c) o-toluidine > aniline> m-toluidine
d) o-toluidine < aniline < m-toluidine

(iii) What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3?

a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$
b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
c) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3$
d) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

(iv) The order of basic strength among the following amines in benzene solution is:

a) $CH_3NH_2 > (CH_3)_3N > (CH_3)_2NH$
b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
d) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

(v) Choose the correct statement.

a) Methylamine is slightly acidic.
b) Methylamine is less basic than ammonia.
c) Methylamine is a stronger base than ammonia.
d) Methylamine forms salts with alkalies.

MCQ Answers-

1. Answer: (c) $(CH_3)_3N$

2. Answer: (d) Ethanamine

3. Answer: (b) p-benzoquinone

4. Answer: (b) 2-Butanamine

5. Answer: (c) trichloromethane

6. Answer: (c) CH_3CH_2Br and AgCN

7. Answer: (c) Wurtz reaction

8. Answer: (c) $LiAlH_4$

9. Answer: (d) Sandmeyer.

10. Answer: (b) Benzanilide

Very Short Answers-

Ans 1.

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

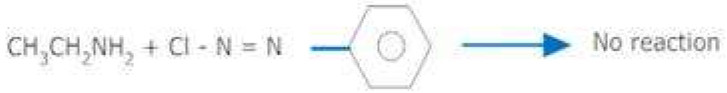
$$K_b = \frac{[RNH_3^+]\ [OH^-]}{[RNH_2]}$$

Ans 2. Quaternary ammonium salts are widely used for manufacture of synthetic detergents.

Ans 3. In Hoffmann – Bromamide reaction an acid amide is reacted with Bromine in presence of a base to give a primary amine having one carbon less than the starting amide.

$$RCONH_2 + Br_2 + 4\,NaOH \rightarrow RNH_2 + Na_2\,CO_3 + 2\,NaBr + 2\,H_2O$$

Ans 4. Ethylamine and aniline can be distinguished by azodye test. On treating aniline with benzene diazonium salt, orange or red coloured azodye is formed which is not formed with ethyl amine.



Ans 5. N- Methylmethanamine.

Ans 6. During diazotization benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273 – 278 K

Ans 7. Diazonium salts are used in preparation of substituted aromatic compounds.

Ans 8. The reactivity of aromatic amines can be controlled by acylation.

Ans 9. Tertiary amines like trimethylamine are used as insect attractants.

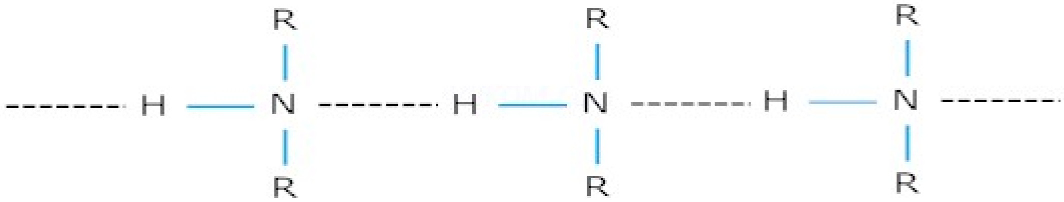
Ans 10. P- Toluenesulphonyl chloride Hinsberg reagent can be used as a distinguishing reagent for primary, secondary and tertiary amines.

Short Answers-

Ans 1. The process of ammonolysis yields a mixture of primary, secondary, tertiary amines and quaternary salts. The separation of this amines is a very complicated process and difficult. Therefore it is difficult to prepare pure amines by ammonolysis of alkyl halides.

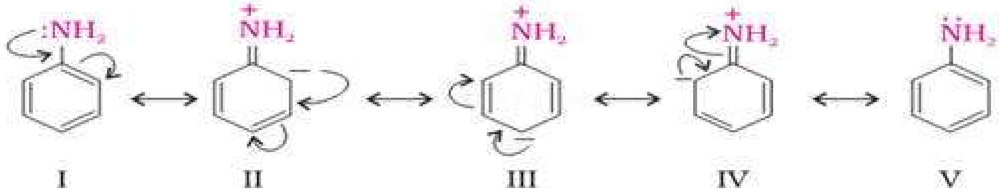
$$Rx \xrightarrow[-Hx]{NH_3} RNH_2 \xrightarrow[-Hx]{Rx} R_2NH \xrightarrow[-Hx]{Rx} R_3N \xrightarrow{Rx} [R_3N]^+ X^-$$

Ans 2. Amines have higher boiling points than hydrocarbons of comparable molecular mass due to the presence of intermolecular hydrogen bond in amines which is absent in hydrocarbons. Therefore, amines exist as associated molecules and have higher boiling points.

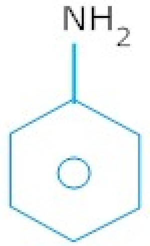


In alcohols and carboxylic acids, the electro- negativity of oxygen is more than nitrogen of amines. Therefore the hydrogen bonds of alcohols and acids are stronger than in amines and alcohols & carboxylic acids have higher boiling points.

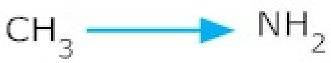
Ans 3. As a result of resonance in aniline; the lone pair on nitrogen delocalized over the benzene ring and is less available for protonation than in cyclohexyl amine which does not undergo resonance. Resonating structure of aniline –



Ans 4. Due to electron donating nature of CH_3, group, electron pair. Availability at N- atom in methyl amine is much higher than that in aniline; in aniline the benzene ring decreases the electron density at N- atom in aniline. Thus CH_3NH_2 is a stronger base than aniline.

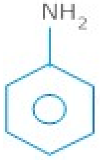


Aniline

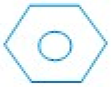


Methylamine

Ans 5. Aniline is very much susceptible to nitration and nitric acid is a strong oxidizing agent. Therefore to avoid oxidation of aniline, $-NH_2$ group is protected by its acetylation to acetanilide which undergo nitration smoothly without any oxidation.



Aniline



Benzene

Ans 6. In aniline, due to +R effect of $-NH_2$ group the benzene ring gets activated to a large extent and it becomes easier to brominates aniline as compared to benzene.

Ans 7. For reduction of nitro compounds to aniline, iron scrap and HCl is preferred because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction & therefore only a small amount of HCl is required to initiate the reaction.

Ans 8. Aromatic amines cannot be prepared by Gabriel pythalimide synthesis as aryl halides do not undergo nucleophilic substitution with the anion formed by pythalimide.

Ans 9. Acylation of amines is carried out in presence of pyridine or another base stronger than amines as it removes HCl so formed and shifts the equilibrium in forward direction.

$$C_2H_5\,NH_2 + CH_3\,COCl \xrightleftharpoons{\text{Base}} C_2H_5\,NHCO\,CH_3 + HCl$$

Ans 10. During Fridel Craft’s reaction, aniline forms salt with aluminum chloride, the catalyst of reaction due to which nitrogen acquires a positive charge and acts as a strong deactivating group for further reaction.

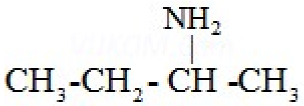
Long Answers-

Ans 1. (i), (ii) The structures and their IUPAC names of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$ are given below:

(a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

Butanamine $(1°)$

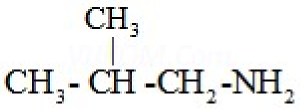
(b)



$CH_3\text{-}CH_2\text{-}\underset{}{\overset{NH_2}{\overset{|}{CH}}}\text{-}CH_3$

Butan-2-amine $(1°)$

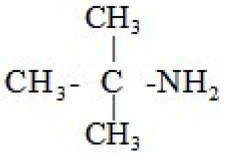
(c)



$CH_3\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}NH_2$

2-Methylpropanamine $(1°)$

(d)



$CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}\text{-}NH_2$

2-Methylpropan-2-amine $(1°)$

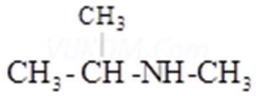
(e) $CH_3\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3$

N-Methylpropanamine $(2°)$

(f) $CH_3\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_3$

N-Ethylethanamine $(2°)$

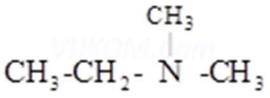
(g)



$CH_3\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}NH\text{-}CH_3$

N-Methylpropan-2-amine $(2°)$

(h)



$CH_3\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{N}}\text{-}CH_3$

N, N-Dimethylethanamine $(3°)$

(iii) The pairs (a) and (b) and (e) and (g) exhibit position isomerism.

The pairs (a) and (c); (a) and (d); (b) and (c); (b) and (d) exhibit chain isomerism.

The pairs (e) and (f) and (f) and (g) exhibit metamerism.

All primary amines exhibit functional isomerism with secondary and tertiary amines and vice-versa.

Ans 2. (i) Considering the inductive effect of alkyl groups, $NH_3, C_2H_5NH_2$ and $(C_2H_5)_2NH$ can be arranged in the increasing order of their basic strengths as:

$NH_3 < C_2H_5NH_2 < (C_2H_5)_5 NH$

Again, $C_6H_5NH_2$ has proton acceptability less than NH_3. Thus, we have:

$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2 NH$

Due to the – I effect of C_6H_5 group, the electron density on the N-atom in $C_6H_5CH_2NH_2$ is lower than that on the N-atom in $C_2H_5NH_2$, but more than that in NH_3. Therefore, the given compounds can be arranged in the order of their basic strengths as:

$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2 NH$

(ii) Considering the inductive effect and the steric hindrance of the alkyl groups, $C_2H_5NH_2,(C_2H_5)2NH_2$ and their basic strengths as follows:

$C_2H_5NH_2 < (C_2H_5)_2 N < (C_2H_5)_2 NH$

Again, due to the – R effect of C_6H_5 group, the electron density on the N atom in $C_6H_5NH_2$ is lower than that on the N atom in $C_2H_5NH_2$. Therefore, the basicity of $C_6H_5NH_2$ is lower than that of $C_2H_5NH_2$. Hence, the given compounds can be arranged in the increasing order of their basic strengths as follows:

$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3 N < (C_2H_5)_2 NH$

(iii) Considering the inductive effect and the steric hindrance of alkyl groups, $CH_3NH_2,(CH_3)_2 NH$, and .$(CH_3)_3 N$.can be arranged in the increasing order of their basic strengths as:

$(CH_3)_3 N < CH_3NH_2 < (CH_3)_2 NH$

In $C_6H_5NH_2$, N is directly attached to the benzene ring. Thus, the lone pair of electrons on the N – atom is delocalized over the benzene ring. In $C_6H_5CH_2NH_2$, N is not directly attached to the benzene ring. Thus, its lone pair is not delocalized over the benzene ring. Therefore, the electrons on the N atom are more easily available for protonation in $C_6H_5CH_2NH_2$ than in $C_6H_5NH_2$ i.e., $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NH_2$.

Again, due to the – I effect of C_6H_5 group, the electron density on the N – atom in $C_6H_5CH_2NH_2$ is lower than that on the N – atom in $(CH_3)_3 N$. Therefore, $(CH_3)_3 N$ is more basic than $C_6H_5CH_2NH_2$. Thus, the given compounds can be arranged in the increasing order of their basic strengths as follows.

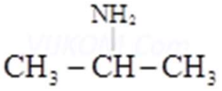
$C_6H_5 < C_6H_5CH_2NH_2 < (CH_3)_3 N < CH_3NH_2 < (CH_3)_2 NH$

Ans 3. The structures of different isomers corresponding to the molecular formula, C_3H_9N are given below:

(a) $CH_3 - CH_2 - CH_2 - NH_2$

Propan-1-amine $(1°)$

(b)



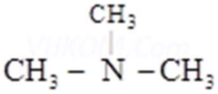
$$CH_3-\underset{}{\overset{NH_2}{CH}}-CH_3$$

Propan-2-amine (1°)

(c)

$$\underset{\text{N-Methylethanamine}(2^\circ)}{CH_3-NH-C_2H_5}$$

(d)

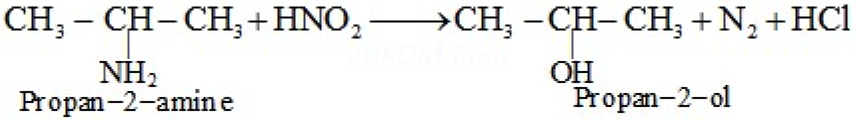


$$CH_3-\overset{CH_3}{N}-CH_3$$

N, N-Dimethylmethanamine (3°)

1° amines, (a) propan-1-amine, and (b) Propan-2-amine will liberate nitrogen gas on treatment with nitrous acid.

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2}+HNO_2 \longrightarrow \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}+N_2+HCL$$

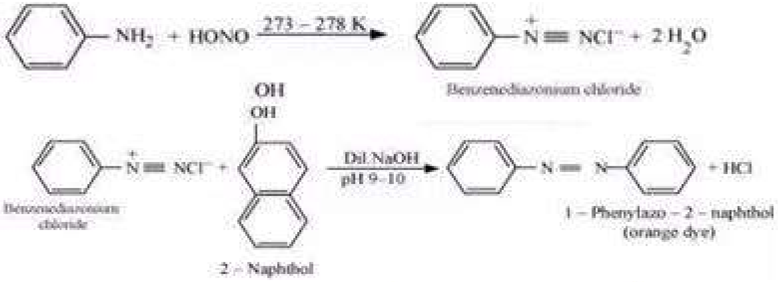


$$\underset{\text{Propan-2-amine}}{CH_3-\underset{NH_2}{CH}-CH_3}+HNO_2 \longrightarrow \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}+N_2+HCl$$

Ans 4. (i) 1-Methylethanamine (1°amine)
(ii) Propan-1-amine (1°amine)
(iii) N-Methyl-2-methylethanamine (2°amine)
(iv) 2-Methylpropan-2-amine (1°amine)
(v) N-Methylbenzamine or N-methylaniline (2°amine)
(vi) N-Ethyl-N-methylethanamine (3°amine)
(vii) 3-Bromobenzenamine or 3-bromoaniline (1°amine)

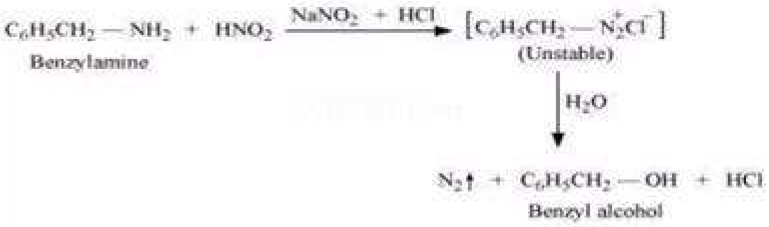
Ans 5. (i) Methylamine and dimethylamine can be distinguished by the carbylamine test.
Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.
(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).
Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N – diethylamine reacts with Hinsberg's reagent to form N, N – diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.
(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with $HNO_2(NaNO_2+\text{dil. }HCl)$ at $0-5^\circ C$, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk

effervescence due (to the evolution of N_2 gas) under similar conditions.



$$CH_3CH_2-NH_2+HONO\xrightarrow{0-5^\circ}C_2H_5OH+N_2\uparrow+H_2O$$

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite. Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

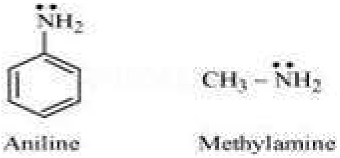


On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

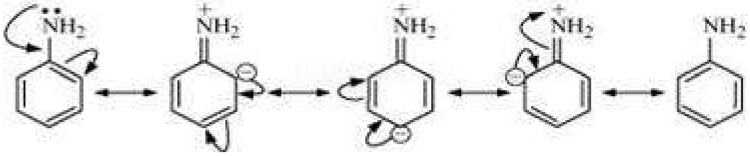
$$C_6H_5NH_2\xrightarrow[273-278K]{NaNO_2+HCl}C_6H_5-\overset{+}{N}_2\bar{C}l+NaCl+2H_2O$$

(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

Ans 6. (i) p*Kb*of aniline is more than that of methylamine:



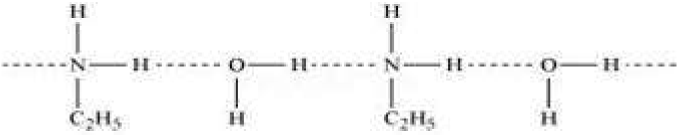
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, *pKb* of aniline is more than that of methylamine.

(ii)Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H – bonds with water. Hence, it is soluble in water.



Ethylamine

But aniline does not undergo H – bonding with water to a very large extent due to the presence of a large hydrophobic – C6H5 group. Hence, aniline is insoluble in water.

Aniline

(iii)Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

$$\underset{\text{Methylamine}}{CH_3 \rightarrow NH_2} \qquad \underset{\text{Water}}{H-OH}$$

Due to the +I effect of – CH_3 group, methylamine is more basic than water. Therefore, in water, methylamine produces OH – ions by accepting H+ ions from water.

$$CH_3-NH_2+H-OH \longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

Ferric chloride $(FeCl_3)$ dissociates in water to form Fe^{3+} *and* CL^- ions.

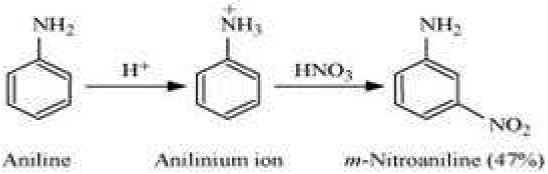
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH – ion reacts with Fe3+ ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\substack{\text{Hydrated} \\ \text{ferric oxide}}}{Fe_2O_3 \cdot 3H_2O}$$

(iv)Although amino group is *o*, *p* – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

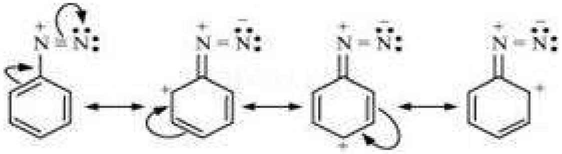
(v)Aniline does not undergo Friedel-Crafts reaction:

A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi)Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii)Gabriel phthalimide synthesis is preferred for synthesising primary amines:

Gabriel phthalimide synthesis results in the formation of amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Ans 7. (i) In $C_2H_5NH_2$, only one – C_2H_5 group is present while in $(C_2H_5)_2NH$, two – C_2H_5 groups are present. Thus, the +I effect is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

Also, both $C_6H_5NHCH_3$ and $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ and $C_6H_5NH_2$, the former will be more basic due to the +T effect of – CH_3 group. Hence, the order of increasing basicity of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

We know that the higher the basic strength, the lower is the p*Kb* values.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

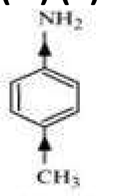
(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the +I effect of two -CH3 groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one – CH_3 group while $(C_2H_5)_2NH$ contains two – C_2H_5 groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

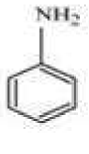
Now, $C_6H_5N(CH_3)_2$ is less basic than CH3NH2 because of the-R effect of – C_6H_5 group.

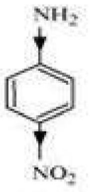
Hence, the increasing order of the basic strengths of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a)


p-Toluidine


Aniline


p-Nitroaniline

In *p*-toluidine, the presence of electron-donating $-CH_3$ group increases the electron density on the N-atom.
Thus, *p*-toluidine is more basic than aniline.
On the other hand, the presence of electron-withdrawing $-NO_2$ group decreases the electron density over the N-atom in *p*-nitroaniline. Thus, *p*-nitroaniline is less basic than aniline.
Hence, the increasing order of the basic strengths of the given compounds is as follows:
p-Nitroaniline< Aniline <*p*-Toluidine

(b) $C_6H_5NHCH_3$ is more basic than $C_6H_5NH_2$ due to the presence of electron-donating $-CH_3$ group in $C_6H_5NHCH_3$.
Again, in $C_6H_5NHCH_3$, $-C_6H_5$ group is directly attached to the N-atom. However, it is not so in $C_6H_5NH_2NH_2$. Thus, in $C_6H_5NHCH_3$, the -R effect of $-C_6H_5$ group decreases the electron density over the N-atom. Therefore, $C_6H_5NHCH_3$ is more basic than $C_6H_5NHCH_3$.
Hence, the increasing order of the basic strengths of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2NH_2$.

(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher is the +I effect. Therefore, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

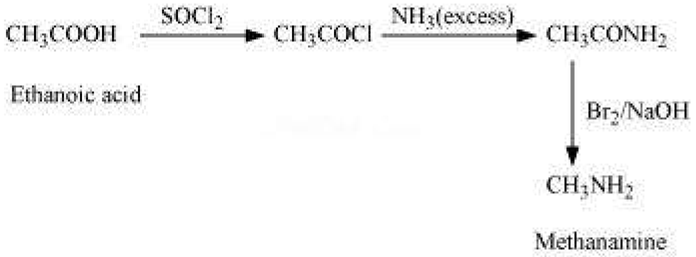
(v) The boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point. $(CH_3)_2NH$ contains only one H-atom whereas $C_2H_5NH_2$ contains two H-atoms. Then, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(CH_3)_2NH$. Hence, the boiling point of $C_2H_5NH_2$ is higher than that of $(CH_3)_2NH$.

Further, O is more electronegative than N. Thus, C_2H_5OH forms stronger H-bonds than $C_2H_5NH_2$. As a result, the boiling point of C_2H_5OH is higher than that of $C_2H_5NH_2$ and $(CH_3)_2NH$.
Now, the given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

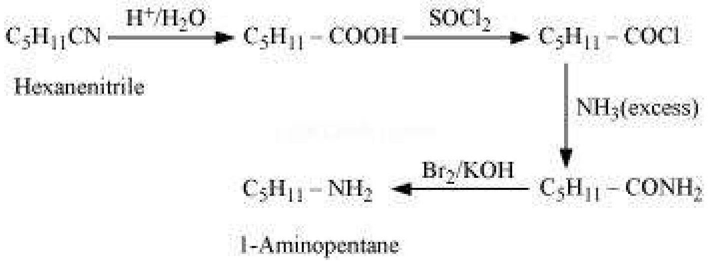
(vi) The more extensive the H-bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)_2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.
Further, the solubility of amines decreases with increase in the molecular mass. This is because the molecular mass of amines increases with an increase in the size of the hydrophobic part. The

molecular mass of $C_6H_5NH_2$ is greater than that of $C_2H_5NH_2$ and $(C_2H_5)_2NH$.
Hence, the increasing order of their solubility in water is as follows:
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

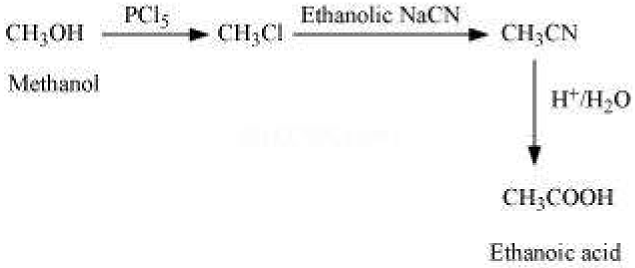
Ans 8. (i)



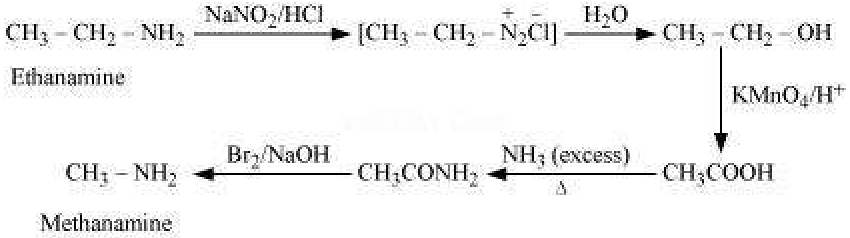
(ii)



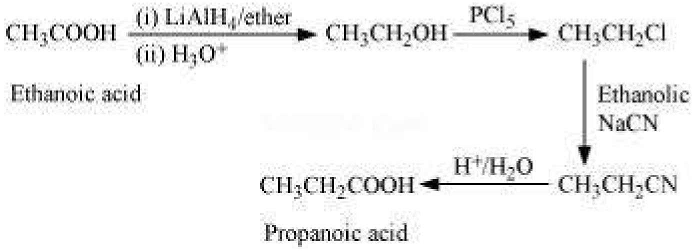
(iii)



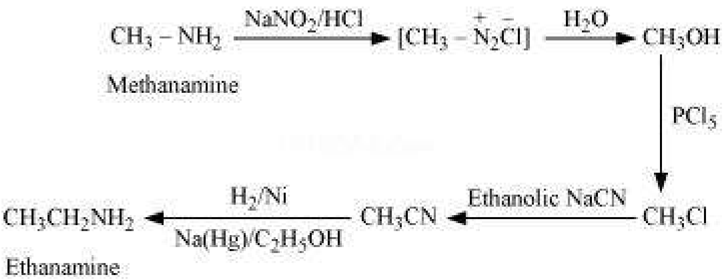
(iv)



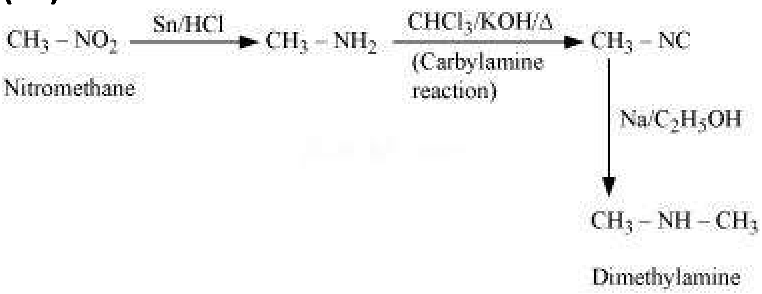
(v)



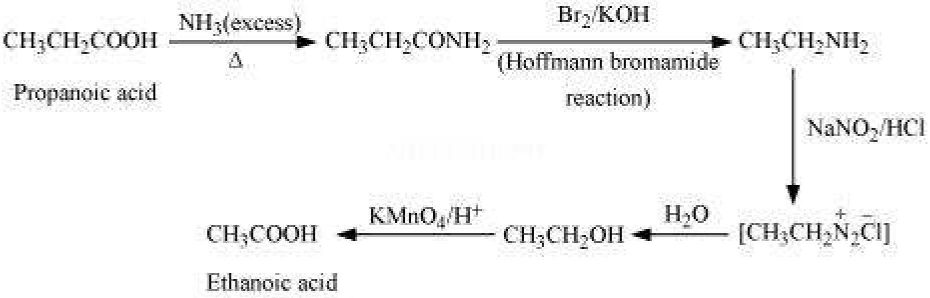
(vi)



(vii)



(viii)



Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

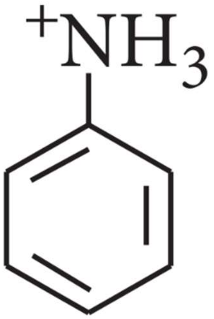
Explanation:

Ortho effect is a consequence of steric and electronic factors.

2. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

In strongly acidic medium, aniline gets protonated and so the lone pair of electrons is not available to produce +E or + M effects. On the other hand, the −N+H3−N+H3 group exerts strong -I effect and thus it causes the deactivation of the ring.



Case Study Answers-

1. Answer :

(i) (d) Azo dye test.

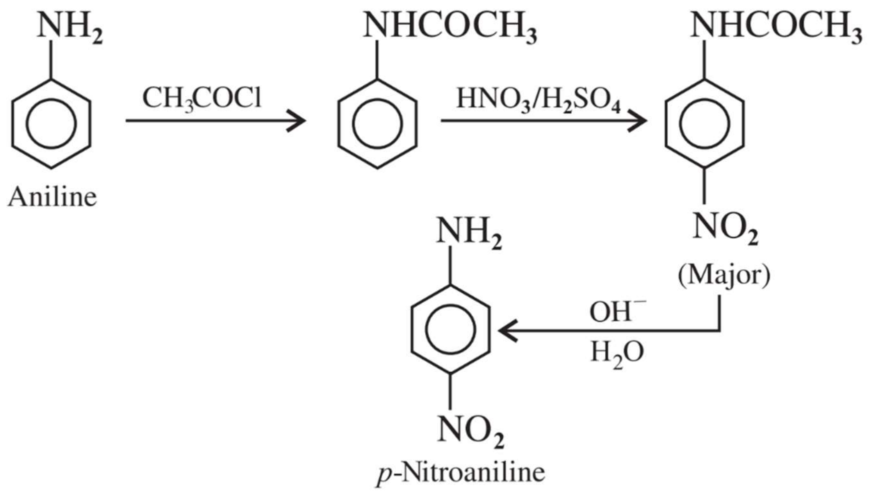
(ii) (a) Aniline.

Explanation:

Aromatic primary amines give dye test.

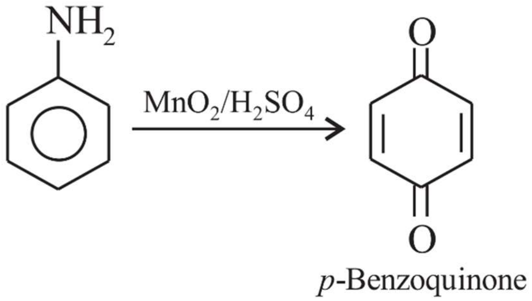
(iii) (c) p-nitroaniline.

Explanation:



(iv) (c) p-benzoquinone.

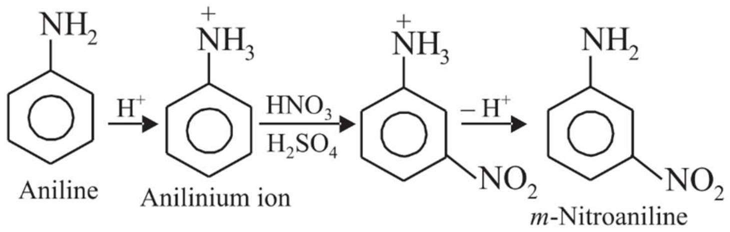
Explanation:



(v) (b) m-nitroaniline.

Explanation:

In acidic medium aniline gets protonated to anilinium ion which is meta-directing.



2. Answer :

(i) (d) Dimethyl amine.

Explanation:

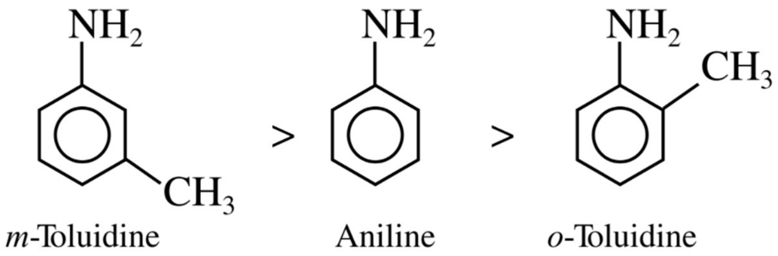
The increasing order of basicity of the given compounds is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$. Due to the +I effect of alkyl groups, the electron density on nitrogen increases and thus, the availability of the lone pair of electrons to proton increases and hence, the basicity of amines also increases. So, aliphatic amines are more basic than aniline. In case of tertiary amine $(CH_3)_3N$, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing groups decrease electron density on nitrogen atom and thereby decreasing basicity.

(ii) (d) o-toluidine < aniline < m-toluidine

Explanation:

In general, electron donating (+R) group which when present on benzene ring ($-NH_2$, -OR, -R, etc.) at the para position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to ortho effect.



(iii) (d) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

Explanation:

In case of ethylamines, the combined effect of (c) inductive effect, steric effect and salvation effect gives the order of basic strength as

$$\underset{(2^\circ)}{(C_2H_5)_2NH} > \underset{(3^\circ)}{(C_2H_5)_3N} > \underset{(1^\circ)}{C_2H_5NH_2} > NH_3$$

(iv) (b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$

Explanation:

In non-aqueous solvents the basic strength of alkyl amines follows the order:

tertiary amines> secondary amines> primary amines.

(v) (c) Methylamine is a stronger base than ammonia.

Explanation:

Methyl amine is stronger base than ammonia due to electron releasing inductive effect of methyl group.